

Solid state physics 1+2

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Official version of this presentation (home.zcu.cz/~jhouška/FPL1+2_CZ.pdf) is available in Czech. This is an unofficial translation to English for foreign PhD students.

The translation is not necessarily word-to-word (let alone that different length of Czech and English sentences sometimes led to grammatical concessions such as omitting articles), does not include translation of several figures, and does not necessarily include updates made in the Czech version after 6/15/2018. This, however, does not affect the information needed to answer the exam questions.

Why physics

from my grandmother's textbook (*1907)

Lost in translation

GUSTA SEDLÁČKOVÁ:

DO ŽIVOTA.

POUČENÍ O VEDENÍ DOMÁCNOSTI, O DOMÁCÍM
LÉČENÍ S DODATKEM O SEBEVÝCHOVĚ.

S 34 VYOBRAZENÍMI.



1924.
ML. BOLESLAV
KAREL VAČLENA,
NAKLADATEL

DÍVKY ČESKOSLOVENSKÉ!

Odrostly jste dětským hřm, jste dívky již, život otevírá se vám plný krás i úskalí, radosti i povinností vážných. A mnohými zkušenostmi musíte se obrnit, abyste kráčely jistě, bezpečně! Práce, jež údělem je všech lidí, čeká i vás a na vás je, abyste se dobře připravovaly k úkolu, který vás čeká, až dospějete.

*Ženě uloženo je býti strážkyní domácnosti, upravit domov milý a útulný, udržovati jej v pořádku a pečovati o zdraví členů rodiny. Žena je srdcem rodiny. **Žena svou jemnou duší** dovede vdechnouti pravou krásu všem místům, kudy kráčí.*

Těchto povinností musíte býti si vědomy, k tomu cíli musí směřovati předběžná vaše příprava. Mnohé z vás sice zvolí si postavení samostatné, ale přes to pravého svého úkolu se nevzdají nikdy. Jak rády vrátí se z denního svého zaměstnání v útulný svůj pokojík, který vlastním vkusem si přizdobily a zkrásnily!

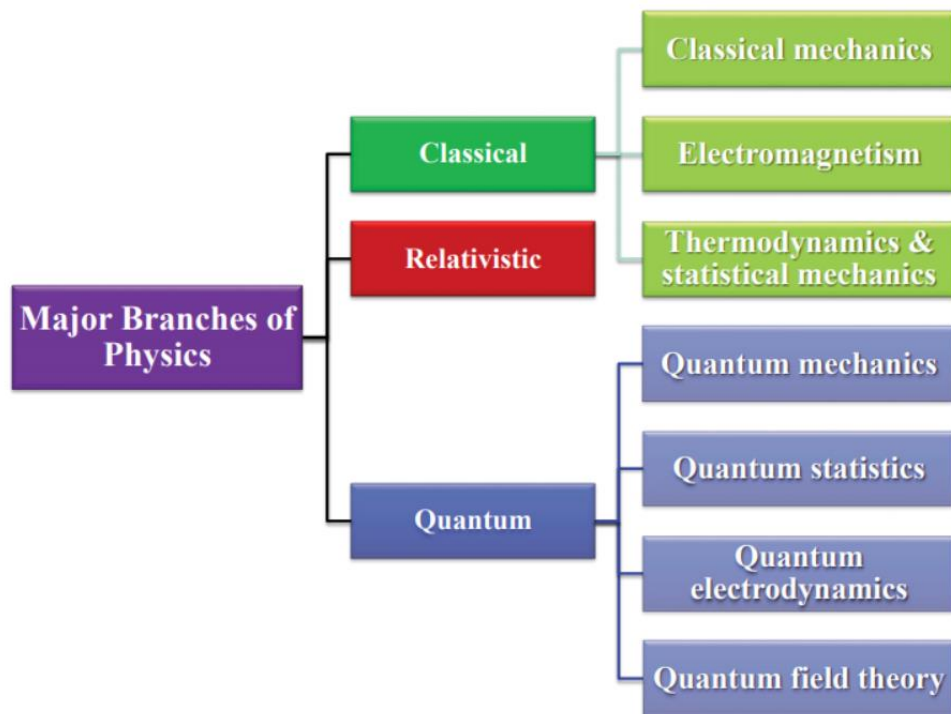
*Žena musí se **naučiti všem pracem**, které s vedením domácnosti souvisejí. I když je sama nemusí konati, dovede poručiti a dohlédnouti na práci zjednané pomocnicí v domácnosti.*

***Své denní práce musí si řádně rozvrhnouti**, aby dobře časem hospodařila.*

*Žena-hospodyně **musí znáti nejdůležitější zákony fyzické**, aby vystríhala se různých nehod při své práci, musí seznámiti se s nejdůležitějšími **strojkami**, kterými by práci svoji usnadnila a drahého času ušetřila.*

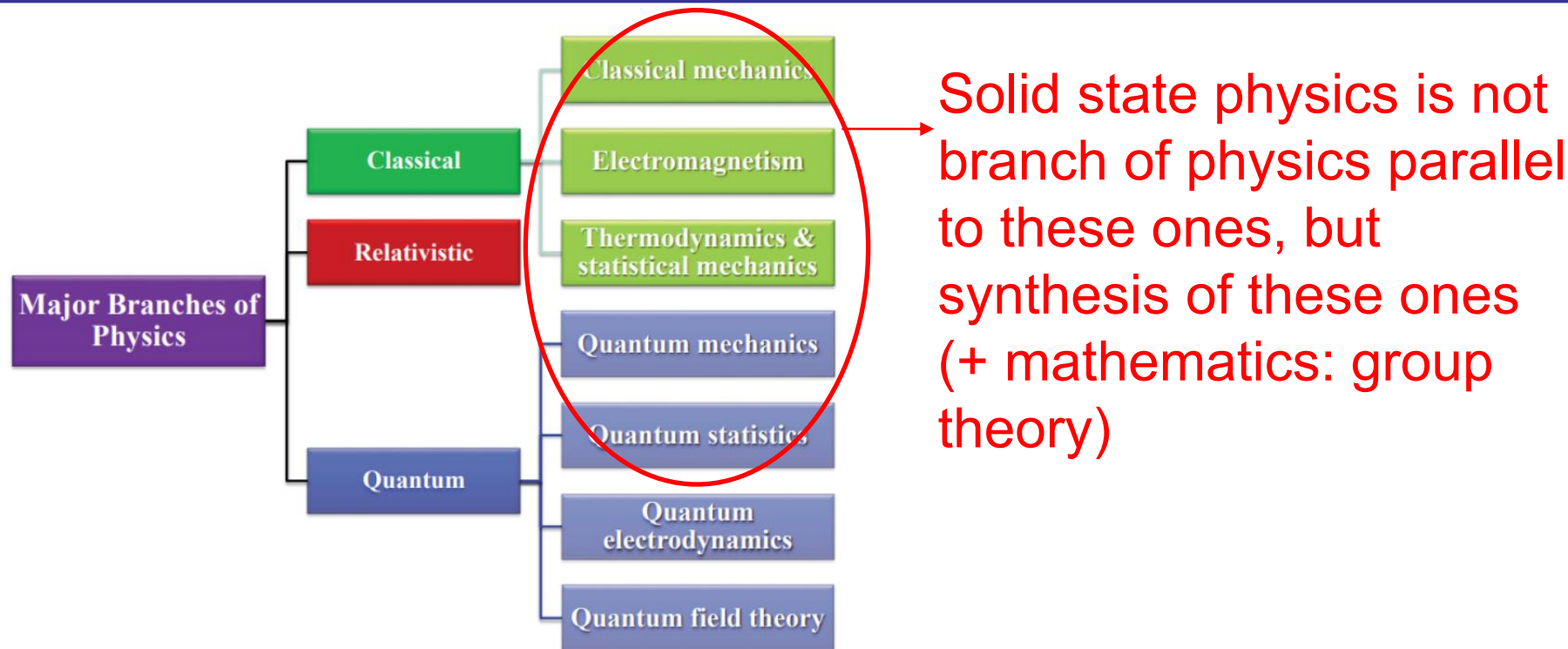
***Přijem svůj rozpočte** si tak, aby kryl všechna vydání nutná, aby zbylo ještě na vydání mimořádná (nemoci a p.). Při tom nesmí zapomenouti, že i **duše potřebuje osvěžení** četbou, divadlem, koncertem a p. Dluhy jsou hrotem spokojenosti rodiny: „Zlárná hospodyně, zlatý sloup v domě“, praví přísloví.*

Why solid state physics



The figure can look like differently (separating cosmology from mechanics, separating vibrations and waves from mechanics, separating optics from electromagnetism, way how to divide the quantum theory, etc.), but it usually does not contain solid state physics

Why solid state physics



Solid state physics (more precisely physics of condensed state) does not bring new physical laws or new elementary particles, but knowledge about collective behavior of elementary particles

If we nevertheless take it as a branch of physics, it is the **widest and most useful** one

Selected solid materials

Glass

Silicon

Ceramics

Rubber

Concrete

Paper

Wood

Plastic

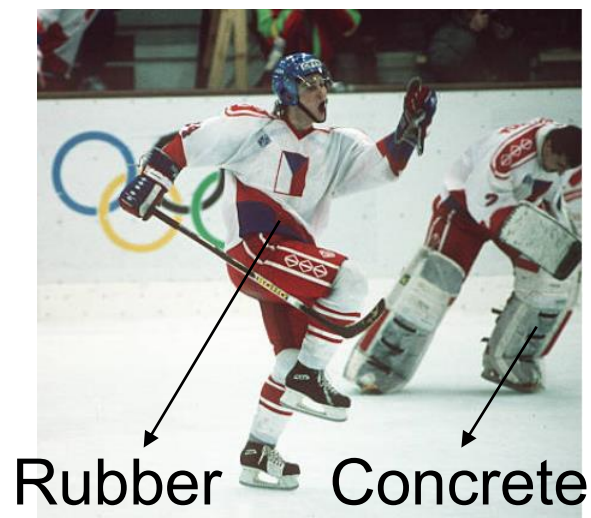
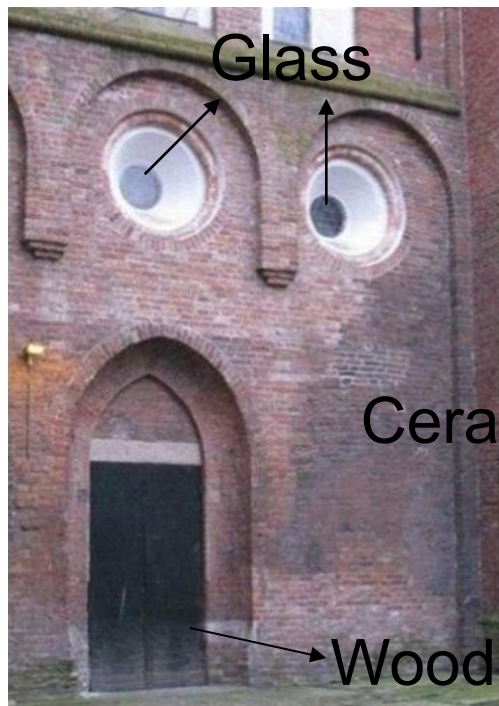
Aluminium

Gold

Textile

Steel

Selected solid materials



Lost in translation



List of chapters

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

1) Introduction, crystal structure

Atomic structure

- 1) Introduction, crystal structure
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Special fields

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Effect of structure on properties

Example 1: **carbon**

- diamond (3D, hard)
- graphite (slices)
- nanotubes, polymers (fibers)
- fullerenes

Example 2: materials based on **SiO₂**

- quartz (3D, hard)
- mica (slices)
- asbestos (fibers)
- glass

The structural differences are also due to the presence of other elements (such as Al or K between planes of mica), but that's not the point: the main differences between properties are due to the structure, not composition

Effect of structure on properties

Example 3: tin

- β -Sn (tetragonal): metal, common at RT
- α -Sn (diamond structure): covalent, fragile

below 13°C (most fast at -48°C) autocatalytic transformation $\beta \rightarrow \alpha$ and the ductile metal becomes dust: **tin pest (plague)**

Effect of structure on properties

Example 3: tin

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example of consequence:
evaporation of tin canned fuel



one of reasons of the death
of Scott and his 4 companions
when returning from
the South pole 1912



Effect of structure on properties

Example 4 (at higher than atomic level): **CaCO₃** (calcite)

- **limestone** = small grains of calcite with many pores
⇒ softer, not so good construction material
- **marble** = limestone which was exposed to high temperatures and pressures ⇒ large and almost pore-free grains of calcite
⇒ harder, better construction material

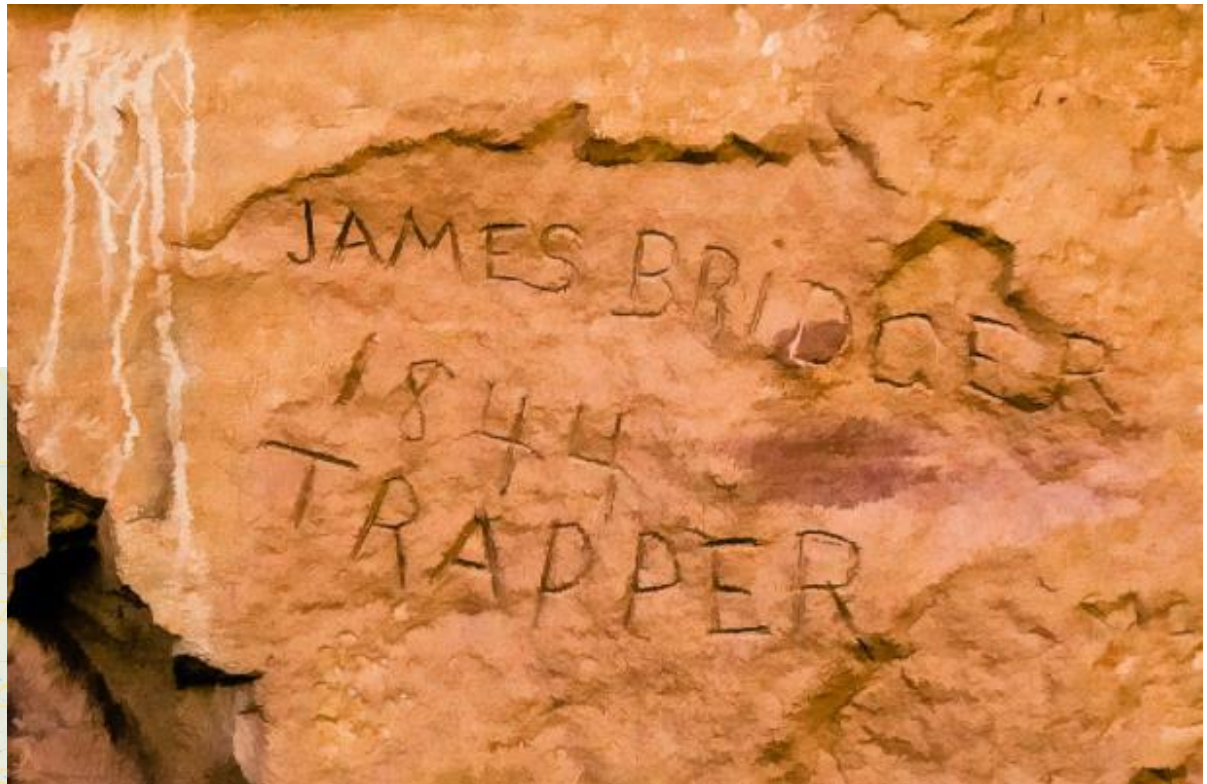
the terminology is blurred by the existence of dolomite limestone and marble (Ca+Mg instead of Ca), possible presence of other elements (different colours of marble) and by aragonite as an alternative to calcite, but this does not change the principle

Effect of structure on properties

Example 4 (at higher than atomic level): CaCO_3 (calcite)

- **limestone** = small grains of calcite with many pores
⇒ softer, not so good construction material

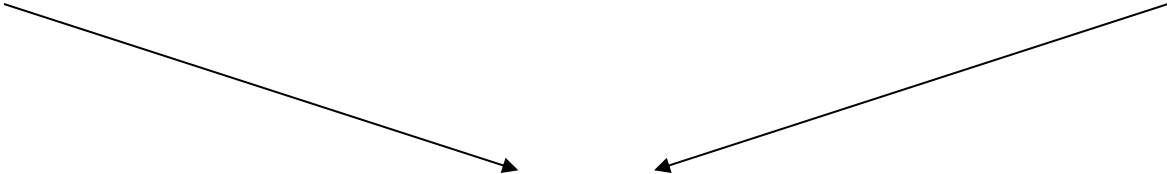
Thus, each trapper
can engrave his
signature there



Overview of crystal structures

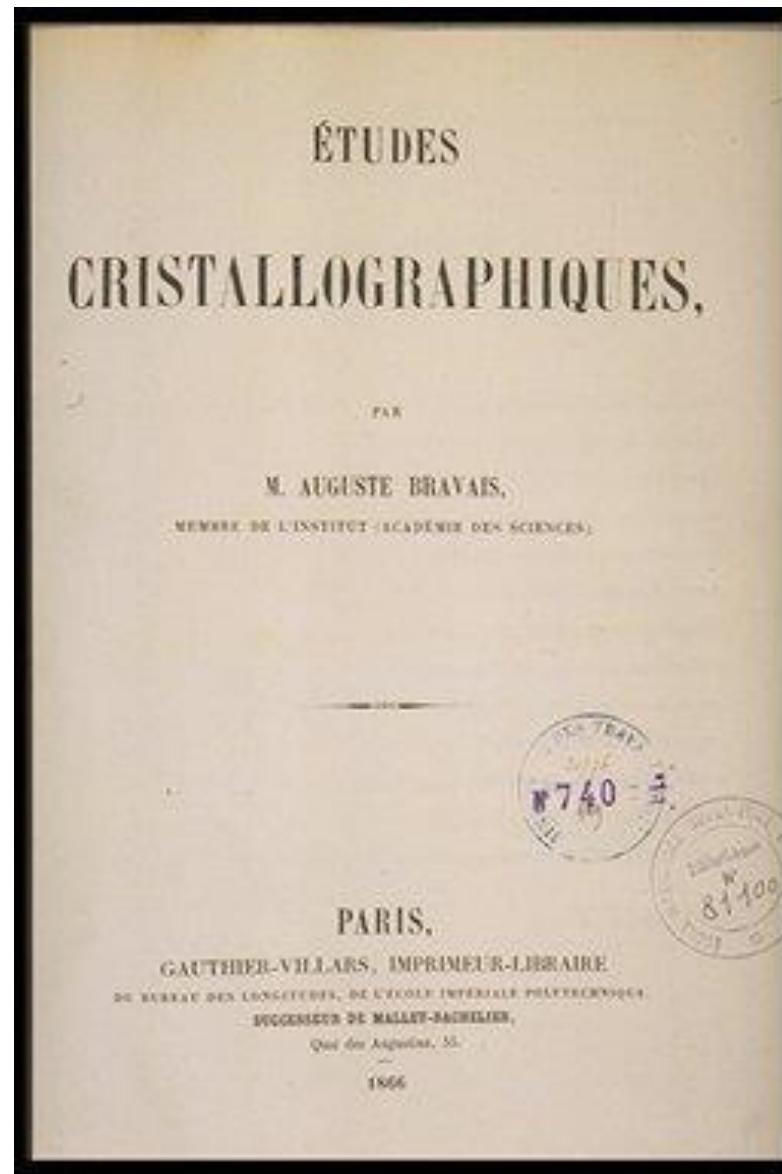
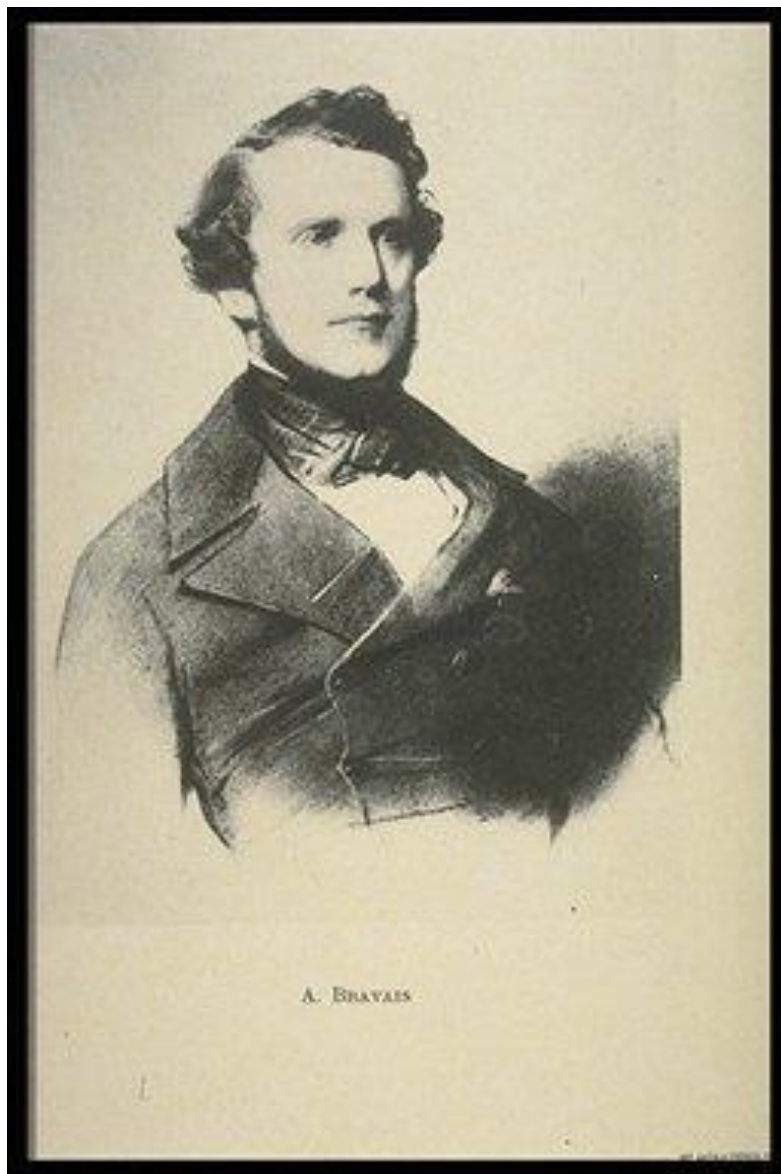
7 crystal systems
(qualitatively different shapes
of the primitive crystal cell)

1-4 types of each cell
(simple and
base / body / face / centered)



14 Bravais lattices

Etudes cristallographiques (1849)



Overview of crystal structures

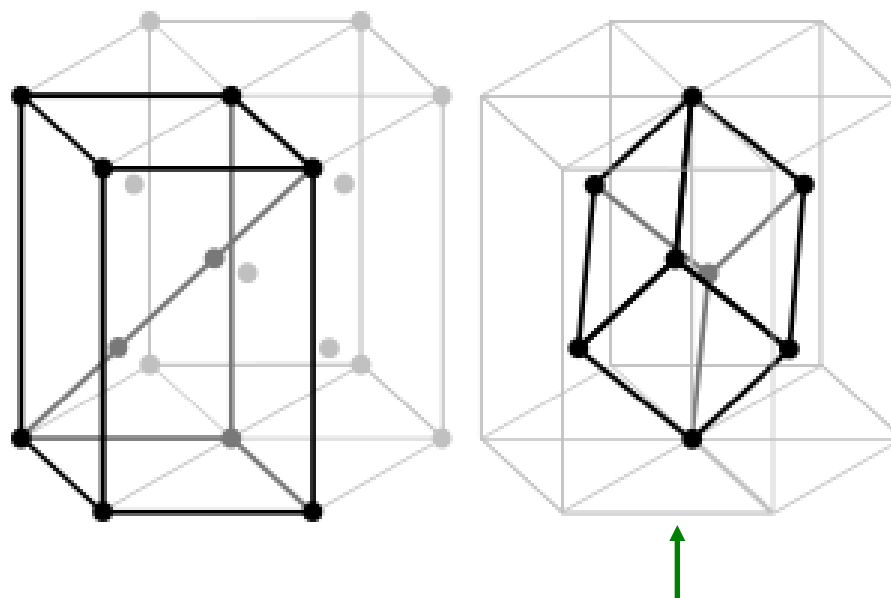
Crystal family	Crystal system	Lattice system	Lattice vectors and angles between them
cubic	cubic	cubic	$a=b=c$ $\alpha=\beta=\gamma=90^\circ$
tetragonal	tetragonal	tetragonal	$a=b\neq c$ $\alpha=\beta=\gamma=90^\circ$
orthorhombic	orthorhombic	orthorhombic	$a\neq b\neq c$ $\alpha=\beta=\gamma=90^\circ$
monoclinic	monoclinic	monoclinic	$a\neq b\neq c$ $\alpha=\gamma=90^\circ, \beta\neq 90^\circ$
triclinic	triclinic	triclinic	$a\neq b\neq c$ $\alpha\neq\beta\neq\gamma$
hexagonal	trigonal <i>threefold rotation axis</i>	rhombohedral <i>can be represented also by rhombohedron</i>	$a=b=c$ $\alpha=\beta=\gamma\neq 90^\circ$
		hexagonal <i>can be represented only using a prism with a hexagonal base</i>	$a=b\neq c$ $\alpha=\beta=90^\circ, \gamma=120^\circ$
	hexagonal <i>sixfold rotation axis</i>		

Overview of crystal structures

Crystal family	Crystal system	Lattice system	Bravais lattice (total 14)
cubic	cubic	cubic	3 (simple, body / face centered)
tetragonal	tetragonal	tetragonal	2 (simple, body centered)
orthorhombic	orthorhombic	orthorhombic	4 (simple, base / body / face centered)
monoclinic	monoclinic	monoclinic	2 (simple, base centered)
triclinic	triclinic	triclinic	1
hexagonal	trigonal <i>threefold rotation axis</i>	rhombohedral <i>can be represented also by rhombohedron ($a=b=c$, $\alpha=\beta=\gamma \neq 90^\circ$)</i>	1
		hexagonal <i>can be represented only using a prism with a hexagonal base</i>	1
	hexagonal <i>sixfold rotation axis</i>		

Overview of crystal structures

rhombohedral × trigonal × hexagonal

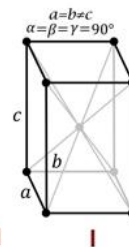
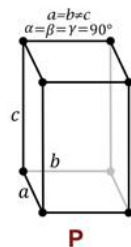
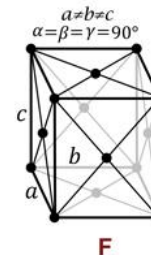
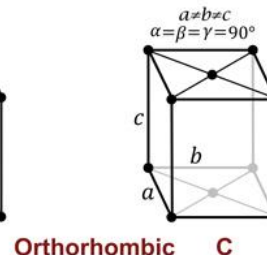
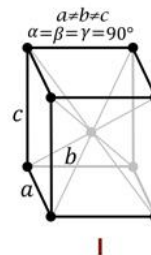
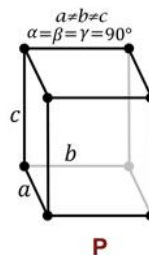
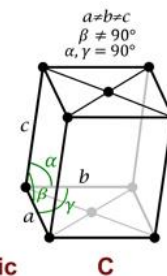
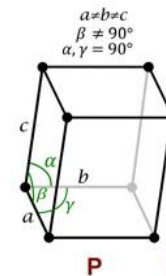
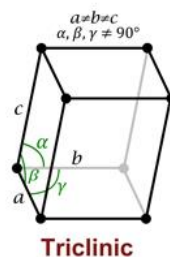


hexagonal	trigonal <i>threefold rotation axis</i>	rhombohedral <i>can be represented also by rhombohedron</i> <i>($a=b=c$, $\alpha=\beta=\chi \neq 90^\circ$)</i>	1
	material which is trigonal but not rhombohedral: e.g. α -quartz		
	hexagonal <i>sixfold rotation axis</i>	hexagonal <i>can be represented only using a prism with a hexagonal base</i>	1

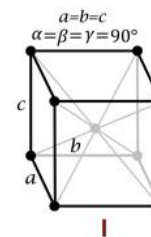
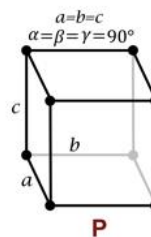
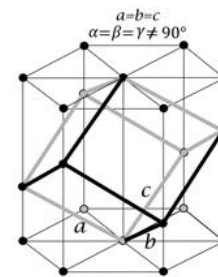
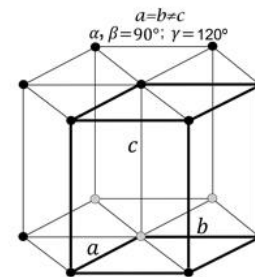
Overview of crystal structures

14 Bravais lattices in a graphical form

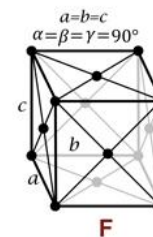
P primitive
I body centered
 (Innenzentriert)
F face centered
 (Flächenzentriert)
A/B/C centered on
 A/B/C faces only
R rhombohedral



Tetragonal



Cubic



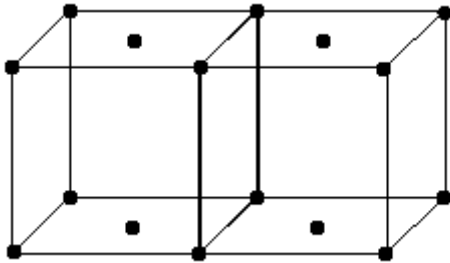
Overview of crystal structures



Atomium in Bruxelles:
body centered cubic (bcc) cell with a lattice constant of 44 m

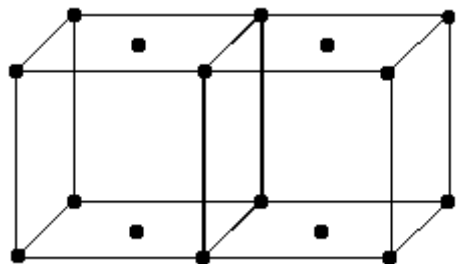
Overview of crystal structures

Are there really only 14 aforementioned Bravais lattices?
Why is there not e.g. base centered cubic/tetragonal?

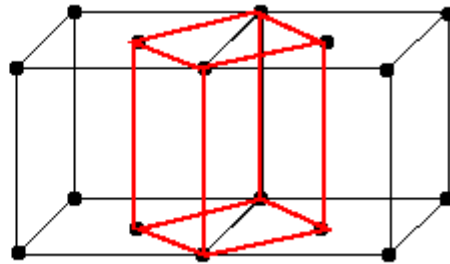
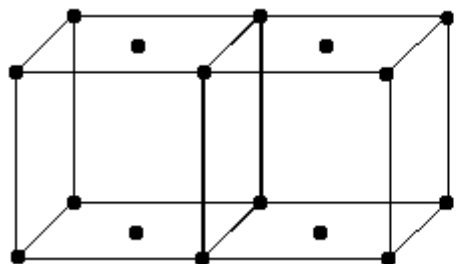


Overview of crystal structures

Are there really only 14 aforementioned Bravais lattices?
Why is there not e.g. base centered cubic/tetragonal?



Because by rotating it of 45° we get simple tetragonal



Bravais was not stupid

Overview of crystal structures

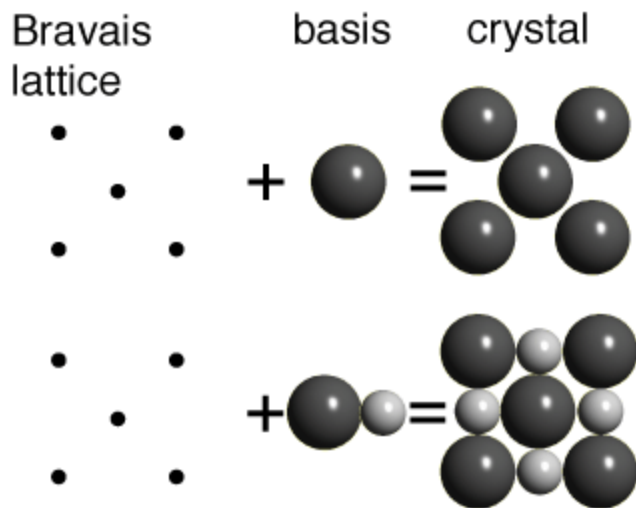
Why are there more crystal structures than the 14 aforementioned Bravais lattices?

Overview of crystal structures

Why are there more crystal structures than the 14 aforementioned Bravais lattices?

Because the Bravais lattice defines only the periodicity.
Basis of any size (not only one-atom basis) can be replicated in space with this period.

Crystal structure = lattice + basis



Crystal atoms and lattice points are two completely different entities
(we can decide that one of basis atoms will overlap with a lattice point, but that's only a convention)

Overview of crystal structures

Crystal structure = lattice + basis



Formation with
one-element basis
(soldier)



Formation with
two-element basis
(soldier + horse)

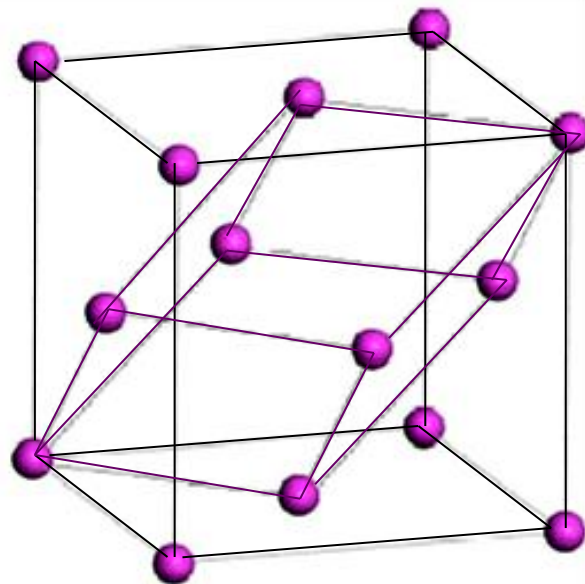
Primitive x conventional unit cell

Primitive unit cell is the smallest possible (one lattice point). Sometimes it also leads to a maximum symmetry (e.g. in the case of simple cubic), but not always.

Conventional unit cell has the maximum possible symmetry ($\Rightarrow$ easier to imagine), at the cost of larger volume (more lattice points $\Rightarrow$ e.g. slower calculations)

Example:

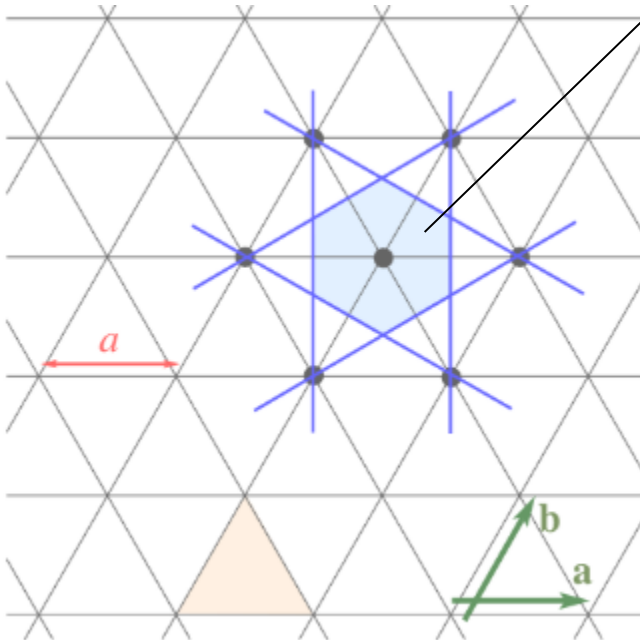
fcc cube can be represented also by a rhombohedron with $4\times$ smaller volume (figure here), similarly for some prisms with a hexagonal base (figure above)



Wigner-Seitz cell

Shape of primitive cell (contrary to its volume) is not specified unambiguously.

The unambiguous thing is Wigner-Seitz cell: part of space around a point of the crystal lattice for which this point is the nearest one. The boundaries are perpendicular to and passing through the midpoints of lines connecting two lattice points.



Reciprocal space and XRD

In the real space the lattice is defined by vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ ($\mathbf{a}_{1-3}$ do not necessarily define "real" primitive crystal cell, but also e.g. its integer multiple - that's not the point now)

Let's define a lattice vector $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ where n_{1-3} are integers

In the reciprocal space the lattice is defined by vectors $\mathbf{A}_1$, $\mathbf{A}_2$, $\mathbf{A}_3$ where $\mathbf{A}_1 = 2\pi \cdot \mathbf{a}_2 \times \mathbf{a}_3 / (\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)$, etc.

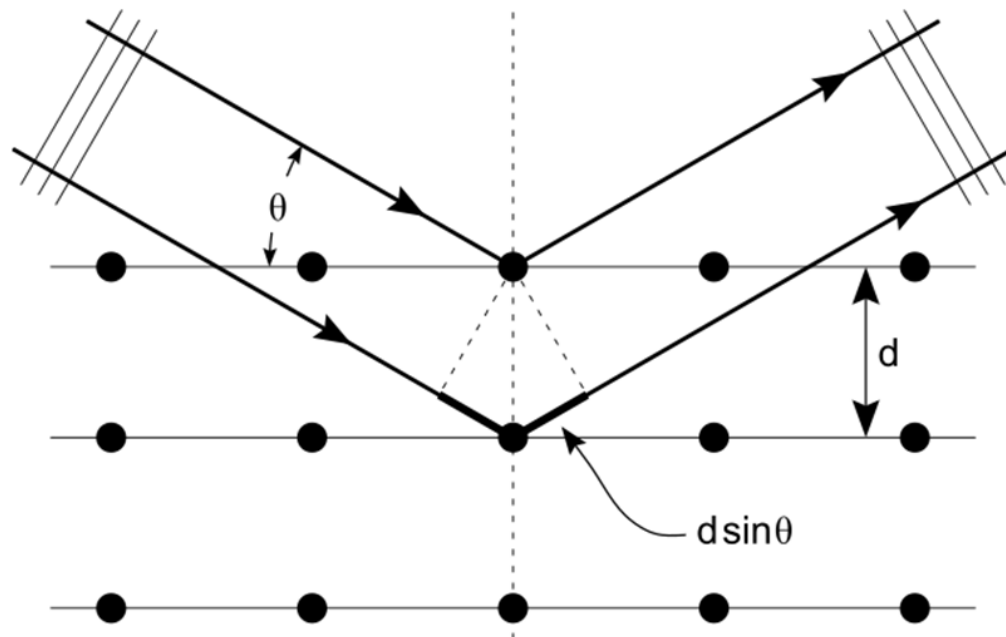
Let's define a reciprocal lattice vector

$$\mathbf{G} = m_1\mathbf{A}_1 + m_2\mathbf{A}_2 + m_3\mathbf{A}_3$$

It holds $\mathbf{G} \cdot \mathbf{R} = 2\pi(n_1 \cdot m_1 + n_2 \cdot m_2 + n_3 \cdot m_3) \Rightarrow e^{i\mathbf{G} \cdot \mathbf{R}} = 1$

Primitive reciprocal lattice cell (= Wigner-Seitz cell in the reciprocal space) is called first Brillouin zone

Reciprocal space and XRD

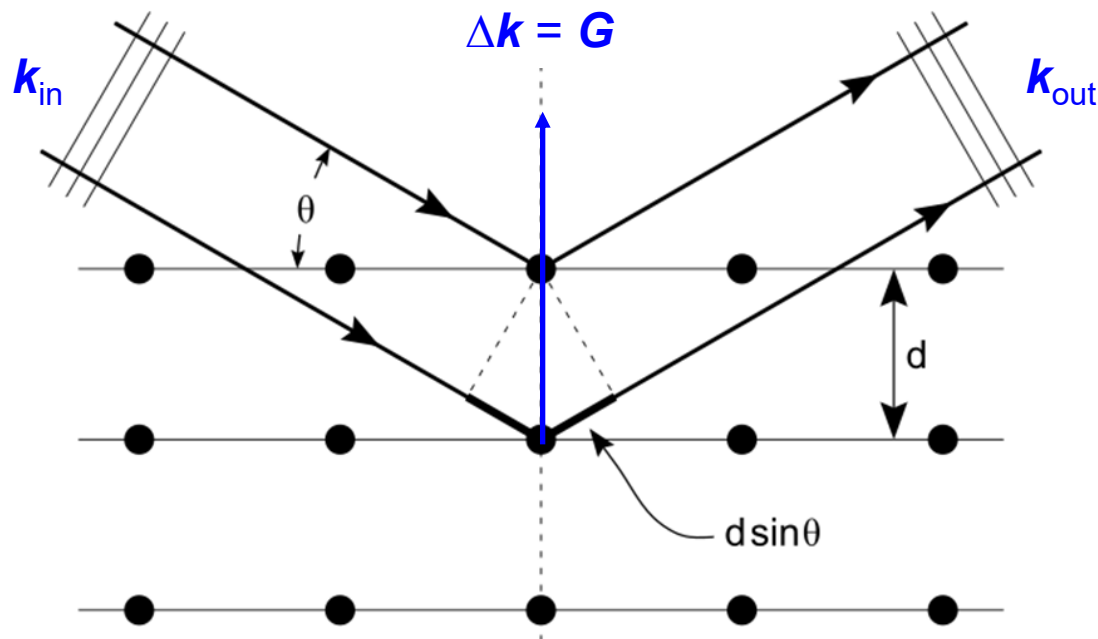


From the wave point of view:

constructive interference for $2.d.\sin\theta = n.\lambda$

Nobel prize 1915 (William Bragg father + son)

Reciprocal space and XRD



From the reflecting atom point of view ($|\mathbf{k}_{in(out)}| = 2\pi/\lambda$):

waves $A_{in} \cos(\omega t - \mathbf{k}_{in} \cdot \mathbf{x})$ and $A_{out} \cos(\omega t - \mathbf{k}_{out} \cdot \mathbf{x})$ must have the same phase (i.e. $\Delta \mathbf{k} \cdot \mathbf{x} = 2\pi n$) when interacting with atom, i.e. where $\mathbf{x}$ is a lattice vector $\Rightarrow \Delta \mathbf{k}$ is a reciprocal lattice vector $\mathbf{G} \Rightarrow 2\mathbf{k}_{in(out)} \cdot \mathbf{G} = \mathbf{G}^2$ where $|\mathbf{G}| = 2\pi n/d \Rightarrow$ again $2.d.\sin \theta = n.\lambda$

Reciproký prostor a XRD

From the reflecting atom point of view ($|\mathbf{k}_{\text{in(out)}}| = 2\pi/\lambda$):

waves $A_{\text{in}} \cos(\omega t - \mathbf{k}_{\text{in}} \cdot \mathbf{x})$ and $A_{\text{out}} \cos(\omega t - \mathbf{k}_{\text{out}} \cdot \mathbf{x})$ must have the same phase (i.e. $\Delta \mathbf{k} \cdot \mathbf{x} = 2\pi n$) when interacting with atom, i.e. where $\mathbf{x}$ is a lattice vector $\Rightarrow \Delta \mathbf{k}$ is a reciprocal lattice vector $\mathbf{G}$

At the same time

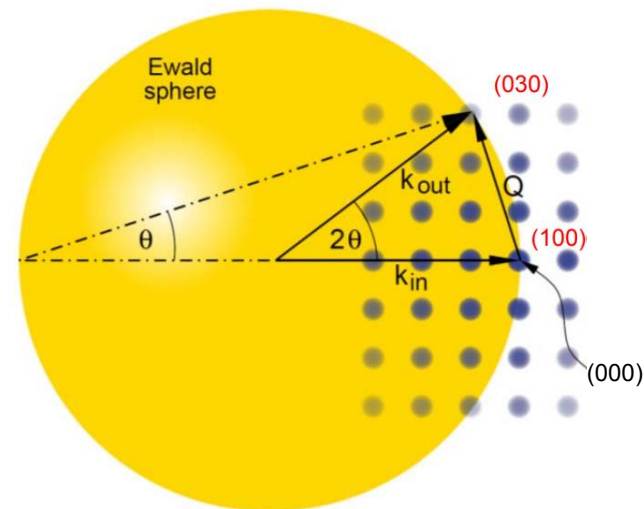
$$|\mathbf{k}_{\text{in}}| = |\mathbf{k}_{\text{out}}| = |\mathbf{k}_{\text{in}} - \Delta \mathbf{k}| = |\mathbf{k}_{\text{in}} - \mathbf{G}|$$

$$\mathbf{k}_{\text{in}}^2 = (\mathbf{k}_{\text{in}} - \mathbf{G})^2$$

$$2\mathbf{k}_{\text{in(out)}} \cdot \mathbf{G} = \mathbf{G}^2 \quad \text{kde } |\mathbf{G}| = 2\pi n/d$$



$$\text{again } 2.d.\sin\theta = n.\lambda$$

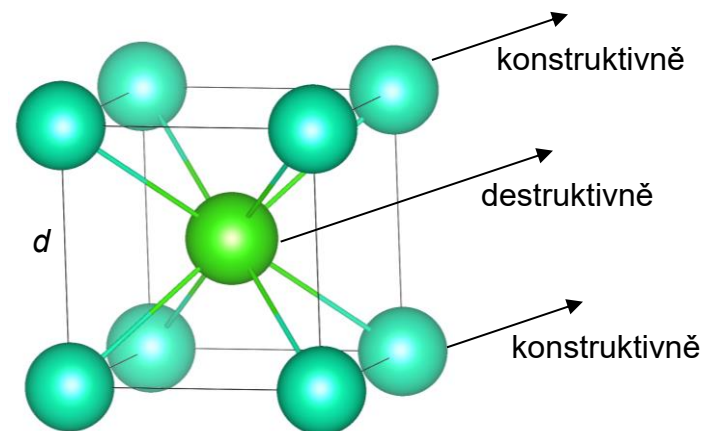


Ewald sphere visualizes this condition for diffraction

Reciprocal space and XRD

The Bragg equation $2.d.\sin\theta = n.\lambda$ is necessary, not sufficient, condition for an interference maximum

There is a plane in the distance d which reflects constructively interfering beam. But there can be a plane in a different distance (see $d/2$ for bcc) which reflects destructively interfering beam.

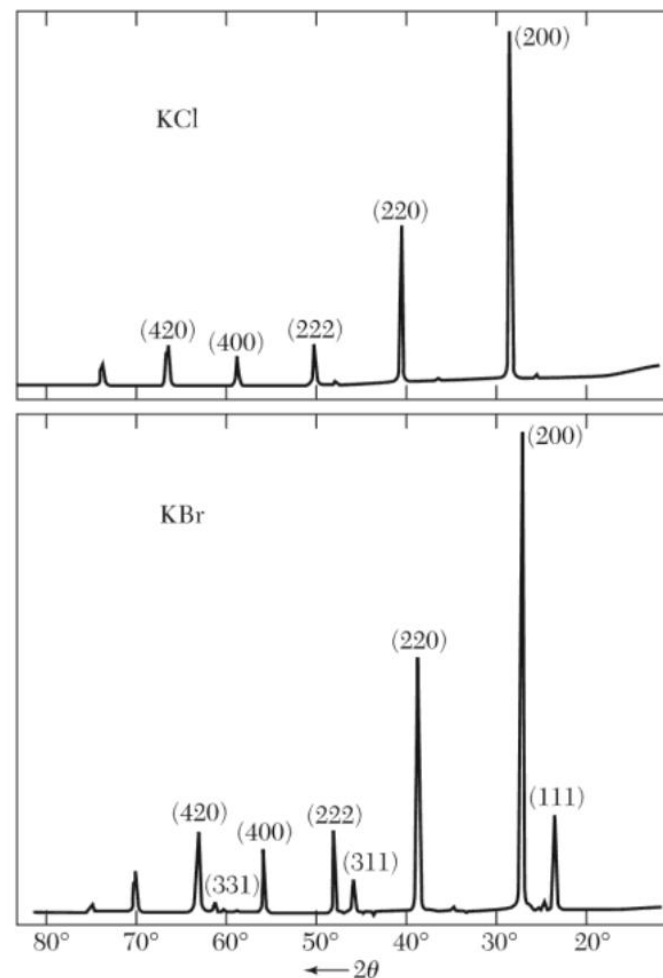


Reciprocal space and XRD

The Bragg equation $2.d.\sin\theta = n.\lambda$ is necessary, not sufficient, condition for an interference maximum

KCl and KBr have the same structure

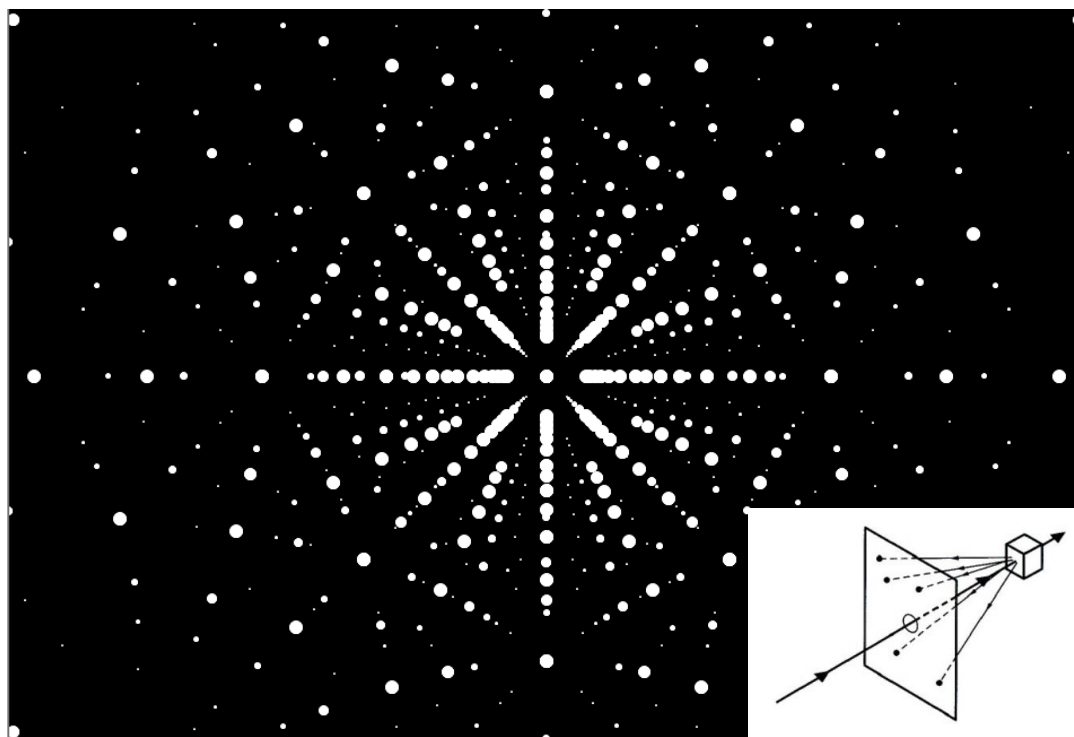
- destructively interfering beams reflected from K planes and Cl planes have similar intensities and almost completely cancel out $\Rightarrow$ less peaks
- destructively interfering beams reflected from K planes and Br planes have different intensities and cancel out only partially $\Rightarrow$ more peaks



Reciprocal space and XRD

Practical realization (further details in KFY/EMSA)

- many wavelengths & fixed crystal (Laue, figure for NaCl)
- one wavelength & rotating crystal (Bragg-Brentano)
- one wavelength & powder sample (Debye-Scherrer)



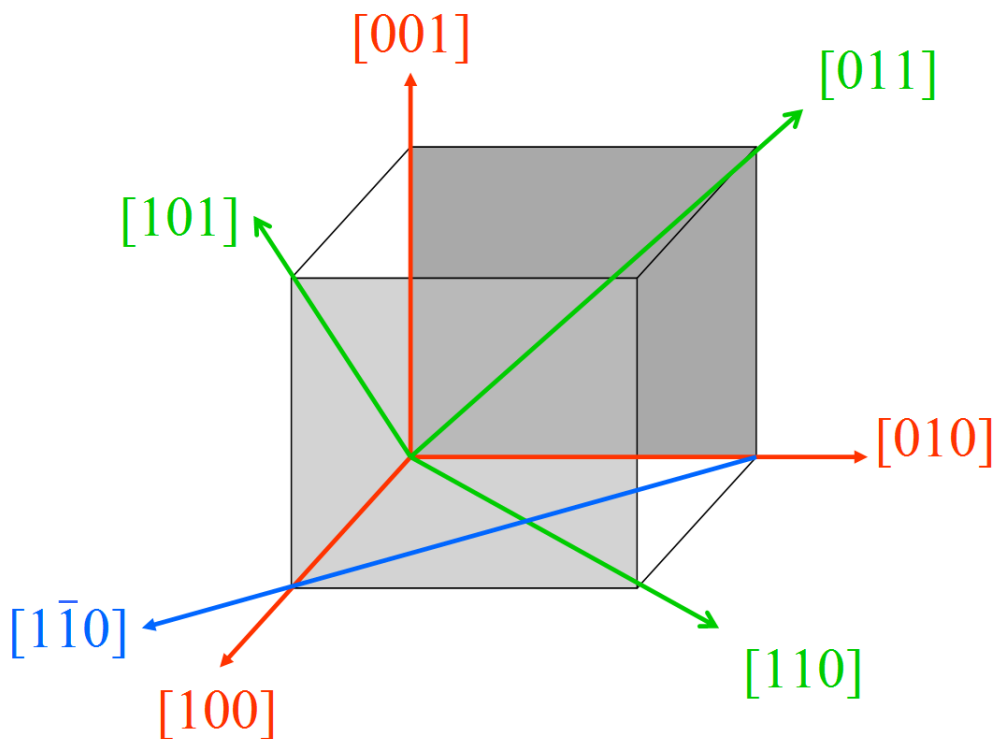
Miller indices for vectors

Vector (direction) is expressed as a least integer multiple (often bar instead of minus) of lattice vectors:

$[hkl]$ for specific direction

$\langle hkl \rangle$ for a set of all equivalent directions

hki instead of hkl ($i = -h-k$) for hexagonal family



Miller indices for planes

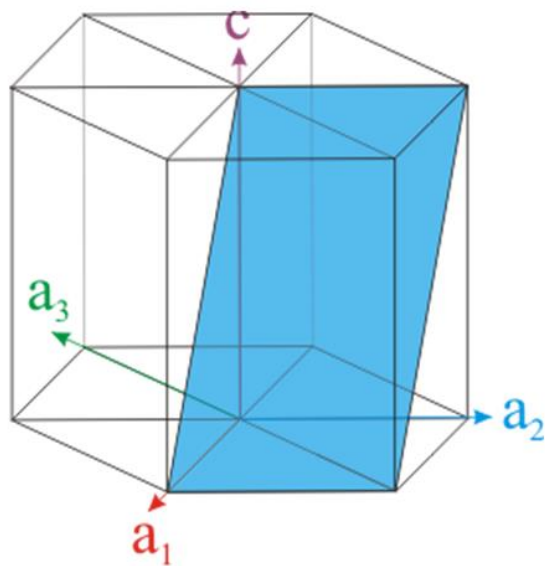
Reciprocal lengths obtained by intercepts of plane with axes:

(hkl) for a specific plane

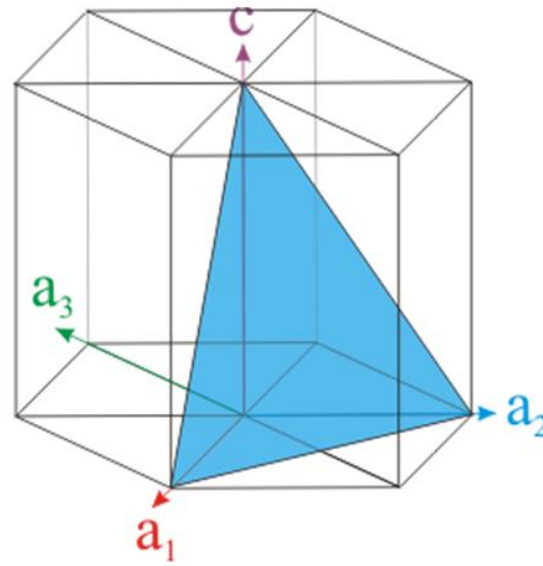
(perpendicular to direction $[hkl]$ for cubic, not in general)

$\{hkl\}$ for a set of all equivalent planes

again hkl instead of hkl ($i = -h-k$) for hexagonal family



intercepts $1 \infty -1$
 $\Rightarrow$ plane $(1 \ 0 \ \bar{1} \ 1)$



intercepts $1 \ 1 \ -\frac{1}{2}$
 $\Rightarrow$ plane $(1 \ 1 \ \bar{2} \ 1)$

Point groups

How many times more are there qualitatively different (differently symmetric) crystal structures than Bravais lattices?

Bravais lattice	Crystal structure
7 (see crystal systems)	32 point groups
14 (see Bravais lattices)	230 space groups

Point groups

first possible notation: Schoenflies

first the most qualitatively different ones (11 groups with different rotation axes)

C_n : only one n-fold rotation axis (C_1 , C_2 , C_3 , C_4 , C_6)

D_n : n-fold rotation axis + n 2-fold axes perpendicular to it (D_2 , D_3 , D_4 , D_6)

O : group of octahedron of cube (3×4-fold + 4×3-fold + 6×2-fold)

T : group of tetrahedron (4×3-fold + 3×2-fold)

now add center and planes of symmetry (other 21 groups)

C_{ni} : C_n + inversion ($C_{1i} = C_i$, C_{3i} , $C_{4i} = S_4$, [$C_{6i} = C_{3h}$ is elsewhere])

C_{nh} : C_n + plane of symmetry perpendicular to the rot. axis ($C_{1h} = C_s$, C_{2h} , C_{3h} , C_{4h} , C_{6h})

C_{nv} : C_n + n planes of symmetry containing the rotation axis (C_{2v} , C_{3v} , C_{4v} , C_{6v})

D_{nh} : D_n + plane of symmetry perpendicular to the n-fold rot. axis (D_{2h} , D_{3h} , D_{4h} , D_{6h})

D_{nd} : D_n + n planes of symmetry containing the n-fold rotation axis (D_{2d} , D_{3d})

O_h : group of octahedron + inversion

T_h : group of tetrahedron + inversion

T_d : group of tetrahedron + diagonal planes of symmetry

sometimes, another group out of a pair of equivalent groups is preferred, e.g.

S_6 (rotation of 60° + mandatory mirroring in a perpendicular plane of sym.) instead of

C_{3i} (rotation of 120° and/or inversion - contrary to S_6 only one of these two can happen)

Point groups

second possible notation: Hermann-Mauguin

first the most qualitatively different ones (11 groups with different rotation axes)

C_1, C_2, C_3, C_4, C_6	→	1, 2, 3, 4, 6
D_2, D_3, D_4, D_6	→	222, 32, 422, 622
O	→	432
T	→	23

now add center and planes of symmetry (other 21 groups)

$C_i, C_{3i}, C_{4i}, [C_{6i}]$	→	$\bar{1}, \bar{3}, \bar{4}, [\bar{6} \text{ is elsewhere}]$
$C_{1h} = C_s, C_{2h}, C_{3h}, C_{4h}, C_{6h}$	→	m, 2/m, 3/m = $\bar{6}$, 4/m, 6/m
$C_{2v}, C_{3v}, C_{4v}, C_{6v}$	→	mm2, 3m, 4mm, 6mm
$D_{2h}, D_{3h}, D_{4h}, D_{6h}$	→	mmm, $\bar{6}m2$, 4/mmm, 6/mmm
D_{2d}, D_{3d}	→	$\bar{4}2m, \bar{3}m$
O_h	→	$m\bar{3}m$
T_h	→	$m\bar{3}$
T_d	→	$\bar{4}3m$

m = mirror = plane of symmetry, m behind slash = plane of symmetry perpendicular to the plane before slash, bar above number = plane of symmetry containing the axis

Point groups

relationship with crystal systems

	Schoenflies	Hermann - Mauguin
triclinic	C_1, C_i	$1, \bar{1}$
monoclinic	C_2, C_s, C_{2h}	$2, m, 2/m$
orthorhombic	D_2, C_{2v}, D_{2h}	$222, mm2, mmm$
tetragonal	$C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h}$	$4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$
cubic	T, T_d, T_h, O, O_h	$23, \bar{4}3m, m\bar{3}, 432, m\bar{3}m$
trigonal	$C_3, C_{3i}, D_3, C_{3v}, D_{3d}$	$3, \bar{3}, 32, 3m, \bar{3}m$
hexagonal	$C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}$	$6, \bar{6}, 6/m, 622, 6mm, \bar{6}m2, 6/mmm$

The order of symbols matters in the Hermann-Mauguin case: the symmetry (rotation axis) of the highest order is at the first place - e.g. 432 in the cubic case. Further convention in this field says that for all groups of the cubic system, the letter '3' will be at the second place. This allows one to distinguish

- $m\bar{3}$ (cubic): there are four 3-fold rotation axes, let alone other axes
- $\bar{3}m$ (trigonal): there is only one 3-fold rotation axis

Point groups

example for cube

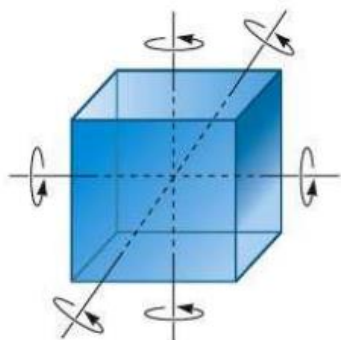
cubic

Schoenflies

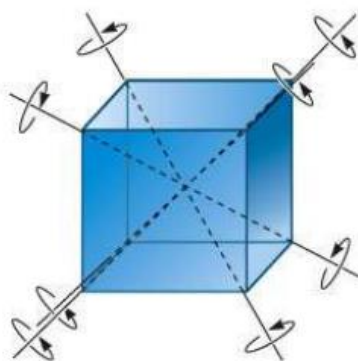
T , T_d , T_h , O , O_h

Hermann - Mauguin

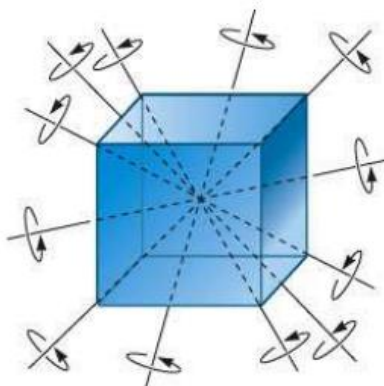
23 , $\bar{4}3m$, $m\bar{3}$, 432 , $m\bar{3}m$



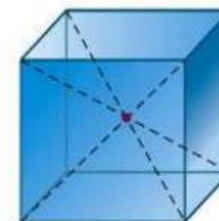
Three 4-fold axes



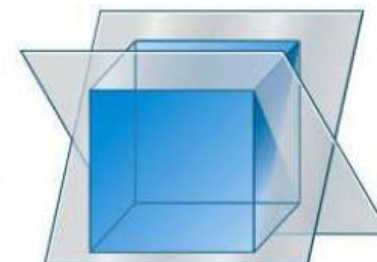
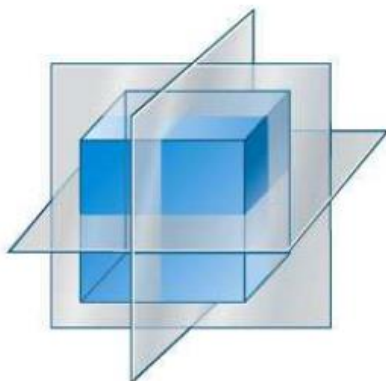
Four 3-fold axes



Six 2-fold axes



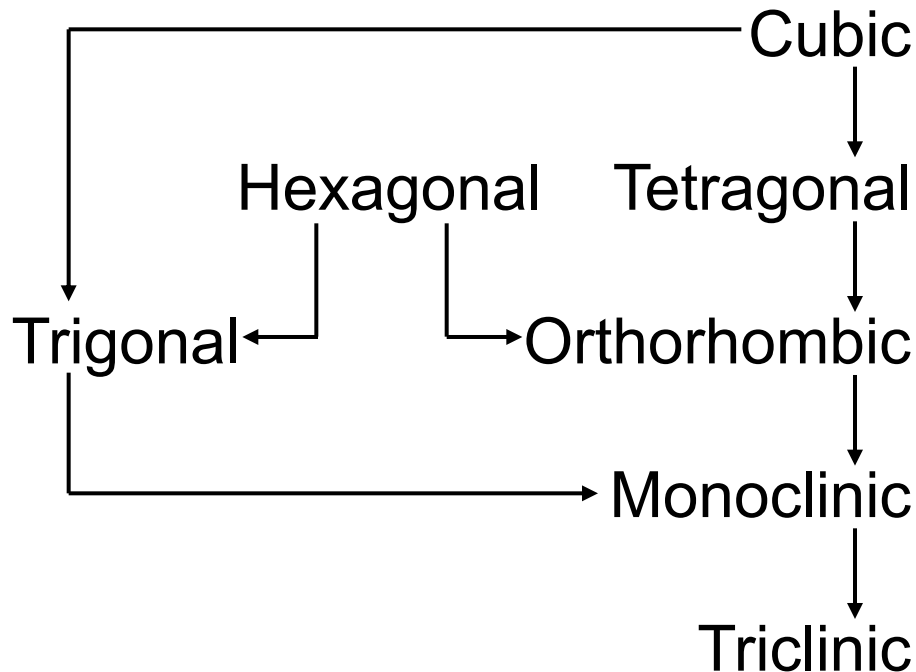
Center of inversion



Nine mirror planes

Hierarchy of crystal systems

Arrows from more symmetrical lattices to the less symmetrical ones (to point groups which are subsets of the starting one)



See also increasing number of independent components of the elastic tensor along the arrows in the chapter about mech. prop.

Laue classes

Crystal family	Crystal system (total 7)	Laue class (total 11)
cubic	cubic	$m\bar{3}$, $m\bar{3}m$
tetragonal	tetragonal	4/m, 4/mmm
orthorhombic	orthorhombic	mmm
monoclinic	monoclinic	2/m
triclinic	triclinic	$\bar{1}$
hexagonal	trigonal	$\bar{3}$, $\bar{3}m$
	hexagonal	6/m, 6/mmm

If we add a center of sym. everywhere, we end up with only 11 out of 32 (see also 11 "most qualitatively different" groups above) ... and the center of sym. does not affect the sym. of the XRD diffraction pattern



only 11 symmetries of the diffraction pattern (Laue classes): 1 centrosym. group which defines the notation of the Laue class, plus 1-3 non-centrosym.

Tensor description of cryst. properties

$$\begin{array}{ccccc} \text{Effect} & = & \text{Property} & \times & \text{Action} \\ n^{\text{th}} \text{ order tensor} & & (n+m)^{\text{th}} \text{ order tensor} & & m^{\text{th}} \text{ order tensor} \end{array}$$

1st order tensor, i.e. vector

- pyroelectricity (vector effect, scalar action)
- electrocaloricity (scalar effect, vector action)

2nd order tensor

- electrical and thermal conductivity (vect. effect, vect. action)
- permittivity and other optical prop. (vect. effect, vect. action)
- thermal expansion (tensor effect, scalar action)

3rd order tensor

- piezoelectricity (vector effect, tensor action)

4th order tensor

- elastic deformation (tensor effect, tensor action)

Tensor description of cryst. properties

$$\begin{array}{ccccc} \text{Effect} & = & \text{Property} & \times & \text{Action} \\ n^{\text{th}} \text{ order tensor} & & (n+m)^{\text{th}} \text{ order tensor} & & m^{\text{th}} \text{ order tensor} \end{array}$$

Neumann principle: tensor of a crystal property is at least as symmetrical as the crystal itself

Thus, the symmetry (as expressed e.g. by providing the corresponding group: the group of symmetry elements of each property contains all symmetry elements of the crystal point group) e.g. defines whether some properties of crystals and molecules can have non-zero values

Point groups

relationship with crystal properties

As pointed out above, the symmetry (as expressed e.g. by the corresponding point group) defines some crystal properties

Example 1: group does not have center or planes of sym., only rotational axes (is enantiomorphous) ... **necessary condition for rotating the plane of polarization of polarized light** (other molecules do that if equally oriented, not in a liquid state)

Example 2: group does not have center of symmetry ... **necessary condition for piezoelectricity**

Example 3: unique polar axis (the only rotation axis, no center of sym., no planes of sym. which do not contain the axis) ... **necessary (and sufficient) condition for pyroelectricity**

Example 4: dependence of birefringence on crystal system

Point groups

relationship with crystal properties

As pointed out above, the symmetry (as expressed e.g. by the corresponding point group) defines some crystal properties

32 point groups				
do not have center of symmetry (21 groups)				do have center of symmetry (11 groups), therefore non-piezoelectric
piezoelectric (20 groups)			group 432 is neither piezoelectric (although it does not have center of symmetry) nor polar	
polar, pyroelectric (10 groups)		piezoelectric but not polar, therefore non-pyroelectric (10 groups)		
ferroelectric materials	non-ferroelectric materials			

Point groups

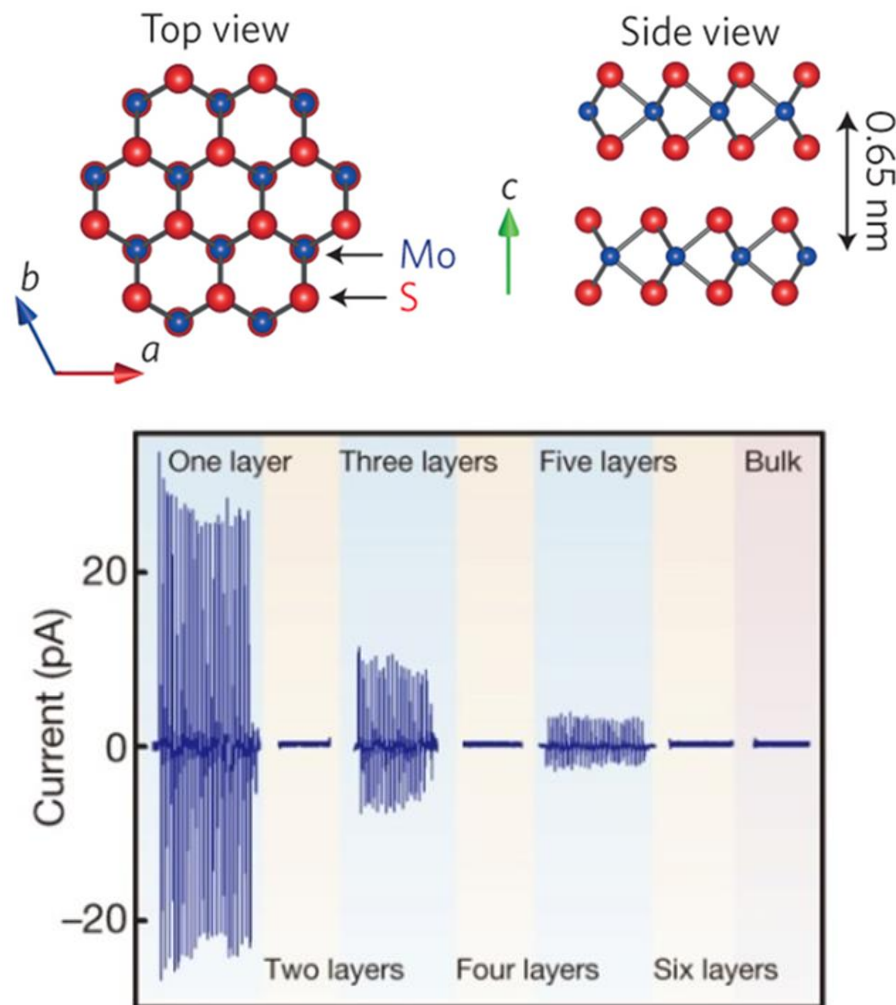
example illustrating the knowledge on previous slides

Hexagonal MoS_2 :

1 monolayer of primitive cells
(3 monolayers of atoms) does
not have center of sym. $\Rightarrow$ is
(allowed to be) piezoelectric

2 monolayers of primitive
cells do have center of sym.
 $\Rightarrow$ piezoelectricity disappears

The same repeats
(with decreasing intensity)
for any odd and even
number of monolayers



[W. Wu et al., Nature 514, 470 (2014)]

Space groups

first possible notation: Schoenflies

notation of space group notation

=

notation of point group (which is behind this space group)

+

serial number in the superscript

E.g. O_h^9 = ninth group of the crystallographic subset O_h

Heavily depends on the knowledge of the convention
(the transition from point to space groups makes
Schoenflies less illustrative than Hermann-Mauguin)

Space groups

second possible notation: Hermann-Mauguin

notation of space group notation

=

notation of point group (which is behind this space group)

+

initial letter defining the lattice (see also above)

P primitive

I body centered (Innenzentriert)

F face centered (Flächenzentriert)

A/B/C centered on A/B/C faces only

R rhombohedral

Space groups

second possible notation: Hermann-Mauguin

notation of space group notation

=

notation of point group (which is behind this space group)

+

initial letter defining the lattice

If there is a glide plane (instead of common plane of symmetry), the letter 'a/b/c/d/e/n' (instead of 'm') denotes the size and direction of the shift which accompanies the reflection

If there is a screw axis (instead of common axis of rotation), the number in subscript denotes the size of shift (along the axis) which accompanies the rotation

E.g. the point group $mm2$ is behind $Pmm2$, $Pma2$, $Cmm2$, $Cmc2_1$, ...

Space groups

relation to the *Strukturbericht* notation

Strukturbericht symbol (A_n , B_n , C_n , etc.) contains:

- info about space group (single group belongs to a symbol)
- info about elements (multiple symbols belong to a group)

Specifically:

- A: single elements e.g. Cu ($\bar{F}m3m \Rightarrow A1$)
- B: two elements XY e.g. NaCl ($\bar{F}m3m \Rightarrow B1$)
- C: two elements X_2Y and XY_2 e.g. CaF_2 ($\bar{F}m3m \Rightarrow C1$)
- D: two elements with other stoichiometry e.g. Al_2O_3
- E: multiple elements with 1-atom ions e.g. $CaTiO_3$
- F: multiple elements with 2 to 3-atom ions e.g. $Na^+(NO_2)^-$
- G: multiple elements with 4-atom ions e.g. $Ca^{2+}(CO_3)^{2-}$
- H: multiple elements with 5-atom ions e.g. $Ca^{2+}(SO_4)^{2-}$
- L: alloys, S: silicates, etc.

Atomic coordinates corresponding to 230 space groups

see e.g. <http://www.cryst.ehu.es/cgi-bin/cryst/programs/nph-wp-list>

Table of Space Group Symbols

No space group has been selected by now.

Click over the group name to see the group Wyckoff positions

1	<i>P</i> 1	2	<i>P</i> -1	3	<i>P</i> 2:unique axis b <i>P</i> 2:unique axis c
4	<i>P</i> 2 ₁ :unique axis b <i>P</i> 2 ₁ :unique axis c	5	<i>C</i> 2:unique axis b <i>C</i> 2:unique axis c	6	<i>P</i> m:unique axis b <i>P</i> m:unique axis c
7	<i>P</i> c:unique axis b <i>P</i> c:unique axis c	8	<i>C</i> m:unique axis b <i>C</i> m:unique axis c	9	<i>C</i> c:unique axis b <i>C</i> c:unique axis c
10	<i>P</i> 2/ <i>m</i> :unique axis b <i>P</i> 2/ <i>m</i> :unique axis c	11	<i>P</i> 2/ <i>m</i> :unique axis b <i>P</i> 2/ <i>m</i> :unique axis c	12	<i>C</i> 2/ <i>m</i> :unique axis b <i>C</i> 2/ <i>m</i> :unique axis c
13	<i>P</i> 2/ <i>c</i> :unique axis b <i>P</i> 2/ <i>c</i> :unique axis c	14	<i>P</i> 2/ <i>c</i> :unique axis b <i>P</i> 2/ <i>c</i> :unique axis c	15	<i>C</i> 2/ <i>c</i> :unique axis b <i>C</i> 2/ <i>c</i> :unique axis c
16	<i>P</i> 222	17	<i>P</i> 22 ₁	18	<i>P</i> 2 ₁ 2 ₁ 2
19	<i>P</i> 2 ₁ 2 ₁ 2 ₁	20	<i>C</i> 222 ₁	21	<i>C</i> 222
22	<i>I</i> 222	23	<i>I</i> 222	24	<i>I</i> 2 ₁ 2 ₁ 2 ₁
25	<i>P</i> m <i>m</i> 2	26	<i>P</i> mc2 ₁	27	<i>P</i> cc2
28	<i>P</i> ma2	29	<i>P</i> ca2 ₁	30	<i>P</i> nc2
31	<i>P</i> mn2 ₁	32	<i>P</i> ba2	33	<i>P</i> na2 ₁
34	<i>P</i> nn2	35	<i>C</i> mm2	36	<i>C</i> mc2 ₁
37	<i>C</i> cc2	38	<i>A</i> mm2	39	<i>A</i> em2
40	<i>A</i> ma2	41	<i>A</i> ea2	42	<i>F</i> mm2
43	<i>F</i> dd2	44	<i>I</i> mm2	45	<i>I</i> ba2
46	<i>I</i> ma2	47	<i>P</i> mmm	48	<i>P</i> nnn:origin choice 1 <i>P</i> nnn:origin choice 2
49	<i>P</i> ccm	50	<i>P</i> ban:origin choice 1 <i>P</i> ban:origin choice 2	51	<i>P</i> m <i>m</i> a
52	<i>P</i> n <i>n</i> a	53	<i>P</i> m <i>n</i> a	54	<i>P</i> cca
55	<i>P</i> b <i>m</i> a	56	<i>P</i> ccn	57	<i>P</i> bcm
58	<i>P</i> n <i>n</i> m	59	<i>P</i> mmn:origin choice 1 <i>P</i> mmn:origin choice 2	60	<i>P</i> bcn
61	<i>P</i> bca	62	<i>P</i> n <i>m</i> a	63	<i>C</i> mc <i>m</i>
64	<i>C</i> mce	65	<i>C</i> mmm	66	<i>C</i> cc <i>m</i>
67	<i>C</i> mme	68	<i>C</i> cce:origin choice 1 <i>C</i> cce:origin choice 2	69	<i>F</i> mmm
70	<i>F</i> ddd:origin choice 1 <i>F</i> ddd:origin choice 2	71	<i>I</i> mmm	72	<i>I</i> bam
73	<i>I</i> bca	74	<i>I</i> mma	75	<i>P</i> 4
76	<i>P</i> 4 ₁	77	<i>P</i> 4 ₂	78	<i>P</i> 4 ₃
79	<i>I</i> 4	80	<i>I</i> 4 ₁	81	<i>P</i> -4
82	<i>I</i> -4	83	<i>P</i> 4/ <i>m</i>	84	<i>P</i> 4 ₂ / <i>m</i>
85	<i>P</i> 4/ <i>n</i> :origin choice 1 <i>P</i> 4/ <i>n</i> :origin choice 2	86	<i>P</i> 4 ₂ / <i>n</i> :origin choice 1 <i>P</i> 4 ₂ / <i>n</i> :origin choice 2	87	<i>I</i> 4/ <i>m</i>
88	<i>I</i> 4 ₁ / <i>a</i> :origin choice 1 <i>I</i> 4 ₁ / <i>a</i> :origin choice 2	89	<i>P</i> 422	90	<i>P</i> 42 ₁ 2
91	<i>P</i> 4 ₂ 2	92	<i>P</i> 4 ₂ 2	93	<i>P</i> 4 ₂ 2

Wyckoff Positions of Group 35 (*C*mm2)

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
			(0,0,0) + (1/2,1/2,0) +
8	f	1	(x,y,z) (-x,-y,z) (x,-y,z) (-x,y,z)
4	e	m..	(0,y,z) (0,-y,z)
4	d	.m.	(x,0,z) (-x,0,z)
4	c	..2	(1/4,1/4,z) (1/4,3/4,z)
2	b	mm2	(0,1/2,z)
2	a	mm2	(0,0,z)

Wyckoff position and site symmetry group of a specific point

Specify the point by its relative coordinates (in fractions or decimals)
Variable parameters (x,y,z) are also accepted

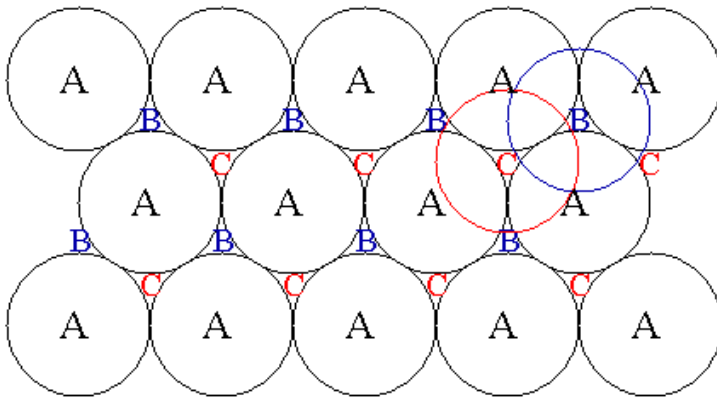
x = y = z =

Show

If you want to see the Wyckoff position in other setting, click here

Close packed structures (cannonball problem)

Crucial for unary metals
(in the case of covalent materials,
role of bonding angles etc.
makes it more complicated)

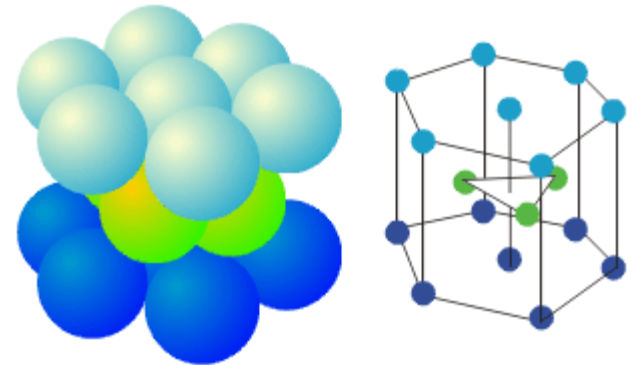


For fixed layers 'A' and 'B', the
third layer can be placed in two
equally meaningful & justified
ways: 'A' or 'C'

Close packed structures

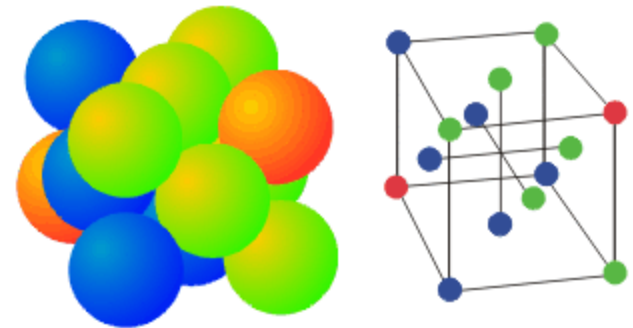
(cannonball problem)

Sequence ABABAB (Ti, Zr, Hf, ...) :
hexagonal close packed lattice, hcp
(= two simple hexagonal Bravais
lattices inside each other
= hexagonal Bravais lattice
with two-atom basis)



Sequence ABCABC (Al, Cu, Ni, ...) :
cubic face centered lattice, fcc

Why do not we look at it like at
a hexagonal Bravais lattice with
a three-atom basis? Possible, but
redundant - it's a fcc cube on a corner.



Are these packings really the closest?

Intuitively already Kepler 1611

Sacrae Caesareae Maiestatis Mathematici
= Mathematician to His Sacred Imperial
Majesty

in Strena Seu de Nive Sexangula
= A New Year's Gift, or On the Six-
Cornered Snow

proof Hales 1998

computer checking of the long proof 2017



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1

A FORMAL PROOF OF THE KEPLER CONJECTURE

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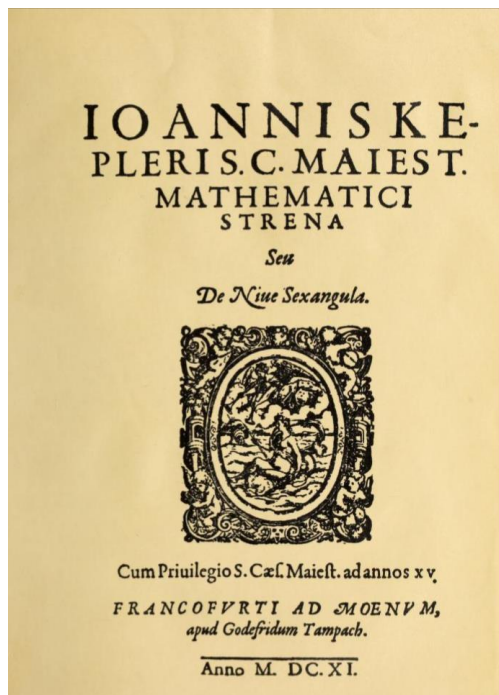
Abstract

This article describes a formal proof of the Kepler conjecture on dense sphere packings in a combination of the HOL Light and Isabelle proof assistants. This paper constitutes the official published account of the now completed Flyspeck project.

2010 Mathematics Subject Classification: 52C17

1. Introduction

The booklet *Six-Cornered Snowflake*, which was written by Kepler in 1611, contains the statement of what is now known as the Kepler conjecture: no packing of congruent balls in Euclidean three-space has density greater than that of the face-centered cubic packing [27]. This conjecture is the oldest problem in discrete geometry. The Kepler conjecture forms part of Hilbert's 18th problem, which raises questions about space groups, anisohedral tilings, and packings in Euclidean space. Hilbert's questions about space groups and anisohedral tiles were answered by Bieberbach in 1912 and Reinhardt in 1928. Starting in the 1950s, Fejes Tóth gave a coherent proof strategy for the Kepler conjecture and eventually suggested that computers might be used to study the problem [6]. The truth of the Kepler conjecture was established by Ferguson and Hales in 1998, but their proof was not published in full until 2006 [18].



In reality it is not that simple

ABABAB (Ti, Zr, Hf, ...) : hexagonal close packed lattice, hcp

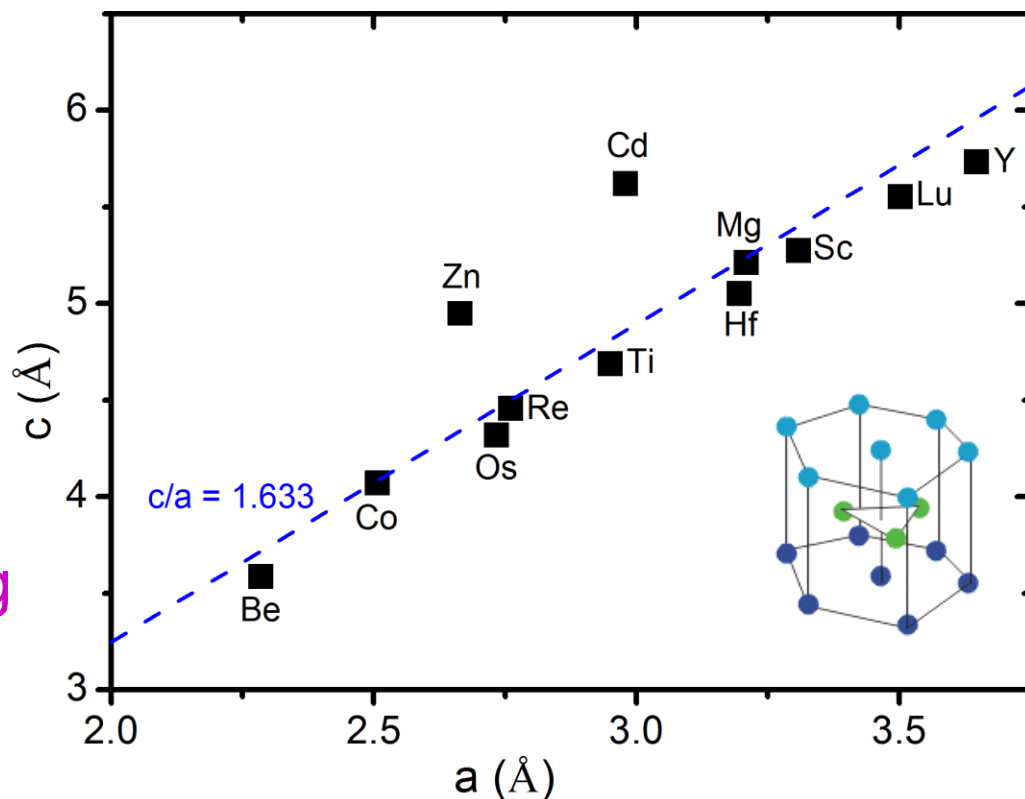
In an ideal case $c/a = 2\sqrt{2/3} = 1.633$

The real value is usually different,
e.g. for two extremal cases

$$(c/a)_{\text{Zn}} = 1.856$$

$$(c/a)_{\text{Cd}} = 1.886$$

The filled orbitals
($nd^{10}.[n+1]s^2$) Zn a Cd
(and liquid Hg) $\Rightarrow$ weaker
interatomic bonds, lower
motivation for close packing

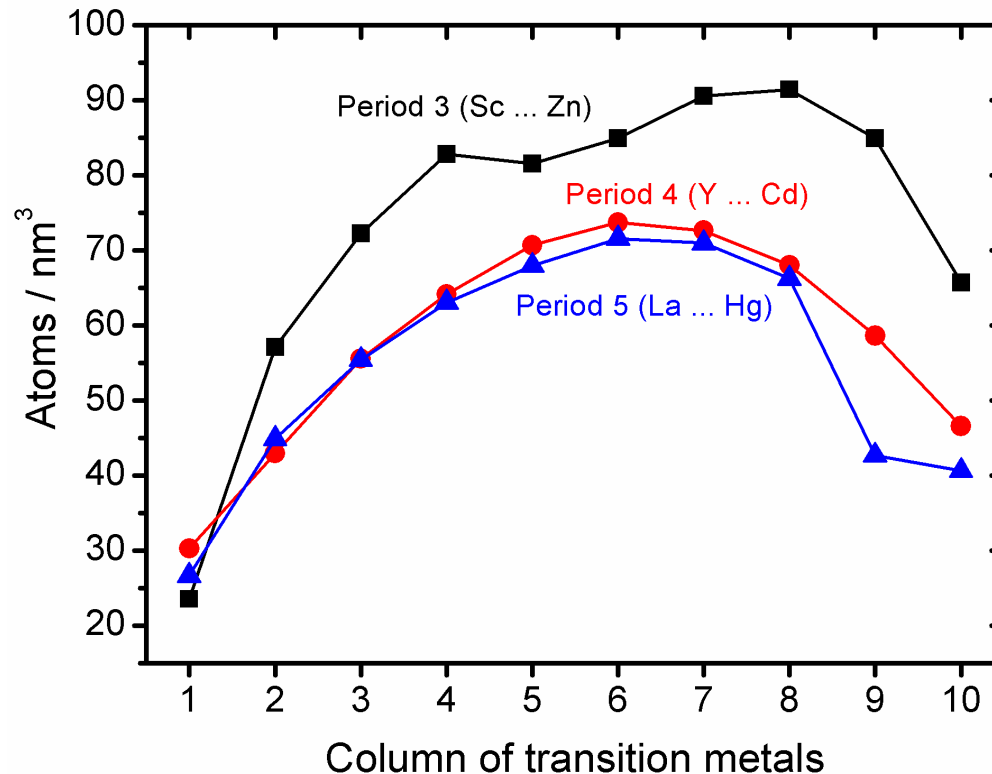


Atomic size $\Leftrightarrow$ lattice constants

example for transition metals (without lanthanoids)

Atomic size is given by the radius of the shell with valence electrons, regardless the number of these electrons.

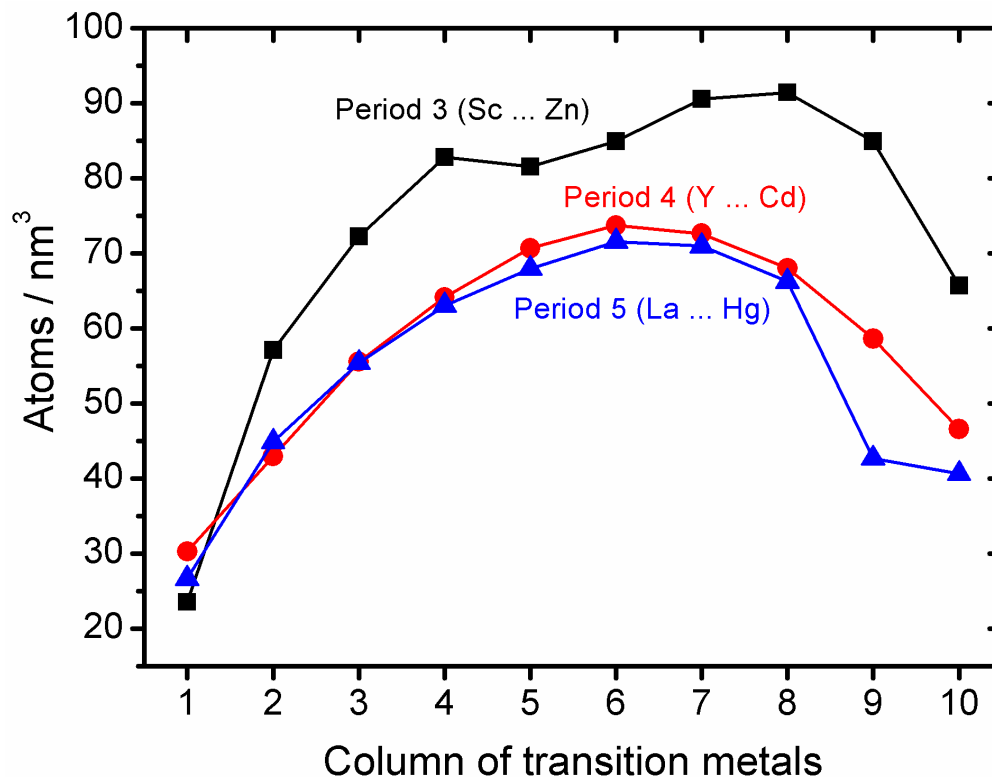
The electrons are attracted by the corresponding number of protons (the rest of the core is shielded by the inner shells).



Atomic size $\Leftrightarrow$ lattice constants

example for transition metals (without lanthanoids)

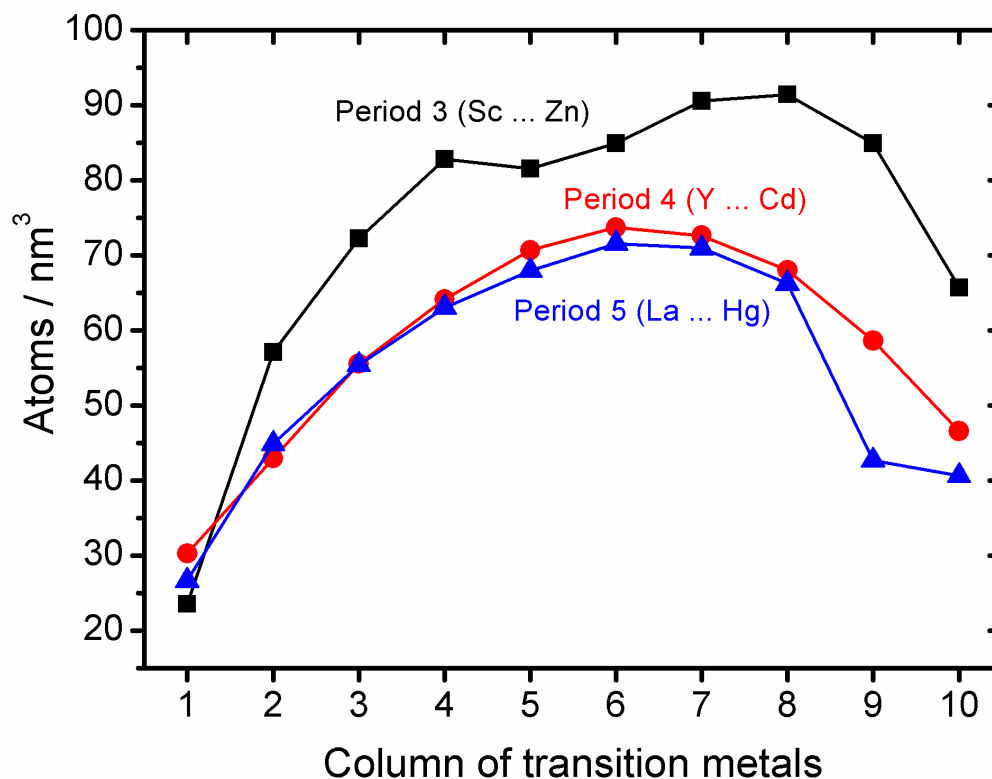
At the start of d-block the atomic size decreases, because valence electrons are attracted by increasing charge. In the second half of the d-block (even before the d-orbital gets filled) the trend turns because the electrons start to interfere



Atomic size $\Leftrightarrow$ lattice constants

example for transition metals (without lanthanoids)

In parallel, we would expect that the size increases with the line number (valence shell number). It indeed does between line 3 and 4, but much less between line 4 and 5. Why so?



Atomic size $\Leftrightarrow$ lattice constants

example for transition metals (without lanthanoids)

In parallel, we would expect that the size increases with the line number (valence shell number). It indeed does between line 3 and 4, but much less between line 4 and 5. Why so?

Because at the same time the size decreases to the right (see above), and metals in line 4 are of 14 columns more on the right due to lanthanoids. D-electrons are attracted by 14 extra protons, which are only partially shielded by 14 extra electrons.

H Hydrogen 1.008																																				He Helium 4.001
3 Li Lithium 6.941	4 Be Beryllium 9.012																	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180													
11 Na Sodium 22.990	12 Mg Magnesium 24.305																	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948													
19 K Potassium 39.098	20 Ca Calcium 40.078																	21 Sc Scandium 44.956	22 Ti Titanium 47.887	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798			
37 Rb Rubidium 85.468	38 Sr Strontium 87.62																	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29			
55 Cs Cesium 132.905	56 Ba Barium 137.327	57 La Lanthanum 138.905	58 Ce Cerium 140.12	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.257	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium 209	85 At Astatine 209	86 Rn Radon 222					
87 Fr Francium 223	88 Ra Radium 226	89 Ac Actinium 227	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.08	99 Es Einsteinium 252.083	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium 262	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 266	107 Bh Bohrium 264	108 Hs Hassium 277	109 Mt Meitnerium 268	110 Ds Darmstadtium 271	111 Rg Roentgenium 272	112 Cn Copernicium 285	113 Nh Nihonium 284	114 Fl Flerovium 289	115 Mc Moscovium 288	116 Lv Livermorium 293	117 Ts Tennessine 294	118 Og Oganesson 294					

Why are alkali metals bcc

(i.e. not close packed, fcc or hcp)

There are only 's' valence electrons (spherical orbitals). All the more we would not expect directionality (dependence on bonding angles etc.) making the material non-close-packed.

Why are alkali metals bcc

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There are only 's' valence electrons (spherical orbitals). All the more we would not expect directionality (dependence on bonding angles etc.) making the material non-close-packed.

While the bcc lattice has slightly higher energy, it has (due to the non-close packing) higher entropy. Thus, metals often transform to bcc at higher temperature, in order to minimize the Gibbs energy $G = H - TS$.

Room temperature is high temperature for alkali metals (note the low melting temperatures - potassium 63°C, sodium 97°C, ...), so they are already transformed to bcc at this temperature (while e.g. sodium is hcp at 0 K)

Possible stacking of layers A,B,C

Hcp and fcc (see also above) are most natural and known, but not the only ones:

Sequence ABABAB (Ti, Zr, Hf, ...) :
hexagonal close packed lattice, hcp

Sequence ABCABC (Al, Cu, Ni, ...) :
cubic face centered lattice, fcc

Sequence AABBAABB :
wurtzite (see below)

Sequence ABACABAC :
NiAs (also see below)

Sequence ABCACBAC and similarly :
MAX phases (also see below)

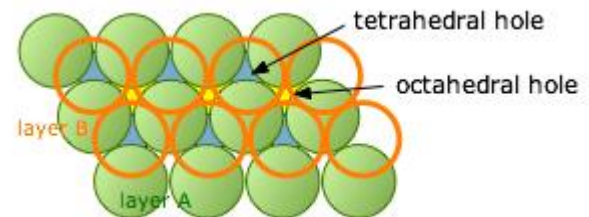
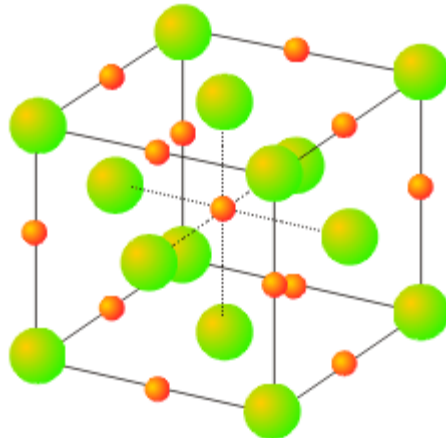
Lattices based on fcc and hcp

Atoms of the first element are often close packed

- the "holes" between them in unary metals are not used
- binary material "based on fcc/hcp" can be obtained by putting atoms of another (smaller) element into the "holes" of fcc/hcp

First option: **octahedral holes**

- centers of octahedrons formed by atoms of the first element
- fcc case: center and centers of edges of the cube
- coordination number 6
- one octahedral hole per one atom of the first element



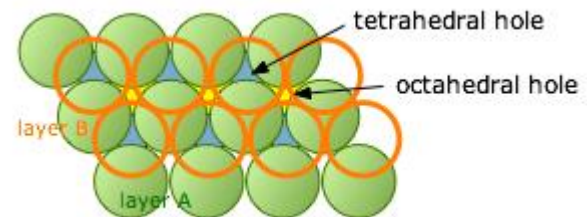
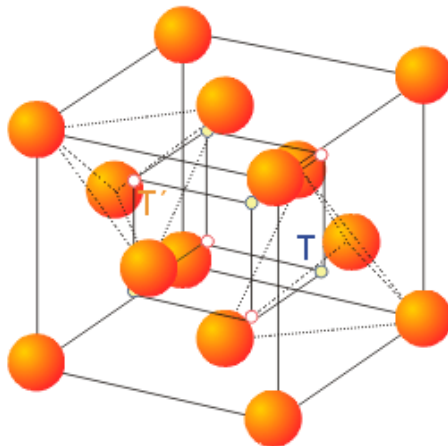
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Second option: **tetrahedral holes**

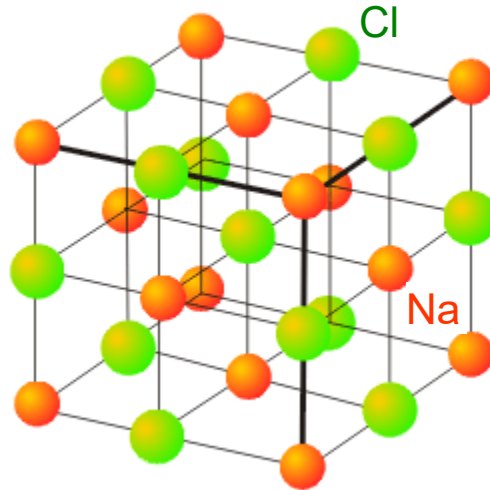
- centers of tetrahedrons formed by atoms of the first element
- fcc case: centers of 8 cubes which the big cube is divided to
- coordination number 4
- two tetrahedral holes (T, T') per one atom of the first element



Important binary structures

Rocksalt structure (prototype NaCl)

- **fcc** lattice of anions (Cl)
- all octahedral holes filled by cations (Na)
(= two fcc lattices shifted by $a/2$ = fcc with two-atom basis)

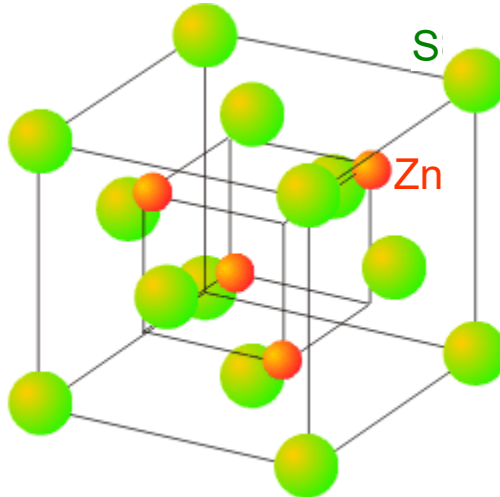


Other materials: MgO, TiN, ZrN, HfN, TiC, ZrC, HfC, ...

Important binary structures

Zincblende structure (prototype ZnS)

- **fcc** lattice of anions (S)
- 1/2 tetrahedral holes filled by cations (Zn)
(= two fcc lattices shifted by $a/4, a/4, a/4$ = fcc with 2-at. basis)
- the same element in both sublattices leads to the diamond structure

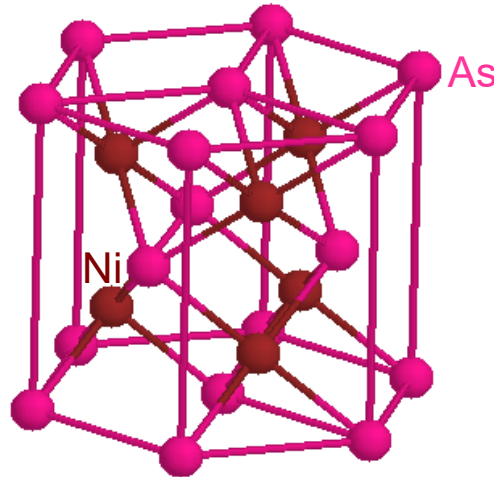


Other materials: c-BN, BP, Si, C (diamond), ...

Important binary structures

NiAs (nickeline, niccolite) structure

- **hcp** lattice of anions (As)
- all octahedral holes filled by cations (Ni)
- i.e. seq. ABACABAC with Ni in planes A (fcc-like environment) and As in planes B and C (hcp-like environment)

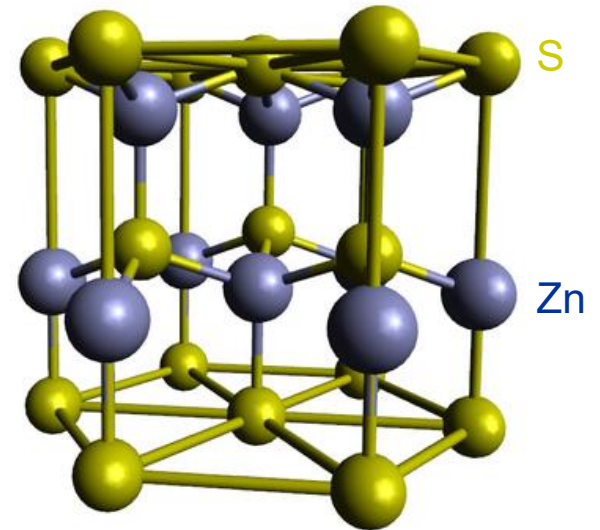


Other materials: MoN, WN (stable phase of both of them, but other phases exist as well, especially NaCl-type a WC-type), ...

Important binary structures

Wurtzite structure (prototype ZnS, not confuse with zincblende)

- **hcp** lattice of anions (S)
- 1/2 tetrahedral holes filled by cations (Zn)
(= two vertically shifted hcp lattices = hcp with two-atom basis)
- the same element in both sublattices leads to the "hexagonal diamond" structure

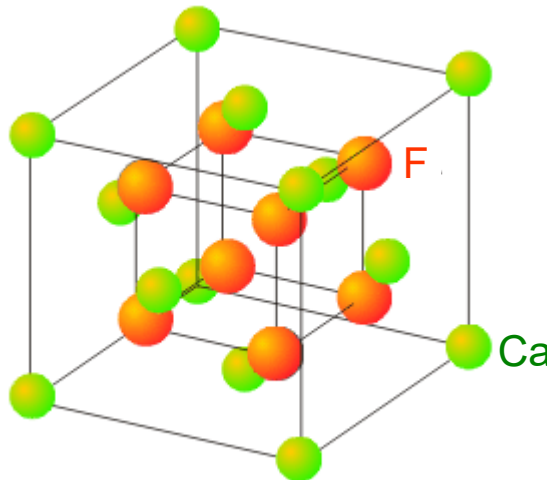


Other materials: ZnO, AlN, 2H-SiC, w-Si, w-C, ...

Important binary structures

Fluorite structure (prototype CaF_2)

- **fcc** lattice of big cations (Ca) ... in this case not anions
- all tetrahedral holes filled by anions (F)
- Antifluorite: exchanged cations and anions (i.e. close-packed lattice of anions like in other discussed structures)



Other materials: c-ZrO_2 , c-HfO_2 , CeO_2 , ...

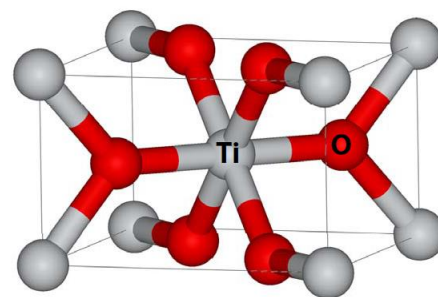
Important binary structures

Smaller size of metal atoms results in surrounding them by lower number of O atoms (lower preferred coord. number)

- big Zr: coordination 8 (c-ZrO₂, t-ZrO₂) or 7 (m-ZrO₂)
- smaller Ti: coordination 6 (both rutile TiO₂ and anatase TiO₂)

Rutile structure (prototype TiO₂)

- body-centered tetragonal lattice of cations (Ti)
- O atom in centers of triangles formed by atoms Ti



Other materials:

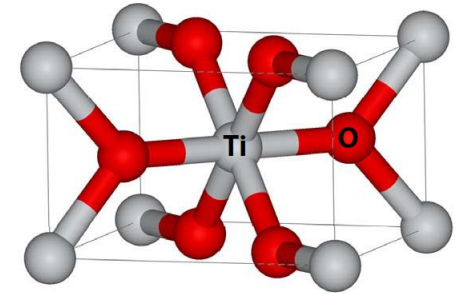
CrO₂, MnO₂, RuO₂, ... (stable)

NbO₂, TaO₂, VO₂, ... (at elevated temperature)

Important binary structures

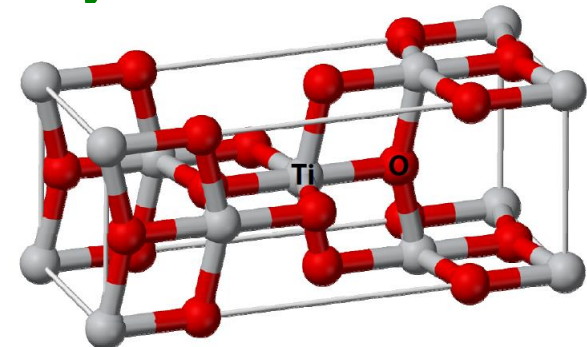
Rutile structure (prototype TiO_2)

- body-centered tetragonal lattice of cations (Ti)
- O atom in centers of triangles formed by atoms Ti
- another point of view:
distorted **hcp** lattice of anions (O)
half of octahedral holes filled by Ti



Anatase structure (prototype TiO_2)

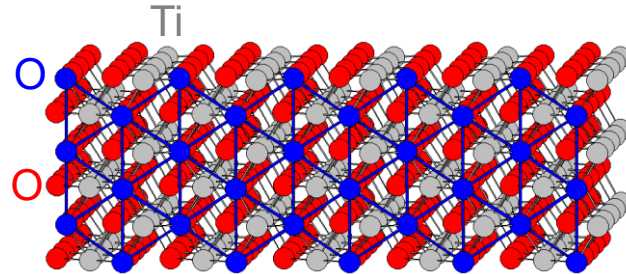
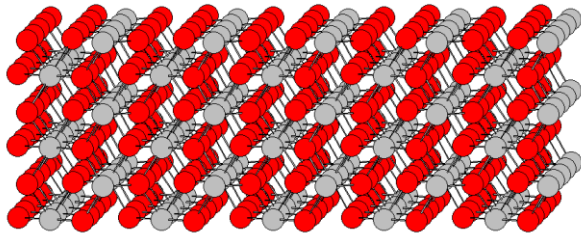
- body-centered tetragonal lattice of cations (Ti) with **2-at. basis** (alternatively triclinic cell with half the volume)
- O atom again in center of triangles formed by atoms Ti
- another point of view:
distorted **fcc** lattice of anions (O)
half of octahedral holes filled by Ti



Important binary structures

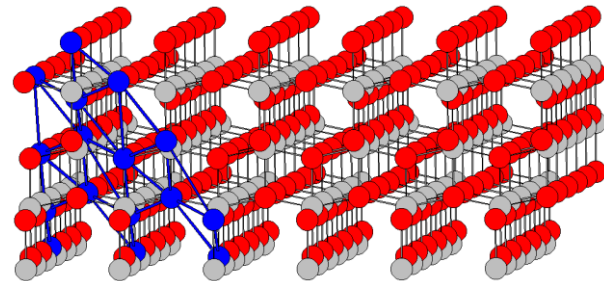
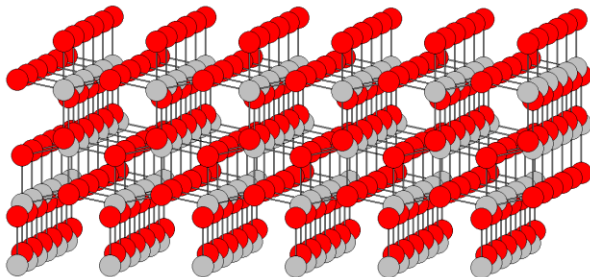
Rutile structure (prototype TiO_2)

- distorted hcp lattice of O + half of octahedr. holes filled by Ti
- close-packed planes of O are (100) (and equivalent (010))



Anatase structure (prototype TiO_2)

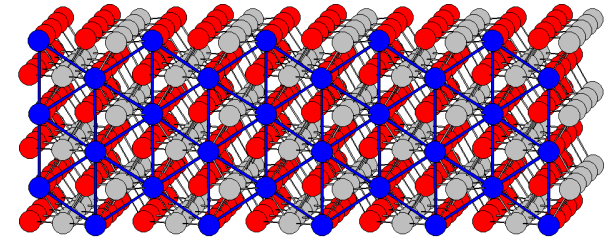
- distorted fcc lattice of O + half of octahedr. holes filled by Ti
- close-packed planes of O are (112) (and equivalent)



Important binary structures

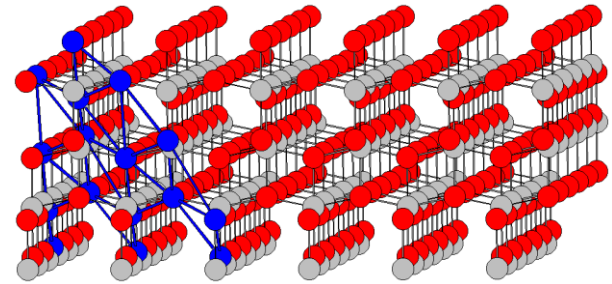
Rutile structure (prototype TiO_2)

- close-packed planes of O are (100)



Anatase structure (prototype TiO_2)

- close-packed planes of O are (112)
(face of trigonal primitive unit cell)



This yields an (approximate) ratio of lattice constants of the tetragonal conventional unit cells of both phases, e.g. for a :

$$a_{\text{rutile}} = a_{\text{O-O}}\sqrt{3}$$

$$a_{\text{anatase}} = a_{\text{O-O}}\sqrt{2}$$

$$\Rightarrow a_{\text{rutile}}/a_{\text{anatase}} = \sqrt{(3/2)} = \mathbf{1.22}$$

Experiment for TiO_2 :

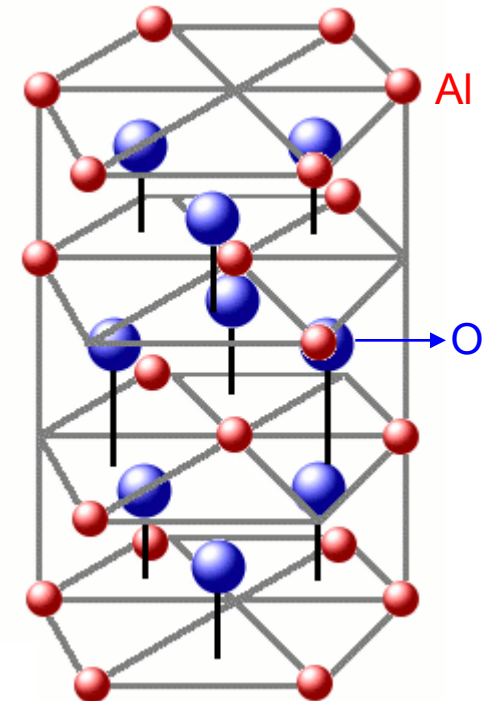
$$a_{\text{rutile}}/a_{\text{anatase}} = 4.594 / 3.785 = \mathbf{1.21}$$

Important binary structures

Corundum structure (prototype $\alpha\text{-Al}_2\text{O}_3$)

- **hcp** lattice of anions (O)
- 2/3 octahedral holes filled by cations (Al)
(alternatively the cell can be converted to rhombohedral)
- all Al atoms have coordination number 6 ($\times \gamma\text{-Al}_2\text{O}_3$ below)

(neighbouring Al atoms
are slightly vertically
shifted from each other)



Other materials:

Cr_2O_3 , Fe_2O_3 (hematite), FeTiO_3 , ...

Important binary structures

Summary of 8 aforementioned structures

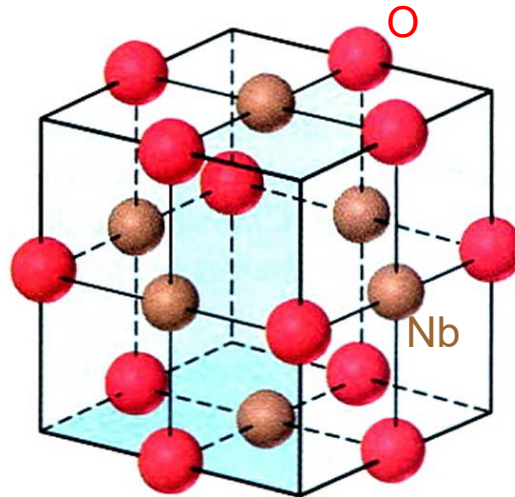
stoichiometry	occupation of O/T holes by B	element A: fcc	element A: hcp
AB	100% O	Rocksalt (NaCl, TiN)	Nickeline (NiAs, MoN)
A₃B₂	66% O	<i>nothing</i>	Corundum (Al ₂ O ₃ , Fe ₂ O ₃)
A₂B	50% O	Anatase (TiO ₂)	Rutile (TiO ₂ , VO ₂)
AB₂	100% T	Fluorite (CaF ₂ , ZrO ₂)	<i>nothing (pairs of T holes too close)</i>
AB	50% T	Zincblende (ZnS, diamond)	Wurtzite (ZnS, w-C)

the table could continue (filling of half of O holes in layers instead of uniform, filling of third of O holes, O and T holes at the same time), but the corresponding materials are less important for us

Important binary structures

NbO structure

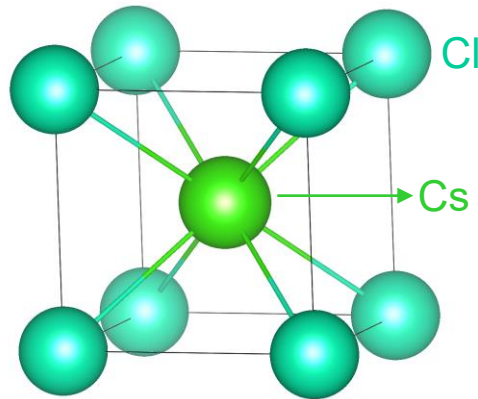
- rocksalt structure with 1/4 atoms missing
(in the figure O in the center and Nb in corners is missing)
- coord. number of both elements therefore drops from 6 to 4
(with all 4 neighbours in a single plane)



Important binary structures

CsCl structure

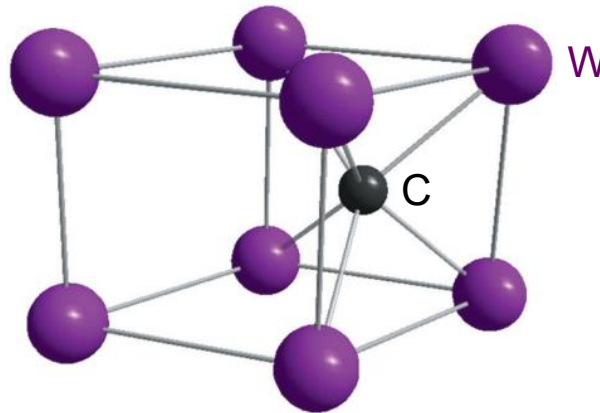
- simple cubic (not fcc) lattice of anions (Cl)
- cations in the middle of the cube (Cs)
- alternative to the rocksalt structure (e.g. NaCl), preferred if the ratio of ionic radii is close to 1 (0.93 for CsCl, 0.52 for NaCl)
- another point of view: bcc with different elements in each sublat.



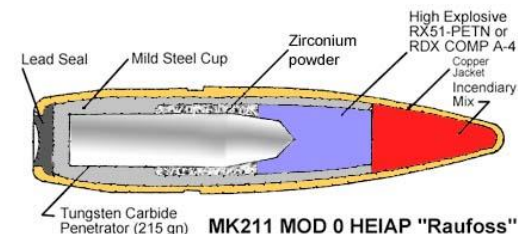
Important binary structures

WC structure

- hexagonal lattice of W (atoms above each other, i.e. not hcp)
- C atoms in the middle of each other triangular prism
- another point of view: hcp with different elements in each sublat.



Exceptionally hard material $\Rightarrow$
applications from armour-piercing
shells to scratch-resistant rings



Important binary structures

MB₂ structure (prototype AlB₂)

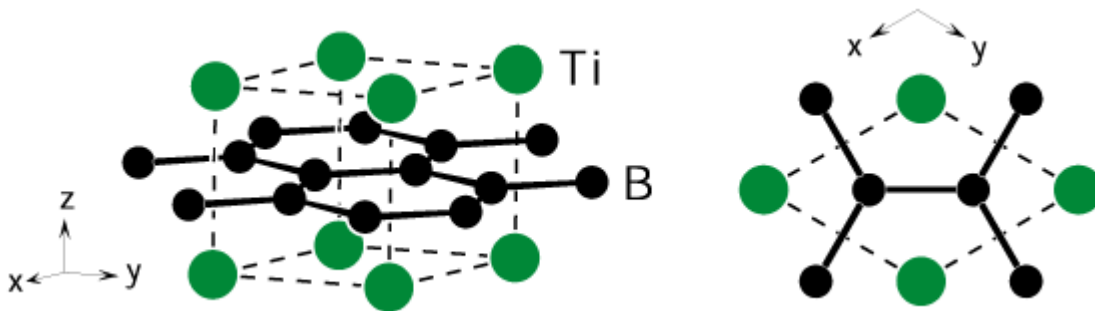
Two alternating hexagonal layers

- simple hexagonal ("graphitic") layer of B
- close-packed hexagonal layer of metal, (metal atoms are above centers of hexagons formed by B)

boron: 2 atoms per hexagon with side a

metal: 3 atoms (one in the center) per hexagon with side $a\sqrt{3}$

⇒ therefore stoichiometry AlB₂



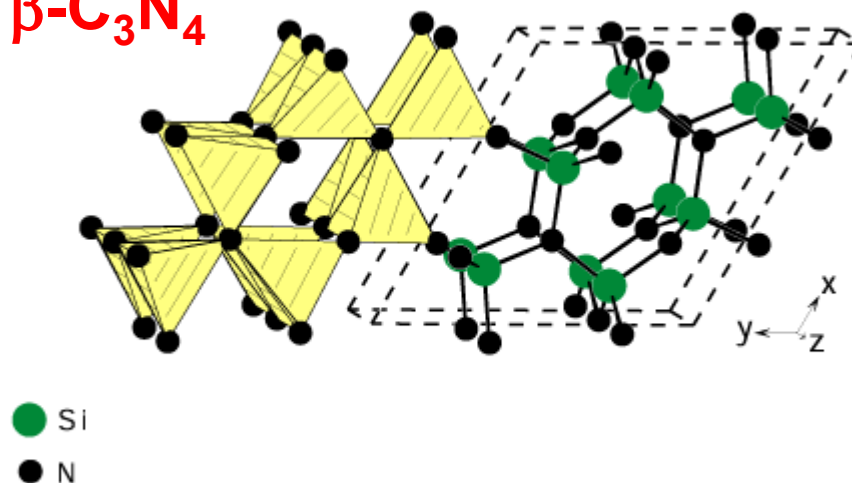
Other materials: TiB₂, ZrB₂, HfB₂, CrB₂, ...

More complicated binary structures

If there is not any template represented by close packing, single-element layers, etc., structures become less intuitive (writing atomic coordinates becomes more difficult) even for simple elemental compositions

Example 1: structure $\beta\text{-Si}_3\text{N}_4$ a $\beta\text{-C}_3\text{N}_4$

- 14 atoms ($\alpha\text{-Si}_3\text{N}_4$: 28)
in a hexagonal cell
- crystal is covalent
 $\Rightarrow$ "template" is given by preferred coordination numbers and bonding angles
 $\Rightarrow$ tetrahedrons with N in corners and Si in the middle



Extremal binary structures

If there is not any template represented by close packing, single-element layers, etc., structures become less intuitive (writing atomic coordinates becomes more difficult) even for simple elemental compositions

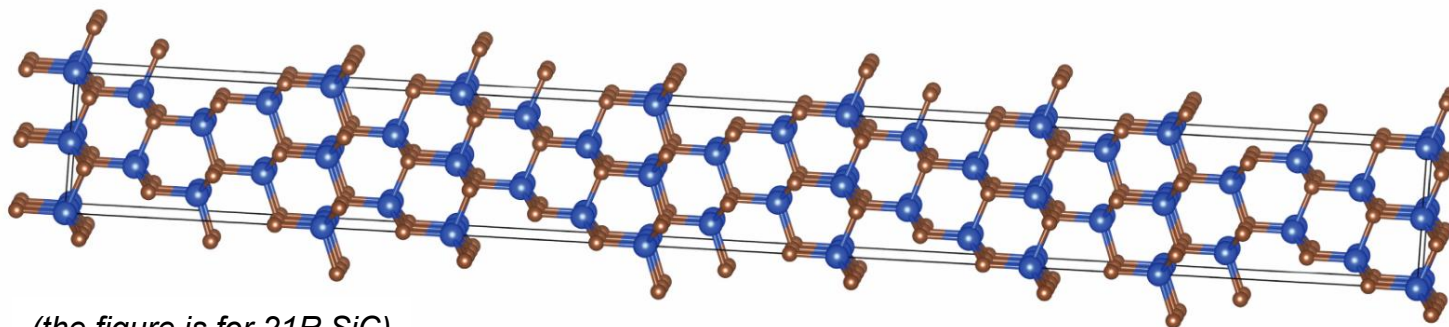
Example 2: some of >250 polymorphs of SiC

- various stackings of bilayers SiC (with atoms Si and C mutually shifted like fcc sublattices in a diamond)
- ABC (3C-SiC; diamond-like)
- AB (2H-SiC; wurtzite-like)
- ABCB (4H-SiC)
- ABCACB (6H-SiC)
- or e.g. ABCACBCABACABCB (15R-SiC)

Extremal binary structures

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- AB (2H-SiC; wurtzite-like)
- ABCB (4H-SiC)
- ABCACB (6H-SiC)
- or e.g. ABCACBCABACABCB (15R-SiC)
- extremal case 393R SiC: 393 bilayers = 786 atoms in a rhombohedral primitive cell $a = 3.073 \text{ \AA}$, $c = 987.6 \text{ \AA}$
- role of spiral stairs caused by dislocations in the crystallization seed



(the figure is for 21R SiC)

Extremal binary structures

If there is not any template represented by close packing, single-element layers, etc., structures become less intuitive (writing atomic coordinates becomes more difficult) even for simple elemental compositions

Example 3: so-called NaCd_2 (actually $\text{NaCd}_{1.92}$)

- 1192 atoms in a cubic primitive cell $\text{Na}_{408}\text{Cd}_{784}$

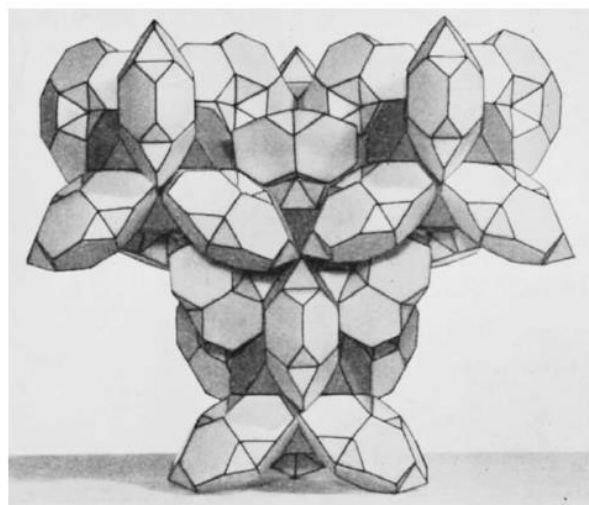


Fig. 4. Four 234-atom complexes arranged about one such complex. The four complexes are at the vertices of a regular tetrahedron

[S. Samson, *Nature* 195, 259 (1962)]

Important ternary structures

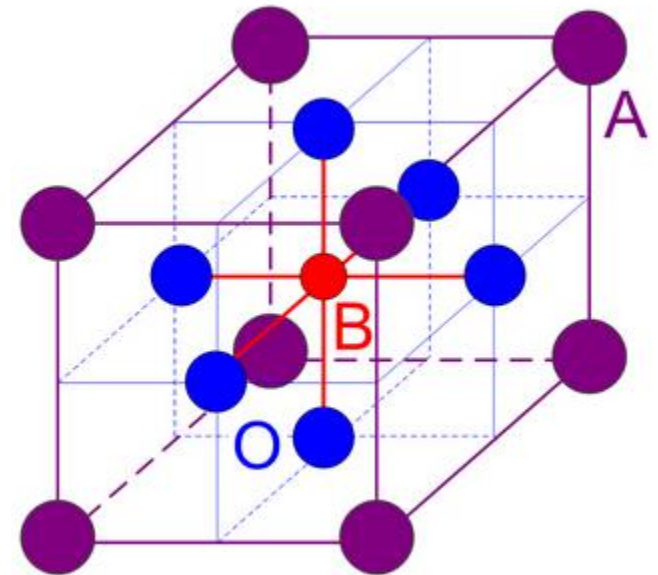
Perovskite structure (prototype CaTiO_3 , in general ABO_3)

- atoms A (bigger cation) in corners of the cube (coord. 12)
- atoms B (smaller cation) in the cube center (coord. 6)
- atoms O in centers of the faces

sometimes given after shift by vector $(a/2, a/2, a/2)$

- *atoms B in cube corners*
- *atoms A in cube center*
- *atoms O in centers of edges*

Other materials: SrTiO_3 , PbTiO_3 ,
 CaSiO_3 , LaMnO_3 , $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, ...

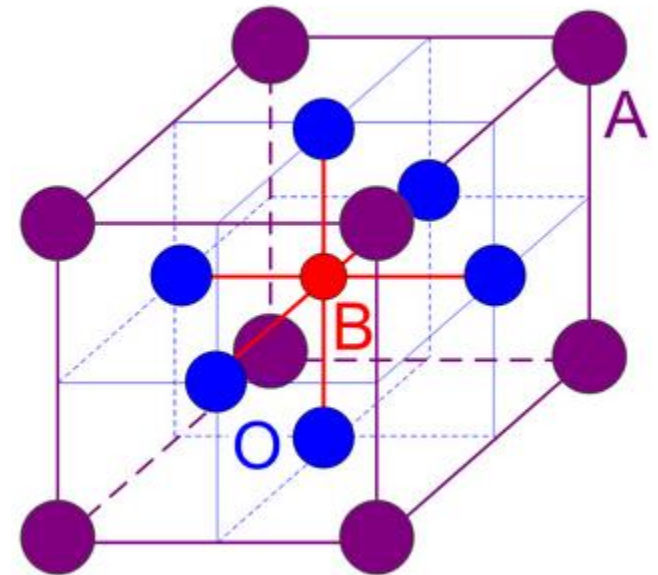
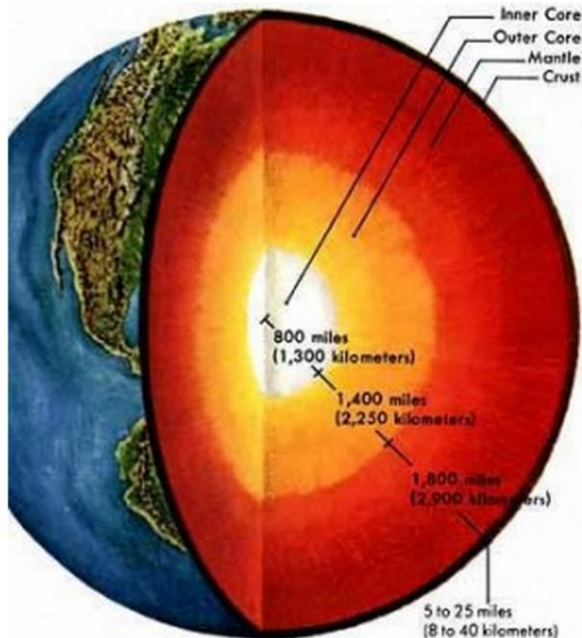


Important ternary structures

What forms most of the Earth mantle? What controls the movement of continents, earthquakes, volcanoes?

Perovskite MgSiO_3

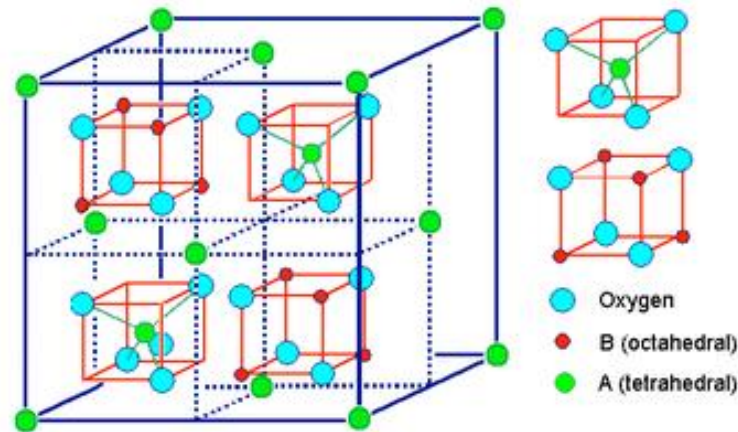
(sometimes given, less precisely, as $\text{MgO} + \text{SiO}_2$)



Important ternary structures

Spinel structure (prototype MgAl_2O_4 , in general AB_2O_4)

- fcc lattice of anions (O), compare to aforementioned cases the cube is doubled in each direction $\Rightarrow$ 32 O at. instead of 4
- 1/8 tetrahedral holes filled by atoms A (smaller cation)
- 1/2 octahedral holes filled by atoms B

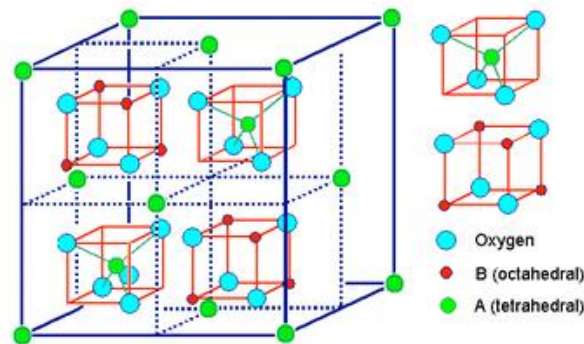


Other materials: CuAl_2O_4 , CuFe_2O_4 , ...

Important ternary structures

Spinel structure (prototype MgAl_2O_4 , in general AB_2O_4)

- the cubic cell shown (conventional unit cell): 56 atoms
- rhombohedral cell (primitive unit cell): 14 atoms
- the same element in sublattices 'A' and 'B': **Fe_3O_4 , Mn_3O_4 , ...**



$\gamma\text{-Al}_2\text{O}_3$

- 3 rhombohedral cells of spinel $\Rightarrow$ fictitious $\text{Al}_{18}\text{O}_{24}$
(6 $\times$ tetrahedral Al, 12 $\times$ octahedral Al, 24 $\times$ O)
- vacancies instead of two octahedral Al $\Rightarrow$ **$\gamma\text{-Al}_{16}\text{O}_{24}$**
(6 $\times$ tetrahedral Al, 10 $\times$ octahedral Al, 24 $\times$ O)

Important ternary structures

MAX phases (M_2AX , M_3AX_2 , M_4AX_3)

$M = \text{Ti, Zr, Hf, V, Cr, ...}$

$A = \text{Al, Si, P, Ga, Ge, ...}$

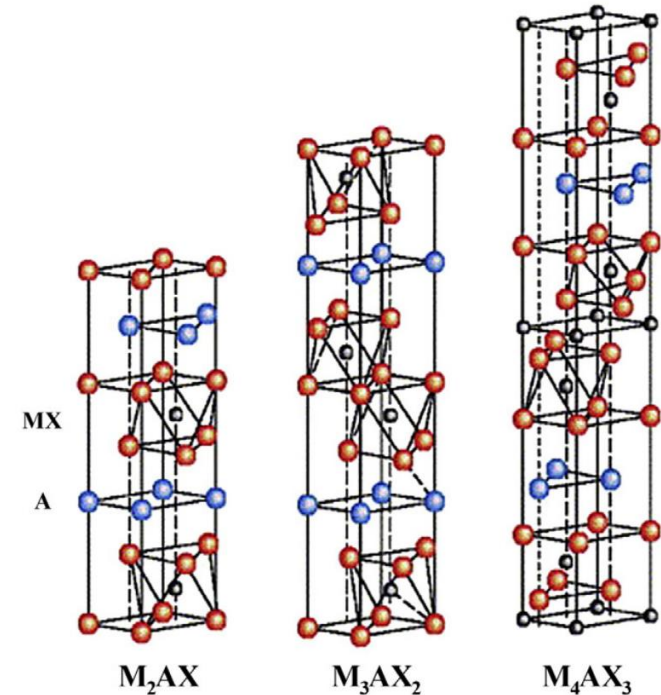
$X = \text{C or N}$

- close packing (layers A,B,C)

M_2AX : MXMA

M_3AX_2 : MXMXMA

M_4AX_3 : MXMXMXMA



- contrary to fcc, layers A,B,C do not alternate regularly, but other layer than which is in line comes after layers occupied by element 'A' (bold and underlined, not confuse with layer A)

M_2AX : ABCACBACBACBA...

M_3AX_2 : ABCABCBACBACBA...

M_4AX_3 : ABCABCBABACBACBACBA...

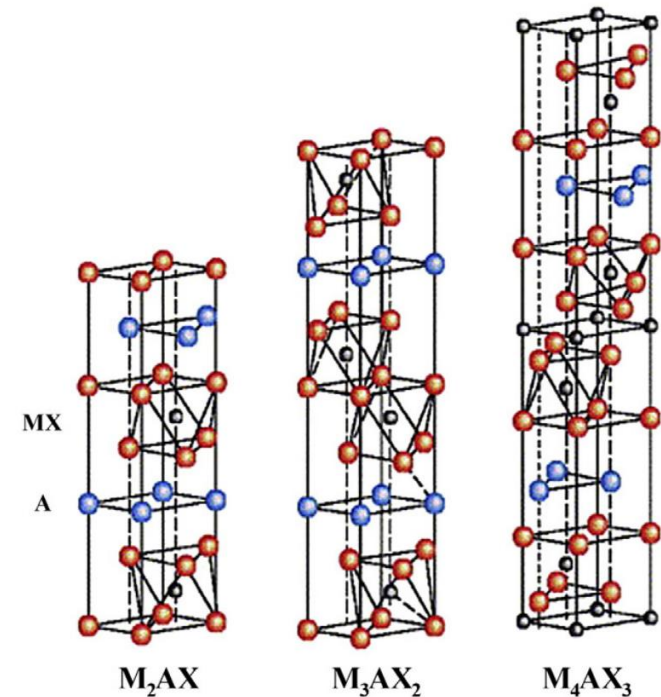
Important ternary structures

MAX phases (M_2AX , M_3AX_2 , M_4AX_3)

M_2AX : ABCACBACABCAC...

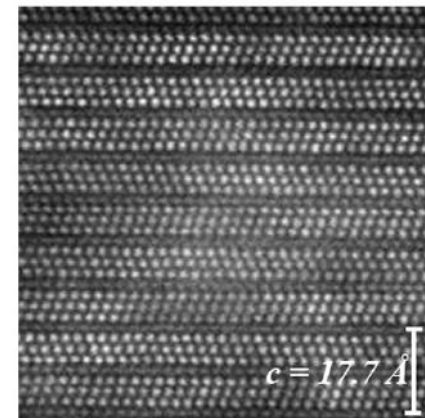
M_3AX_2 : ABCABCBACBACA...

M_4AX_3 : ABCABCABACBACBACA...



TEM photo of Ti_3SiC_2 -
experimental observation of
changes or ordering of layers
after each layer of atoms 'A'

[P. Eklund et al., *Thin Solid Films* 518, 1851 (2010)]



Selected structures in the national museum of the Czech Republic



2) Bonding in solid materials

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Bonding mechanisms

From an "ultra-theoretical" point of view, the mechanism / shared origin of bonding forces is only one (electrostatic forces between cores and electrons respecting Schrödinger equation)

However, in praxis it makes sense to distinguish bonds

- ionic
- covalent
- metallic
- van der Waals
- hydrogen (not so relevant for "our" materials)

The aforementioned joint origin of all bonding forces often results to a mixed character of bonds (e.g. partially metallic and partially covalent), see also below

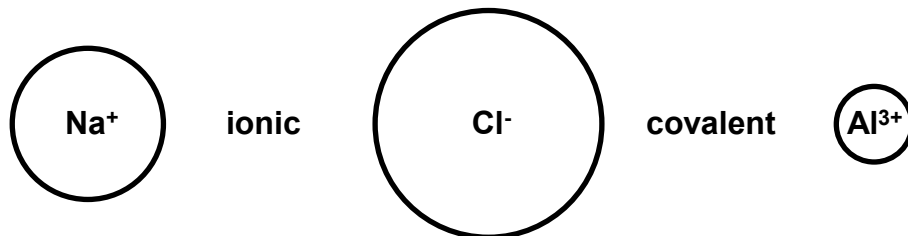
Bonding mechanisms

However, in praxis it makes sense to distinguish bonds

- ionic
- covalent
- metallic
- van der Waals
- hydrogen (not so relevant for "our" materials)

Fajan's rules:

- comparable size of cation and anion, low charge of cation:
ionic bond (e.g. Na^+Cl^-)
- cation much smaller than anion, high formal charge of cation:
covalent bond (e.g. $\text{Al}^{3+}\text{Cl}^-$)

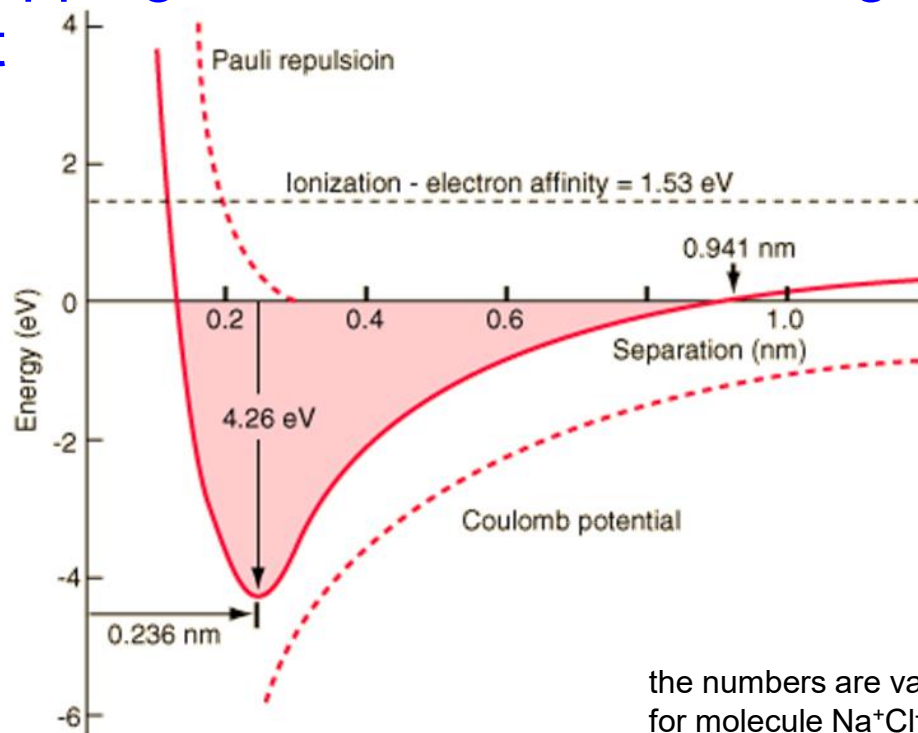


Ionic bonding

Elements with very different electronegativities, e.g. Na^+Cl^-
(see also Fajan's rules)

The valence electron of cation is completely given to anion
 $\Rightarrow$ attractive component of the interaction

Pauli principle prevents overlapping of orbitals when atoms get close
 $\Rightarrow$ repulsive component



Ionic bonding

Elements with very different electronegativities, e.g. NaCl (Na^+Cl^-)

The valence electron of cation is completely given to anion

⇒ attractive component of the interaction

Pauli principle prevents overlapping of orbitals when atoms get close ⇒ repulsive component

Properties:

- high bonding energy

⇒ stability (high melting temperature)

- energy strongly depends on (dis)placement of atoms

⇒ hardness, brittleness, low thermal expansion

- electrons trapped by their anion, i.e. not delocalized

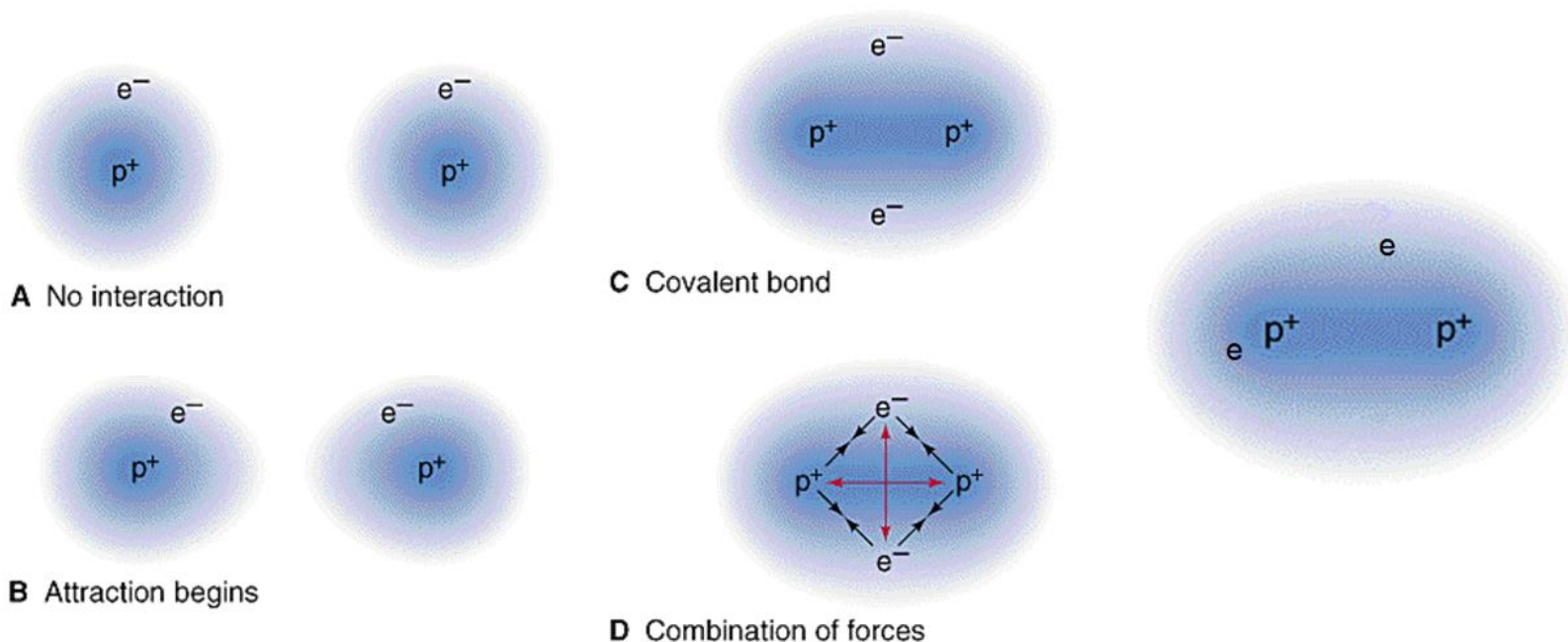
⇒ low electrical conductivity

Unsaturated - number of neighbours is not limited by the number of valence electrons (is given by numbers and sizes of the ions)

Covalent bonding

Single element, or elements with similar electronegativities
(see also Fajan's rules)

Electrons are shared by bonded atoms (the highest probability of their occurrence is between atoms); term "molecular orbital" (valid for molecules as well as for solids)

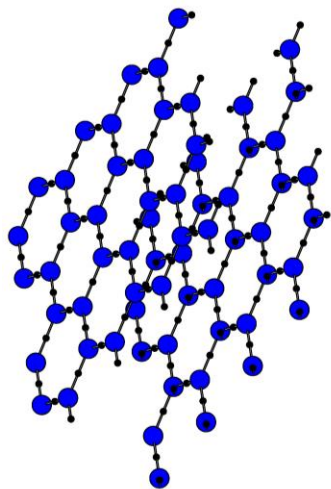


Covalent bonding

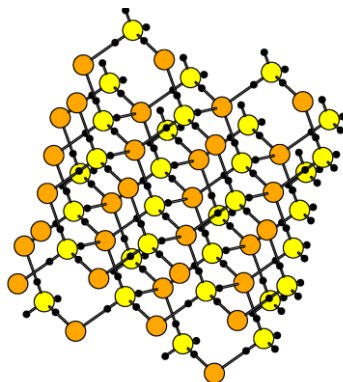
Single element, or elements with similar electronegativities

Electrons are shared by bonded atoms (the highest probability of their occurrence is between atoms); term "molecular orbital" (valid for molecules as well as for solids)

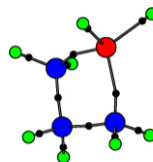
graphite



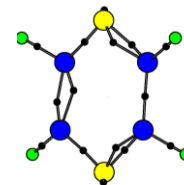
c-BN



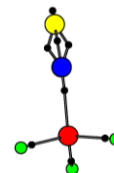
SiC_3H_8



$\text{N}_2\text{C}_4\text{H}_4$



NCSiH_3



black dots:
most probable positions of
pairs of valence electrons

Covalent bonding

Single element, or elements with similar electronegativities

Electrons are shared by bonded atoms (the highest probability of their occurrence is between atoms); term "molecular orbital" (valid for molecules as well as for solids)

Properties qualitatively similar to ionic bonding:

- high bonding energy (although smaller than for ionic)
⇒ stability (high melting temperature)
- energy strongly depends on bonding angles etc.
⇒ hardness, brittleness
- electrons trapped close to the middle of the bond which they represent, i.e. not delocalized
⇒ low electrical conductivity

Saturated - number of neighbours is limited by the number of valence electrons (and by the bond orders)

Covalent bonding

Single element, or elements with similar electronegativities

Electrons are shared by bonded atoms (the highest probability of their occurrence is between atoms); term "molecular orbital" (valid for molecules as well as for solids)

Saturated - number of neighbours is limited by the number of valence electrons (and by the bond orders)

Special case: **coordinate covalent bond** (also called just coordinate bond): covalent bond with all usual properties, but **both electrons are provided by the same atom**

Examples: molecule H_3O^+ in water, adsorption of H_2O on a solid surface (see the hydrophobicity & hydrophilicity in chapter 11)

Covalent bonding

Gilbert Lewis, who discovered (for example) covalent bonding:
41 nominations for NP in chemistry between 1922-1946
until he - probably - committed suicide

Nobelprize.org
The Official Web Site of the Nobel Prize

Home | Nobel Prizes and Laureates | Nomination | Ceremonies | Alfred Nobel

Lists of Nobel Prizes and Laureates
Choose a list

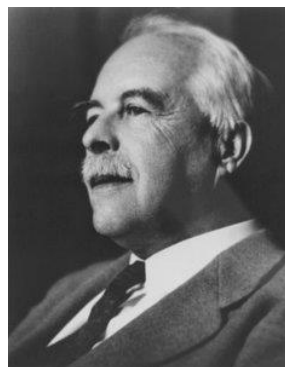
Nomination Database

Gilbert N Lewis

Lastname/org:	Lewis
Firstname:	Gilbert
Initial:	N
Gender:	M
Year, Birth:	1875
Year, Death:	1946

Nominee in 41 nominations:

- Chemistry 1922 by Frederick Donnan
- Chemistry 1924 by James Clark
- Chemistry 1924 by Theodore Richards
- Chemistry 1924 by Charles Walcott
- Chemistry 1925 by Victor Lenher
- Chemistry 1926 by William Campbell
- Chemistry 1929 by James Clark
- Chemistry 1929 by Arthur Allmand



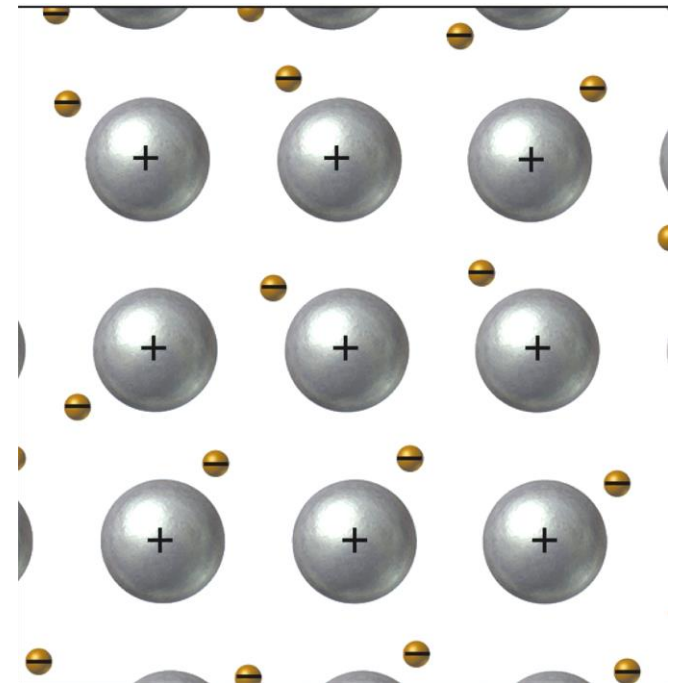
Metallic bonding

Transition metals with 'd' valence electrons ($\Rightarrow$ valence configuration 's'+ 'd' instead of 's'+ 'p') plus some other (e.g. Al)

Sea of delocalized electrons, and inside the sea cations = atom cores + inner electron shells (molecular orbitals like in the case of covalent bonds, but extremely delocalized)

Within the configuration 's'+ 'd'

- 's' electrons are more delocalized ($\Rightarrow$ responsible for metallic character),
- 'd' electrons are more localized ($\Rightarrow$ partially filled 'd' orbitals contribute to bonding, but more covalent one)



Metallic bonding

Transition metals with 'd' valence electrons ($\Rightarrow$ valence configuration 's'+ 'd' instead of 's'+ 'p') plus some other (e.g. Al)

Sea of delocalized electrons, and inside the sea cations = atom cores + inner electron shells (molecular orbitals like in the case of covalent bonds, but extremely delocalized)

Properties:

- electrical (and electronic component of thermal) conductivity
- weak dependence of energy on deformation
(bonding angles etc.) $\Rightarrow$ toughness, lower hardness

Unsaturated - the number of neighbours is limited neither by the number of valence electrons (similarly to ionic crystals) nor by ratios of number and size of ions (contrary to ionic crystals)
 $\Rightarrow$ close packing, high coordination numbers $\Rightarrow$ higher interatomic distances $\Rightarrow$ lower bonding energies per 1 bond

Van der Waals bonding

Electrostatic force between dipoles (incl. temporary dipoles - electrons circulate, electronic density fluctuates, atoms/molecules induce dipole moments of each other due to a positive feedback) formed by neutral atoms/molecules

Weak (energy on the order of percents of that of covalent bond - contrary to the mechanisms above, there is not any overlap of electron shells), but important where it is the only interaction

Example 1: forces between graphitic planes

Example 2: forces between molecules which form a solid material (molecular solid) - rubber, wax, ... (see also below)

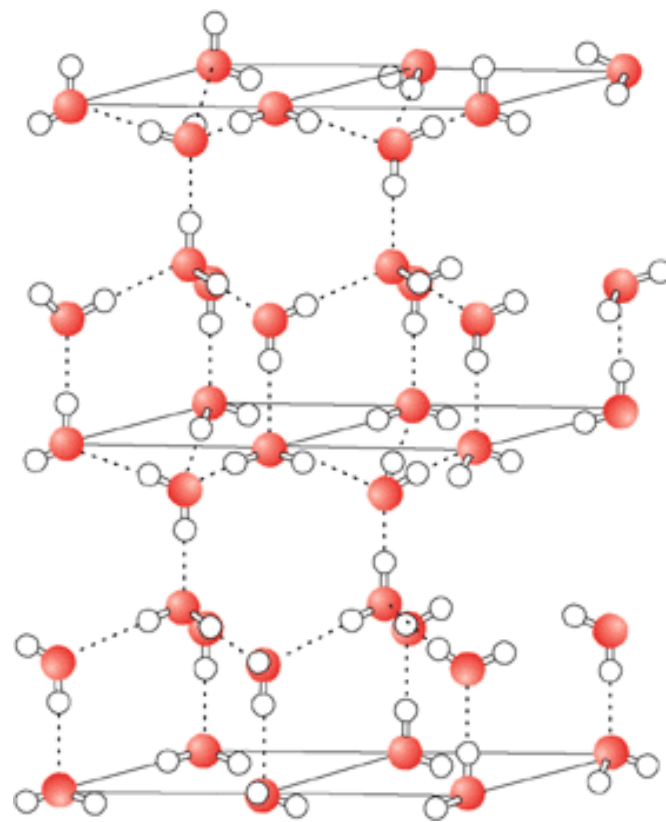
Hydrogen bonds (bridges)

Electrostatic force between cation of H and anion of other mol.

Usually weak (exceptions exist)

Example 1: forces between H_2O molecules in ice - see figure

Example 2: organic chemistry



Hydrogen bonds (bridges)

anomaly of water

O has high electronegativity, therefore there are strong H bonds between H_2O molecules



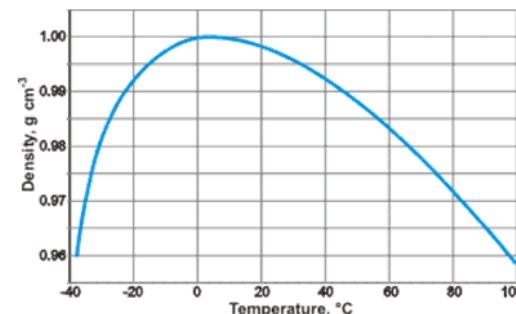
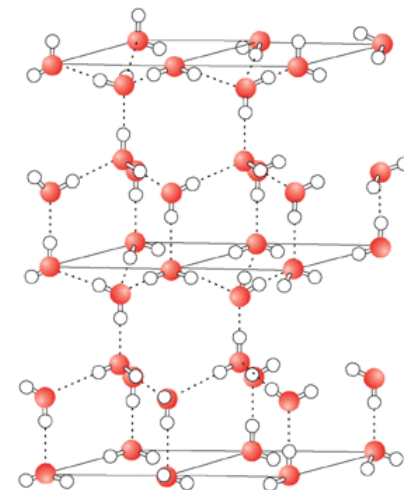
ice molecules require tetrahedral coordination (one bond from each H, two from each O):
less close packed than liquid water



melting leads to a more optimum coordination 3.4 (even less than 4.0 - not spheres) and density increases (similarly to that of materials tetrahedrally coordinated because of covalent bonds, like Si), then T expansion takes place



thermal dependence of density has maximum (4°C - temperature at the bottom below ice)

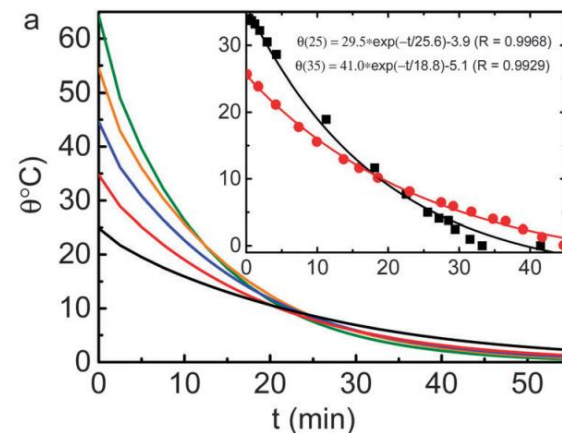


Hydrogen bonds (bridges)

Mpemba effect

Hot water freezes sooner than cold water under the same conditions (already Aristotle).

Part of explanation in the cited paper: hot water does not save energy into elongating all bonds (like other materials), but into elongating of hydrogen bonds between molecules and shortening of covalent bonds in molecules. Modelling of simultaneous release of such "springs" indicates a memory effect: faster release of energy (at given T) for higher starting temperature ("more deformed springs").



PCCP

PAPER

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2014, 16, 22995

Hydrogen-bond memory and water-skin supersolidity resolving the Mpemba paradox

Xi Zhang,^{a,b} Yongli Huang,^{a,c} Zengsheng Ma,^c Yichun Zhou,^c Ji Zhou,^d
Weitao Zheng,^e Qing Jiang^d and Chang Q. Sun^{f,g,h}

Bonding mech. - graphical overview

Type	Schematic	Cohesive Energy	Examples
Van der Waals		Very weak: 1-10 meV	Noble Gases (Ar, Ne, etc), Liquid O ₂
H bonding		Weak: 0.1-0.5 eV	Water, Ice, Proteins
Covalent		Strong: ≤11 eV (molecules) ≤8 eV (solids)	C (graphite, diamond), Si
Metallic		Strong: ≤9 eV	Na, Al, Transition Metals
Ionic		Strong: ≤8 eV	NaCl; NaBr, KI

Bonding mech. × melting temperature

First approximation: melting temperature increases with bonding energy (energy per atom, not per bond $\Rightarrow \times$ coordination).

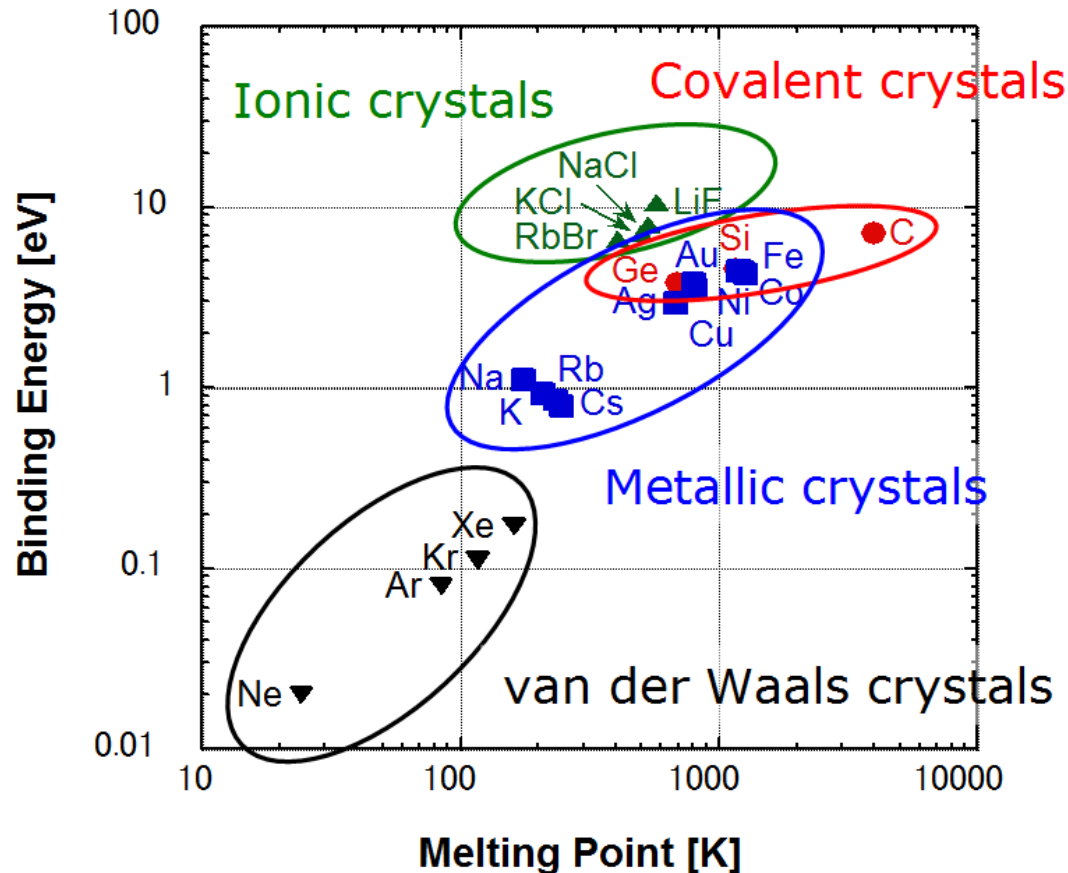
- ionic: very high bonding energy
- covalent: high bonding energy
- metallic: low energy per 1 bond, but high coordination
- van der Waals: very low energy

Second approximation: what matters is the difference of energies in solid and liquid state. Liquid state does not respect directionality of bonds $\Rightarrow$ covalent materials (which require directionality) may have higher melting temperature than that indicated by bonding energy. Graphite does not melt at all and prefers to stay solid until sublimation ($>3500\text{ }^{\circ}\text{C}$).

Bonding mech. × melting temperature

First appr.: melting temperature increases with bonding energy

Second appr.: what matters is the difference of energies in solid and liquid state. C does not melt at all (sublimation >3500 °C).



Bonding mech. × melting temperature

What matters in metals is the number of bonding electrons

- thus, last 2 columns of transition metals with completely full 'd' orbital (**Au, Ag, Hg, ...**) or metals completely without 'd' electrons (**In, Sn, Li, Na, ...**) have low melting temperature (note also the low reactivity of gold and silver)
- metals where electrons from partially filled 'd' orbital readily contribute to reactivity (**Cr, Mo, W, ...** ; including partially covalent character of bonds) have high melting temperature

Some elements (phosphorus, sulfur) are known as covalent, but they have low melting temperatures (44 and 115 °C) - why so?

Bonding mech. × melting temperature

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Some elements (phosphorus, sulfur) are known as covalent, but they have low melting temperatures (44 and 115 °C) - why so?

They do not constitute an infinite network of covalent bonds (like Si or C), but another example of molecular solids. Molecules P_4 and S_8 are held together only by van der Waals bonds.

Bonding mech. $\times$ melting temperature

The same in a graphical form

Local maxima for C, Si, Ge

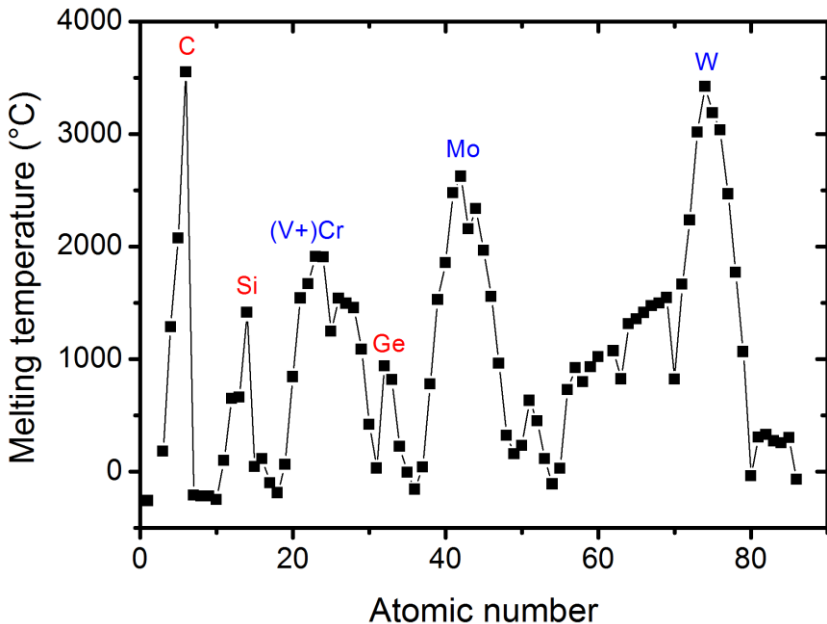
$\rightleftharpoons$ strong covalent bonds

Local maxima for Cr, Mo, W
(val. configuration $nd^5.[n+1]s^1$)

$\Leftrightarrow$ d-orbital is exactly half filled (5 of 10)

⇔ maximum contribution
of d-electrons to (relatively
covalent) bonds

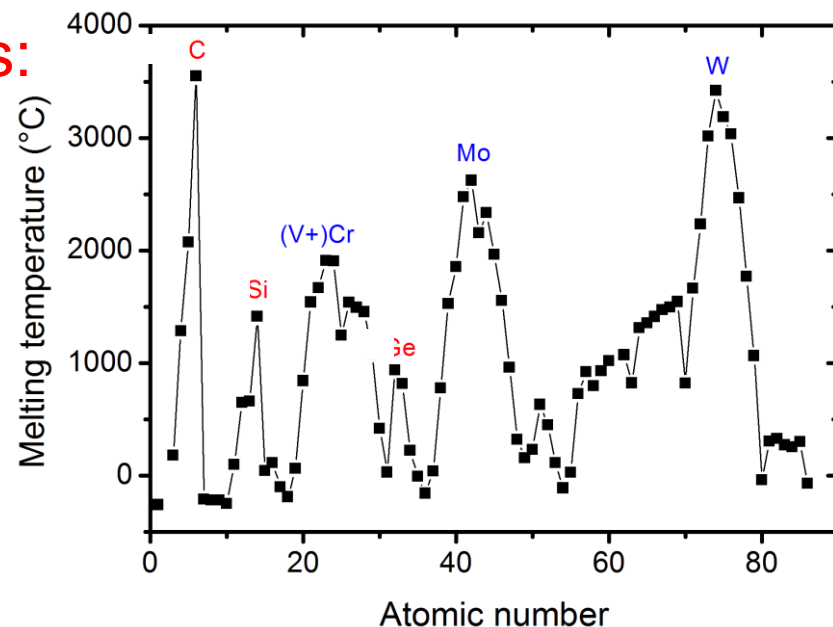
Do not confuse el. configuration of material (projection of molecular orbitals on atomic) and isolated atom



1A	2A																	8A							
1	2																	2							
H Hydrogen 1.008																		He Helium 4.003							
3	4																	5	6	7	8	9	10	11	12
Li Lithium 6.941	Be Beryllium 9.012																	B Boron 10.811	C Carbon 12.011	N Nitrogen 14.007	O Oxygen 15.999	F Fluorine 18.998	Ne Neon 20.180		
13	14																	15	16	17	18	19	20		
Na Sodium 22.990	Mg Magnesium 24.305																	Al Aluminum 26.982	Si Silicon 28.086	P Phosphorus 30.974	S Sulfur 32.06	Cl Chlorine 35.453	Ar Argon 39.948		
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38								
K Potassium 39.098	Ca Calcium 40.078	Sc Scandium 44.956	Ti Titanium 47.88	V Vanadium 50.942	Cr Chromium 51.996	Mn Manganese 54.938	Fe Iron 55.845	Co Cobalt 58.933	Ni Nickel 58.693	Cu Copper 63.546	Zn Zinc 65.38	Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.922	Se Selenium 78.971	Br Bromine 79.904	Kr Krypton 83.798								
39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56								
Rb Rubidium 85.468	Sr Strontium 87.62	Y Yttrium 88.906	Zr Zirconium 91.224	Nb Niobium 92.906	Mo Molybdenum 95.94	Tc Technetium 98.907	Ru Ruthenium 101.07	Rh Rhodium 101.07	Pd Palladium 106.90	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.757	Te Tellurium 127.6	I Iodine 126.905	Xe Xenon 131.29									
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86								
Cs Cesium 132.905	Ba Barium 137.328	Lanthanides 57-71					Hf Hafnium 178.49	Ta Tantalum 180.948	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.22	Pt Platinum 195.084	Au Gold 196.967	Hg Mercury 200.592	Tl Thallium 204.383	Pb Lead 207.2								
87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118								
Fr Francium 223.020	Ra Radium 226.025	Actinides 89-103					Rf Rutherfordium 261	Sg Seaborgium 266	Bh Bohrium 264	Hs Hassium 265	Mt Meitnerium 268	Ds Darmstadtium 271	Rg Roentgenium 272	Cn Copernicium 285	Uut Ununtrium 288	Uuq Ununquadium 291	Uuo Ununhexium 294								

Bonding mech. × melting temperature

Application related to strong bonds:
addition of Mo or W to gun barrels
(range of fire), armour, projectiles,
etc. $\Rightarrow$ strategic resource



Bartlett Mountain in Colorado, USA:
the main worldwide source of
molybdenum in its time. During
WW1 mining in still-neutral USA by
German company American Metal
(branch of Metallgesellschaft AG ;-))
and smuggling to Germany

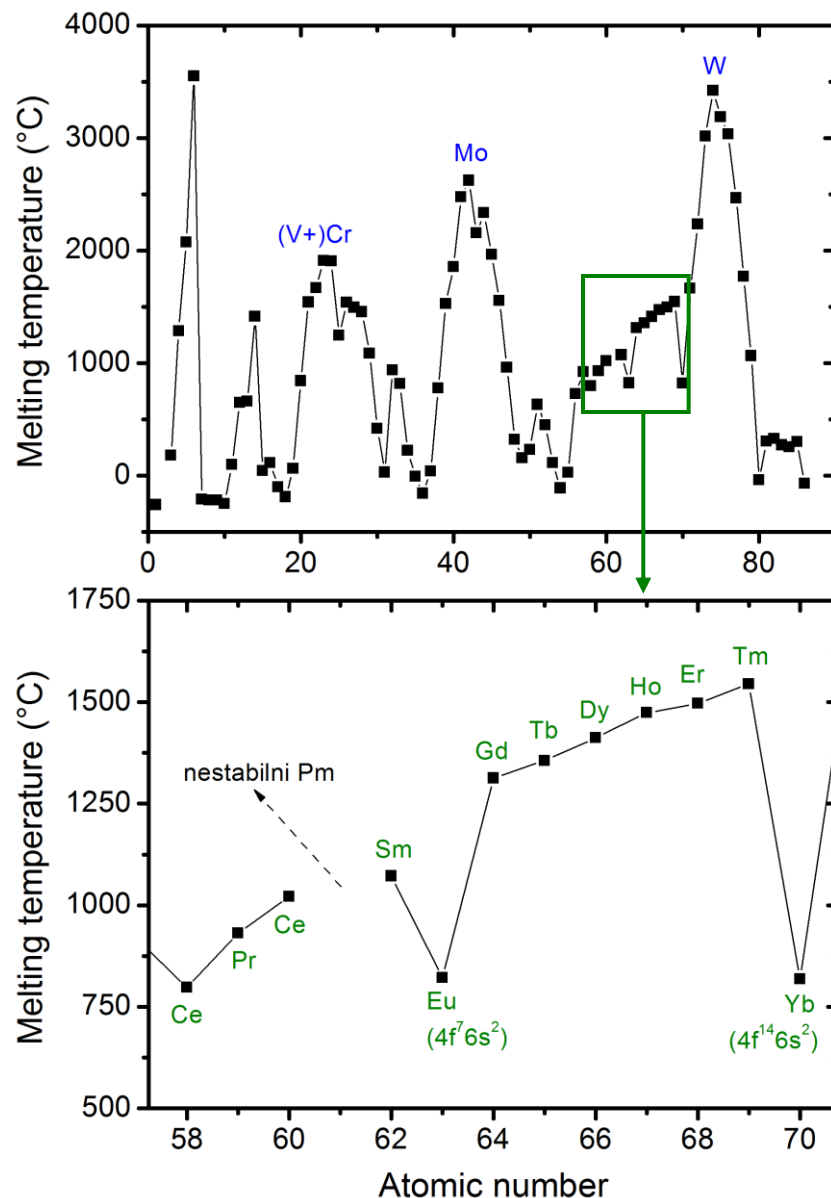


The rule cannot be extrapolated

f-electrons are close to atom cores $\Rightarrow$ they do not contribute to covalent bonds independently of their number

Furthermore, half-filled (7/14) f-band is energ. favorable, so atoms watch these electrons and do not let them to contribute to metallic bonds

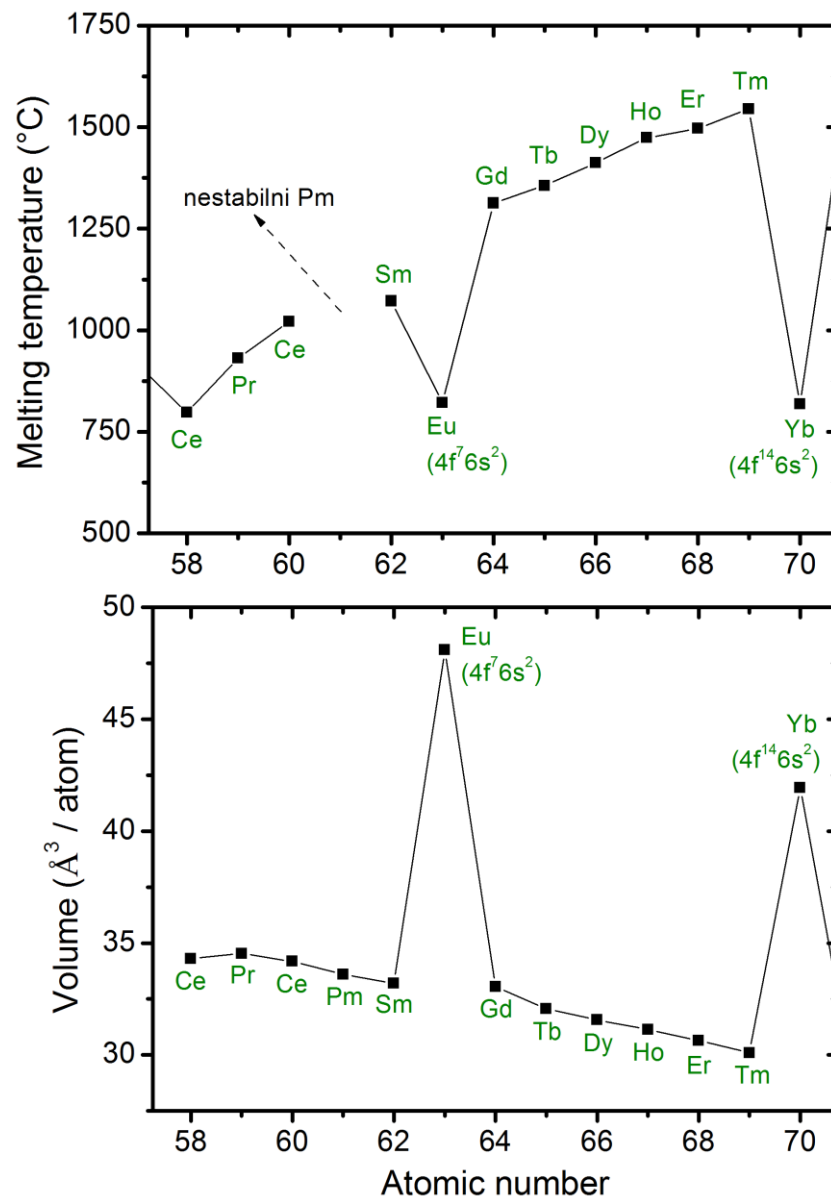
$\Rightarrow$ minimum not only for 14 electrons (Yb; similarly to d-elements like Hg) but also for 7 f-electrons (Eu; **opposite to d-elements like W**)



The rule cannot be extrapolated

Weaker metallic bonds
between cations Eu and Yb
(and higher volume of these
cations, because they keep
more localized electrons)

⇒ not only local minimum of
melting temperature, but also
local minimum of atomic
density (local maximum
of volume per atom)

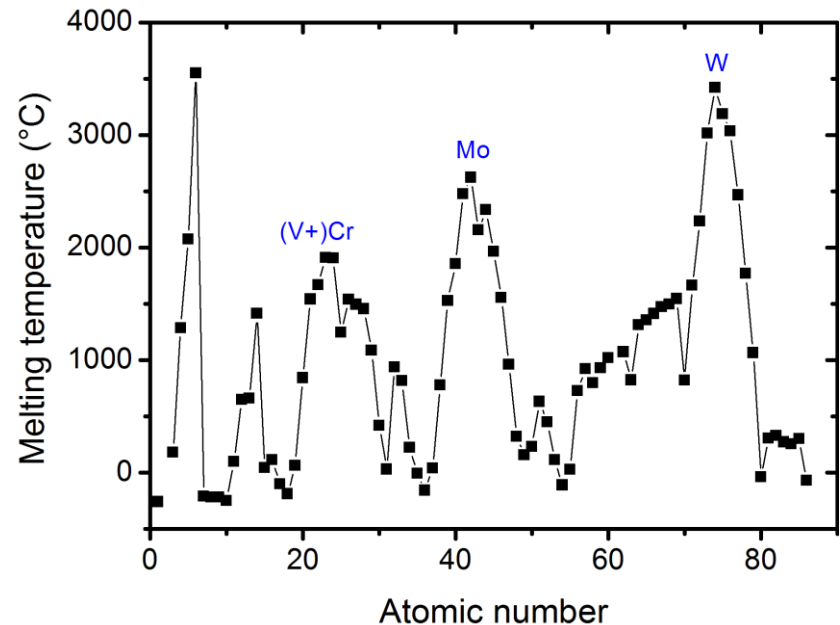


Role of line number (atomic size)

Previous slides: local maxima for Cr, Mo, W

⇔ maximum contribution of d-electrons to (relatively covalent) bonds

So much for the differences between columns of periodic table. In parallel, the melting temperature (⇔ strength of covalent bonds) increases with the line number (elements around Cr → around Mo → around W). Why so?

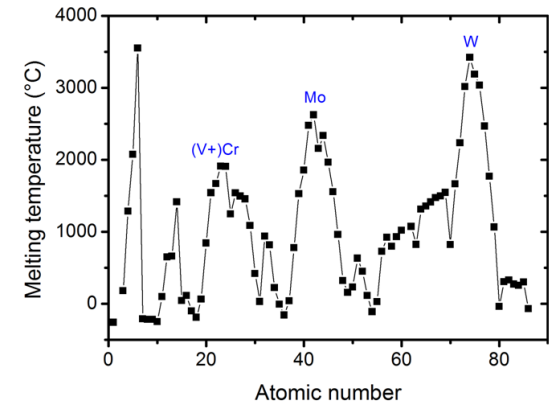


Role of line number (atomic size)

The strength of covalent bonds increase with the line number



Atomic size matters as well.



For a higher line number, the valence d-orbitals of transition metals overlap more and form covalent bond to a higher extent ($\Rightarrow$ paired spins $\Rightarrow$ nonmagnetic materials).

For a lower line number the orbitals overlap less $\Rightarrow$ interact less $\Rightarrow$ electrons do not have to end up in the same covalent bonding orbital ($\Rightarrow$ can choose spin $\Rightarrow$ magnetism).

(See chapter 14 for details about magnetism)

Role of line number (atomic size)

Figure related to previous slide: thus, space for magnetism is open in the first line of d-elements + first/only line of f-elements

Antiferromagnetic: Cr, Mn (below RT), Ce-Tm except Gd and unstable Pm (below RT)

Ferromagnetic: Fe, Co, Ni, Gd (just RT), Tb-Tm (below RT)

1 IA H Hydrogen 1.008																	18 VIIIA He Helium 4.003																	
3 Li Lithium 6.941	4 Be Beryllium 9.012																	10 Ne Neon 20.180																
11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 B Boron 10.811	14 C Carbon 12.011	15 N Nitrogen 14.007	16 O Oxygen 15.999	17 F Fluorine 18.998	18 Ar Argon 39.948																	36 Kr Krypton 83.80										
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80																	54 Xe Xenon 131.29
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29																	86 Rn Radon 222.018
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon 222.018																	118 Og Oganesson [294]
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [277]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [271]	111 Rg Roentgenium [272]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [288]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]																	118 Og Oganesson [294]
			57 La Lanthanum 138.905	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.255	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967																	103 Lr Lawrencium [262]
			89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [252]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]																	103 Lr Lawrencium [262]

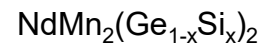
Role of line number (atomic size)

Figure related to previous slide: thus, space for magnetism is open in the first line of d-elements + first/only line of f-elements

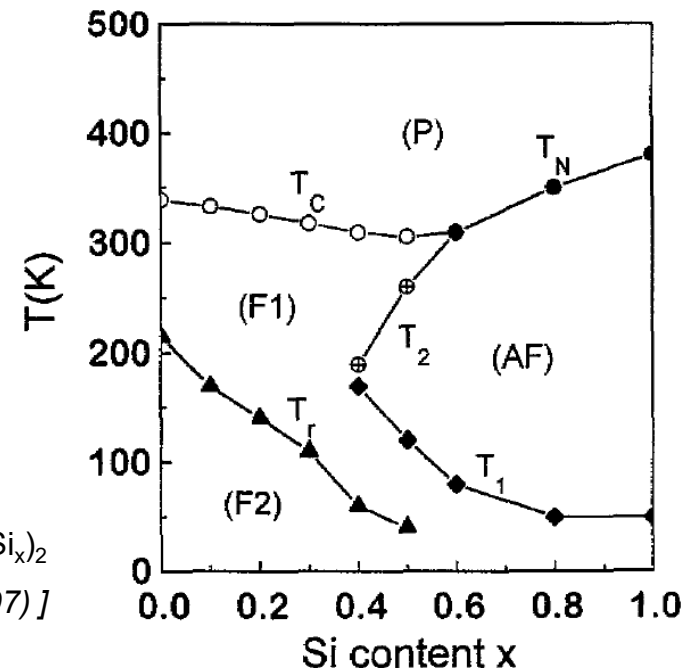
Antiferromagnetic: Cr, Mn (below RT), Ce-Tm except Gd and unstable Pm (below RT)

Ferromagnetic: Fe, Co, Ni, Gd (just RT), Tb-Tm (below RT)

The situation is more complex in more complex materials: while the magnetic moments (unpaired spins) are still associated with the aforementioned elements, their size depends on the overall composition and structure



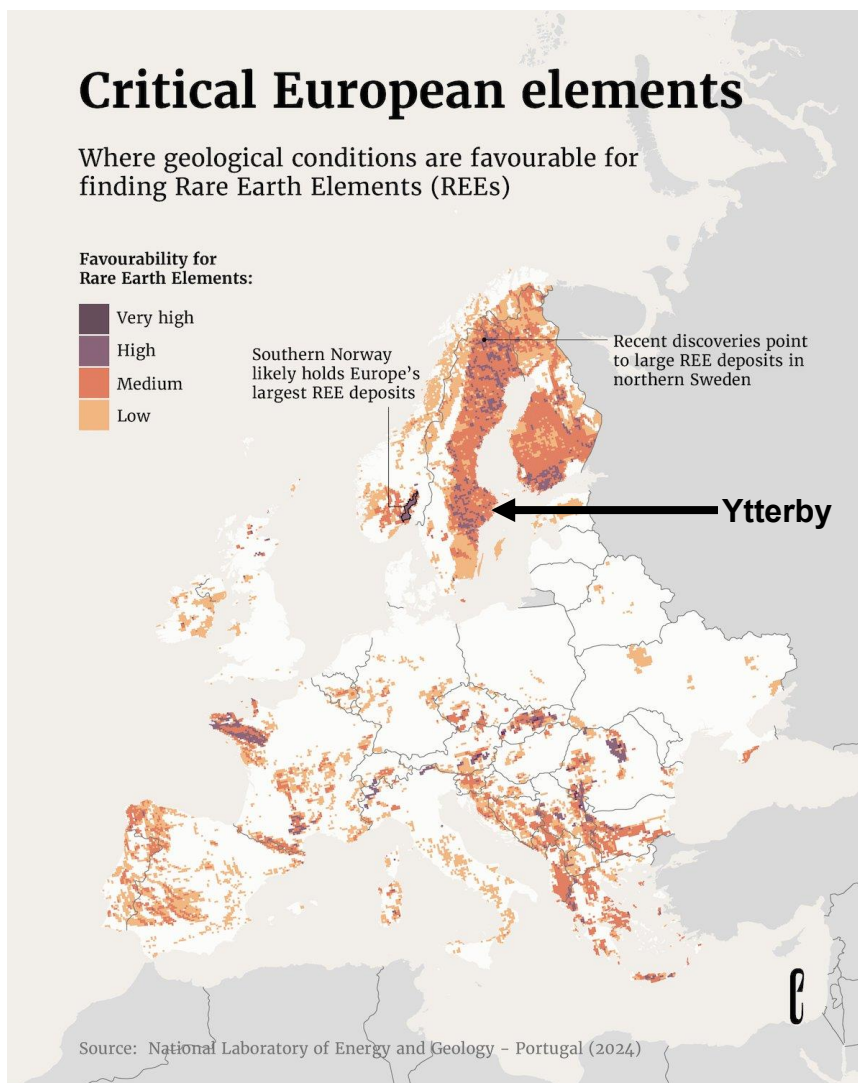
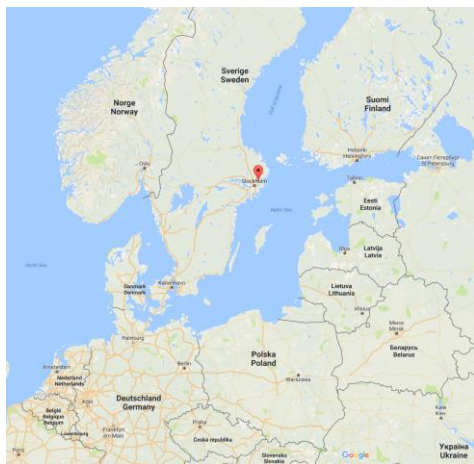
[Y. Wang et al, J. Alloy. Compd. 257, 19 (1997)]



Where to remind many aforementioned elements: map of village Ytterby



Where to remind many aforementioned elements: map of village Ytterby

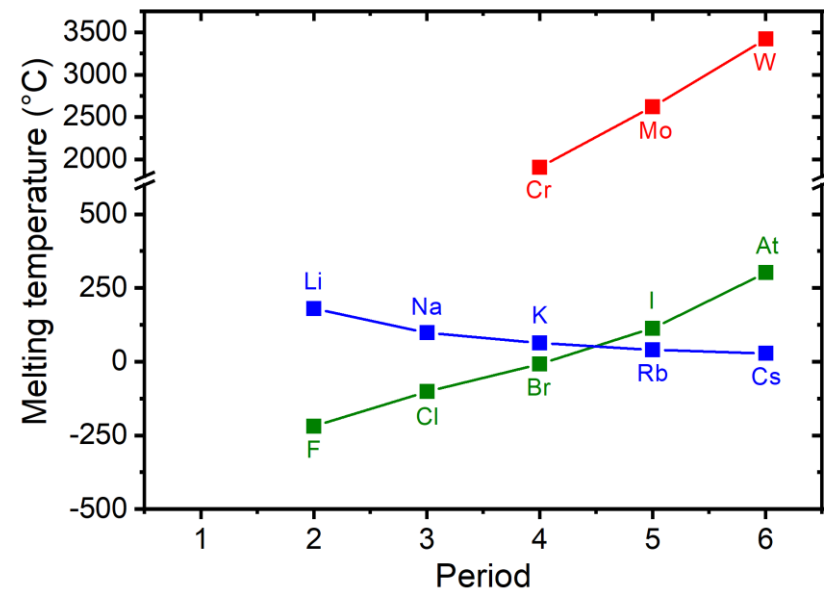


Role of line number (atomic size)

VIB (Cr, Mo, W): melting temp. **increases** downwards (larger atoms $\Leftrightarrow$ bonds are less metallic and more **covalent**)

IA (Li, Na, K, ...): melting temp. **decreases** downwards (larger atoms $\Leftrightarrow$ weaker **metallic** bonds formed by same number of s-el.)

IIIA (F, Cl, Br, ...): melting temp. **increases** downwards (larger atoms $\Leftrightarrow$ stronger **vdW** bonds between more polarizable molecules F_2 , Cl_2 , etc.)



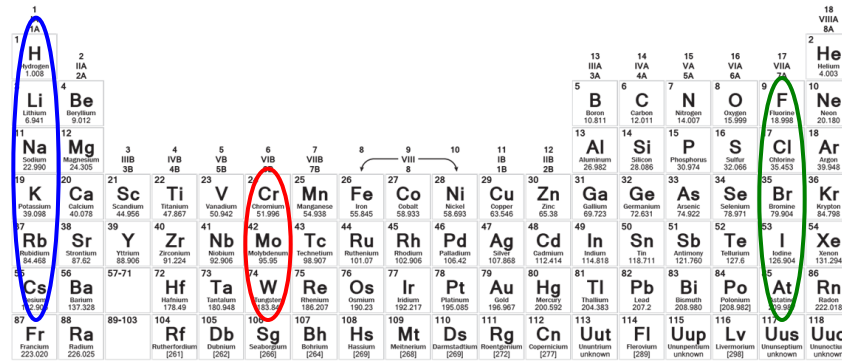
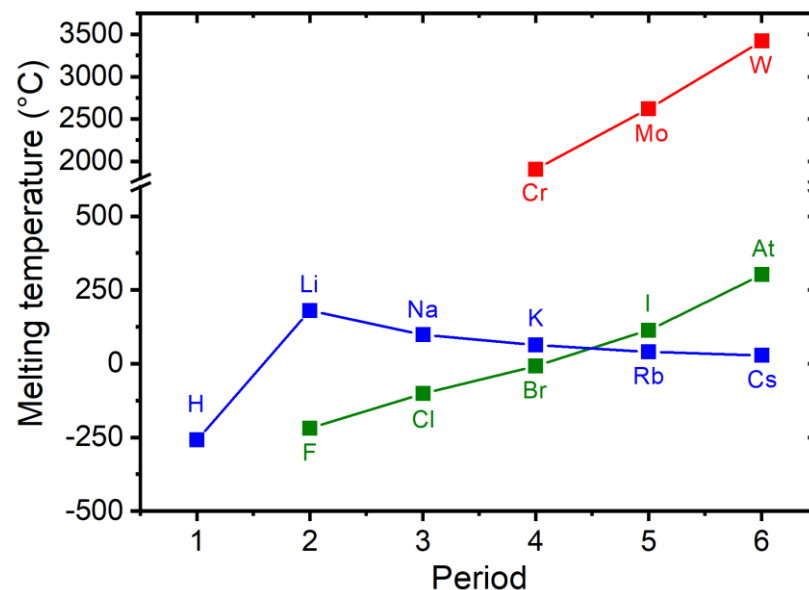
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Na Sodium 22.990	Mg Magnesium 24.305																	Al Aluminum 26.982	Si Silicon 28.086	P Phosphorus 30.974	S Sulfur 32.06	Cl Chlorine 35.453	Ar Argon 39.948																																																																																																																																		
11	12																	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																																																																																																																						
K Potassium 39.098	Ca Calcium 40.078	Sc Scandium 44.956	Ti Titanium 47.88	V Vanadium 50.942	Cr Chromium 51.996	Mn Manganese 54.938	Fe Iron 55.845	Co Cobalt 58.933	Ni Nickel 58.693	Cu Copper 63.546	Zn Zinc 65.38	Ga Gallium 69.723	Ge Germanium 72.631	As Arsenic 74.922	Se Selenium 78.971	Br Bromine 79.904	Kr Krypton 83.798																																																																																																																																								
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Rb Rubidium 85.468	Sr Strontium 87.62	Y Yttrium 88.906	Zr Zirconium 91.224	Nb Niobium 92.906	Mo Molybdenum 95.95	Tc Technetium 98.907	Ru Ruthenium 101.07	Rh Rhodium 101.07	Pd Palladium 106.36	Cd Cadmium 112.411	In Indium 114.818	Sb Antimony 121.757	Te Tellurium 127.6	I Iodine 126.905	Xe Xenon 131.29																																																																																																																																										
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Cs Cesium 132.905	Ba Barium 137.328																	La Lanthanum 138.905	Ce Cerium 140.12	Pr Praseodymium 140.908	Nd Neodymium 144.24	Pm Promethium 144.913	Sm Samarium 150.36	Eu Europium 151.964	Gd Gadolinium 157.25	Tb Terbium 158.925	Dy Dysprosium 162.50	Ho Holmium 164.930	Er Erbium 167.259	Tm Thulium 168.934	Yb Ytterbium 173.054	Lu Lutetium 174.967	Scandium 44.956	Titanium 47.88	Vanadium 50.942	Chromium 51.996	Manganese 54.938	Iron 55.845	Cobalt 58.933	Nickel 58.693	Copper 63.546	Zinc 65.38	Gallium 69.723	Germanium 72.631	Arsenic 74.922	Selenium 78.971	Bromine 79.904	Krypton 83.798	Rubidium 85.468	Strontium 87.62	Yttrium 88.906	Zirconium 91.224	Niobium 92.906	Molybdenum 95.95	Technetium 98.907	Ruthenium 101.07	Rhodium 101.07	Palladium 106.36	Cadmium 112.411	Indium 114.818	Antimony 121.757	Tellurium 127.6	Iodine 126.905	Xenon 131.29	Cesium 132.905	Barium 137.328	Lanthanum 138.905	Cerium 140.12	Praseodymium 140.908	Neodymium 144.24	Promethium 144.913	Samarium 150.36	Europium 151.964	Gadolinium 157.25	Terbium 158.925	Dysprosium 162.50	Holmium 164.930	Erbium 167.259	Thulium 168.934	Ytterbium 173.054	Lutetium 174.967	Unlabeled [258]	Unlabeled [260]	Unlabeled [262]	Unlabeled [264]	Unlabeled [266]	Unlabeled [268]	Unlabeled [270]	Unlabeled [272]	Unlabeled [274]	Unlabeled [276]	Unlabeled [278]	Unlabeled [280]	Unlabeled [282]	Unlabeled [284]	Unlabeled [286]	Unlabeled [288]	Unlabeled [290]	Unlabeled [292]	Unlabeled [294]	Unlabeled [296]	Unlabeled [298]	Unlabeled [300]	Unlabeled [302]	Unlabeled [304]	Unlabeled [306]	Unlabeled [308]	Unlabeled [310]	Unlabeled [312]	Unlabeled [314]	Unlabeled [316]	Unlabeled [318]	Unlabeled [320]	Unlabeled [322]	Unlabeled [324]	Unlabeled [326]	Unlabeled [328]	Unlabeled [330]	Unlabeled [332]	Unlabeled [334]	Unlabeled [336]	Unlabeled [338]	Unlabeled [340]	Unlabeled [342]	Unlabeled [344]	Unlabeled [346]	Unlabeled [348]	Unlabeled [350]	Unlabeled [352]	Unlabeled [354]	Unlabeled [356]	Unlabeled [358]	Unlabeled [360]	Unlabeled [362]	Unlabeled [364]	Unlabeled [366]	Unlabeled [368]	Unlabeled [370]	Unlabeled [372]	Unlabeled [374]	Unlabeled [376]	Unlabeled [378]	Unlabeled [380]	Unlabeled [382]	Unlabeled [384]	Unlabeled [386]	Unlabeled [388]	Unlabeled [390]	Unlabeled [392]	Unlabeled [394]	Unlabeled [396]	Unlabeled [398]	Unlabeled [400]

Hydrogen

IA (Li, Na, K, ...): melting temp. **decreases** downwards (larger atoms $\Leftrightarrow$ weaker **metallic** bonds formed by same number of s-el.)

IIIA (F, Cl, Br, ...): melting temp. **increases** downwards (larger atoms $\Leftrightarrow$ stronger **vdW** bonds between more polarizable molecules F_2 , Cl_2 , etc.)

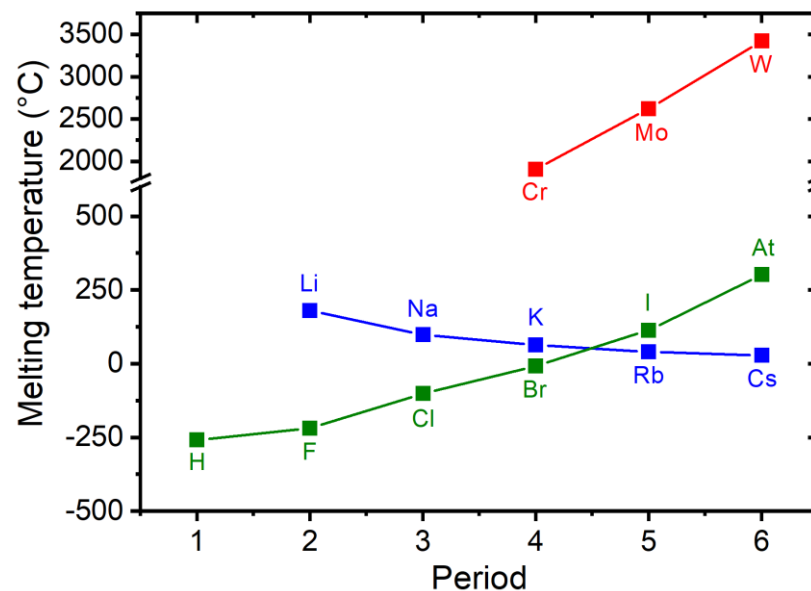
So why is H an exception?



Hydrogen

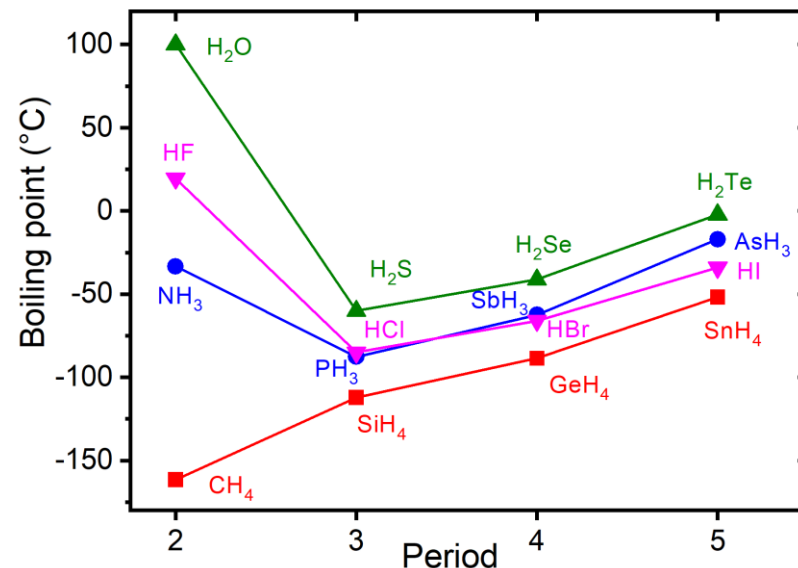
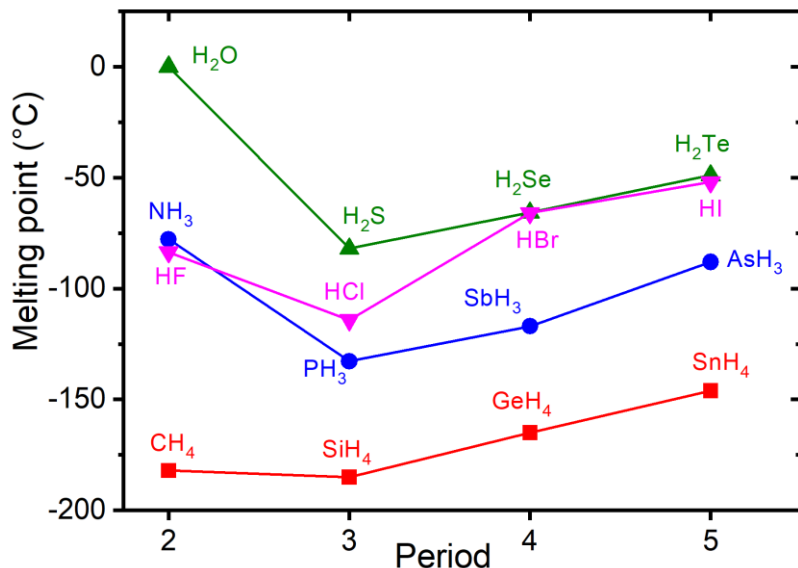
So why is H an exception?

Because 1 of 2 positions in its only shell is occupied, there is one missing and excess electron at the same time and H belongs to both columns IA and VIIA ... rather VIIA from this point of view



A standard periodic table with Hydrogen (H) highlighted in a blue oval and Helium (He) highlighted in a green oval. The table includes element symbols, atomic numbers, and names. The groups are labeled at the top: IA, IIA, IIIA, IVA, VA, VIA, VIIA, and VIIIA. The periods are numbered 1 through 7 on the left side.

Role of line number - molecular solids



Central atom in equivalent molecules is from lower line $\Rightarrow$ melting & boiling temperature increases - why?

NH₃, H₂O, HF are exceptions - why?

CH₄ constitutes an exception less (melting) or not at all (boiling) - why?

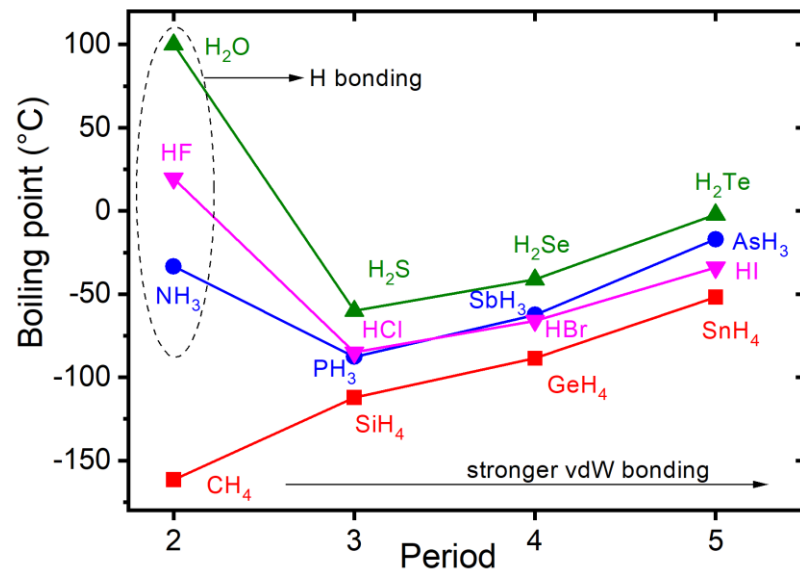
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																		18 Ar 39.948
																		36 Kr 83.80
																		54 Xe 131.29
																		86 Rn 222.018
1 H 1.008	3 Li 6.941	4 Be 9.012	5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180	11 Na 22.990	12 Mg 24.305	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948	19 K 39.098	20 Ca 40.078
21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.631	33 As 74.922	34 Se 78.971	35 Br 79.904	36 Kr 83.80	37 Rb 85.468	38 Sr 87.62	
39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98.906	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.414	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.6	53 I 126.905	54 Xe 131.29	55 Cs 132.905	56 Ba 137.327	
57 La 138.905	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm 144.913	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.259	69 Tm 168.933	70 Yb 173.054	71 Lu 174.967	72 Hf 178.49	73 Ta 180.948	74 W 183.84	
75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.084	79 Au 196.967	80 Hg 200.592	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po 209	85 At 210	86 Rn 222	87 Fr 223	88 Ra 226	89 Ac 227	90 Th 232.0377	91 Pa 231.03688	92 U 238.02891	
93 Np 237.04817	94 Pu 244.06422	95 Am 243.06136	96 Cm 247.07035	97 Bk 247.07035	98 Cf 251.0832	99 Es 252.0832	100 Fm 257.10	101 Md 258.10	102 No 259.10	103 Lr 262.10	104 Rf 261.10	105 Db 262.10	106 Sg 266.10	107 Bh 264.10	108 Hs 277.10	109 Mt 268.10	110 Ds 271.10	
111 Rg 272.10	112 Cn 285.10	113 Nh 286.10	114 Fl 289.10	115 Uup 288.10	116 Lv 293.10	117 Uus 294.10	118 Uuo 294.10	119 Ts 294.10	120 Og 294.10	121 Lr 262.10	122 Hf 178.49	123 Ta 180.948	124 W 183.84	125 Re 186.207	126 Os 190.23	127 Ir 192.22	128 Pt 195.084	

Role of line number - molecular solids

Increasing size of central atom in otherwise equivalent molecules (increasing line number) $\Rightarrow$ stronger vdW forces (larger dipole has higher dipole moment) $\Rightarrow$ increasing melting & boiling temp.

Molecules from the second line (NH_3 , H_2O , HF) are exceptions: stability is enhanced by stronger hydrogen bonds

Molecule CH_4 is not an exception: C does not have (contrary to N, O, F) lonepairs, so the anion charge is less localized and H bonds weaker



																18 VIIA He 4.003
																2
																10 Ne 20.180
																18 Ar 39.948
																36 Kr 83.80
																54 Xe 131.29
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1 IA H 1.008	2 IIA He 4.003	3 IIIA B 10.811	4 IVA C 12.011	5 VA N 14.007	6 VIA O 15.999	7 VIIA F 18.998	8 VIIIA Ne 20.180	9 IIIA Al 26.982	10 IIIA Si 28.086	11 IIIA P 30.974	12 IIIA S 32.06	13 IIIA Cl 35.453	14 IIIA Ar 39.948	15 IIIA K 39.098	16 IIIA Ca 40.078	17 IIIA Sc 44.956
18 IIIA Ti 47.88	19 IIIA V 50.942	20 IIIA Cr 51.996	21 IIIA Mn 54.938	22 IIIA Fe 55.845	23 IIIA Co 58.933	24 IIIA Ni 58.693	25 IIIA Cu 63.546	26 IIIA Zn 65.38	27 IIIA Ga 69.723	28 IIIA Ge 72.631	29 IIIA As 74.922	30 IIIA Se 78.971	31 IIIA Br 79.904	32 IIIA Kr 83.80	33 IIIA Rb 85.468	34 IIIA Sr 87.62
35 IIIA Y 88.906	36 IIIA Zr 91.224	37 IIIA Nb 92.906	38 IIIA Mo 95.94	39 IIIA Tc 98.906	40 IIIA Ru 101.07	41 IIIA Rh 102.905	42 IIIA Pd 106.42	43 IIIA Ag 107.868	44 IIIA Cd 112.414	45 IIIA In 114.818	46 IIIA Sn 118.710	47 IIIA Sb 121.757	48 IIIA Te 127.6	49 IIIA I 126.905	50 IIIA Xe 131.29	51 IIIA Ba 137.327
52 IIIA La 138.905	53 IIIA Ce 140.12	54 IIIA Pr 140.908	55 IIIA Nd 144.24	56 IIIA Pm 144.913	57 IIIA Sm 150.36	58 IIIA Eu 151.964	59 IIIA Gd 157.25	60 IIIA Tb 158.925	61 IIIA Dy 162.50	62 IIIA Ho 164.930	63 IIIA Er 167.259	64 IIIA Tm 168.934	65 IIIA Yb 173.054	66 IIIA Lu 174.967	67 IIIA Hf 178.49	68 IIIA Ta 180.948
69 IIIA W 183.84	70 IIIA Re 186.207	71 IIIA Os 190.23	72 IIIA Ir 192.22	73 IIIA Pt 195.084	74 IIIA Au 196.967	75 IIIA Hg 200.592	76 IIIA Tl 204.383	77 IIIA Pb 207.2	78 IIIA Bi 208.980	79 IIIA Po 209	80 IIIA At 210	81 IIIA Rn 222	82 IIIA Fr 223	83 IIIA Ra 226	84 IIIA Ac 227	85 IIIA Th 232.0377
86 IIIA Pa 231.036	87 IIIA U 238.02891	88 IIIA Np 237.04817	89 IIIA Pu 239.05216	90 IIIA Am 243.06136	91 IIIA Cm 247.07035	92 IIIA Bk 247.07035	93 IIIA Cf 251.0832	94 IIIA Es 252.0832	95 IIIA Fm 257.10	96 IIIA Md 258.10	97 IIIA No 259.10	98 IIIA Lr 262.10	99 IIIA La 138.905	100 IIIA Ce 140.12	101 IIIA Pr 140.908	102 IIIA Nd 144.24

Graphite

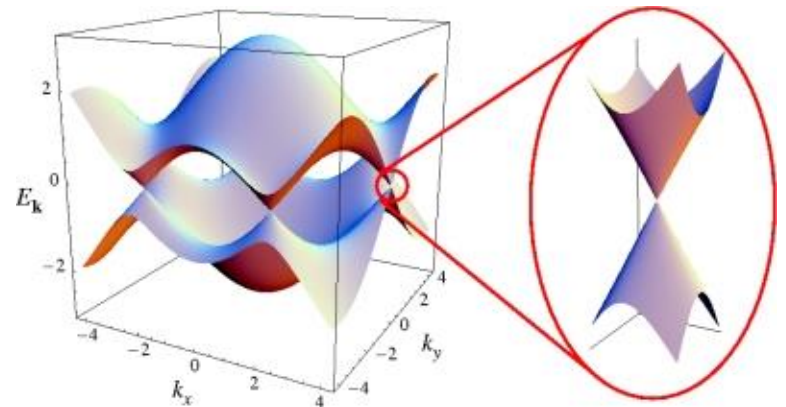
(and graphene and derived materials: we are talking about the plane of hexagons, not about the perpendicular vdW bonds)

We remember this material as covalent, but each fourth valence electron is delocalized

Thus, three covalent bonds are joined by a metallic bond. This does not much increase the total bonding strength, so saying that hexagons are covalent bonded is meaningful simplification.

However, this is enough to fulfil one characteristics of metallic bonding (delocalization) $\Rightarrow$ el. cond. parallel to the hexagons

Border case from the electronic structure point of view as well: valence and conductive band do not overlap, but touch at one point



Mixed character of bonds

(summary of selected examples; further info above)

Graphite: 3 out of 4 electrons constitute a covalent frame, fourth delocalized electron is responsible for the metallic character

Metals: d-electrons (if present) form a relatively covalent frame, s- (after hybridization sp-) electrons are delocalized and responsible for the metallic character. Similar mixed character for **conductive materials** like TiN.

SiO₂: predominantly covalent (coordination numbers correspond to the number of pairs of available valence electrons), non-negligible ionic character due to high electronegativity of O (incl. ionic bonds between slices of mica or fibers of asbestos)

Metal oxides (TiO₂, ZrO₂, ...): predominantly ionic character (coordinations higher than the number of pairs of valence el.)

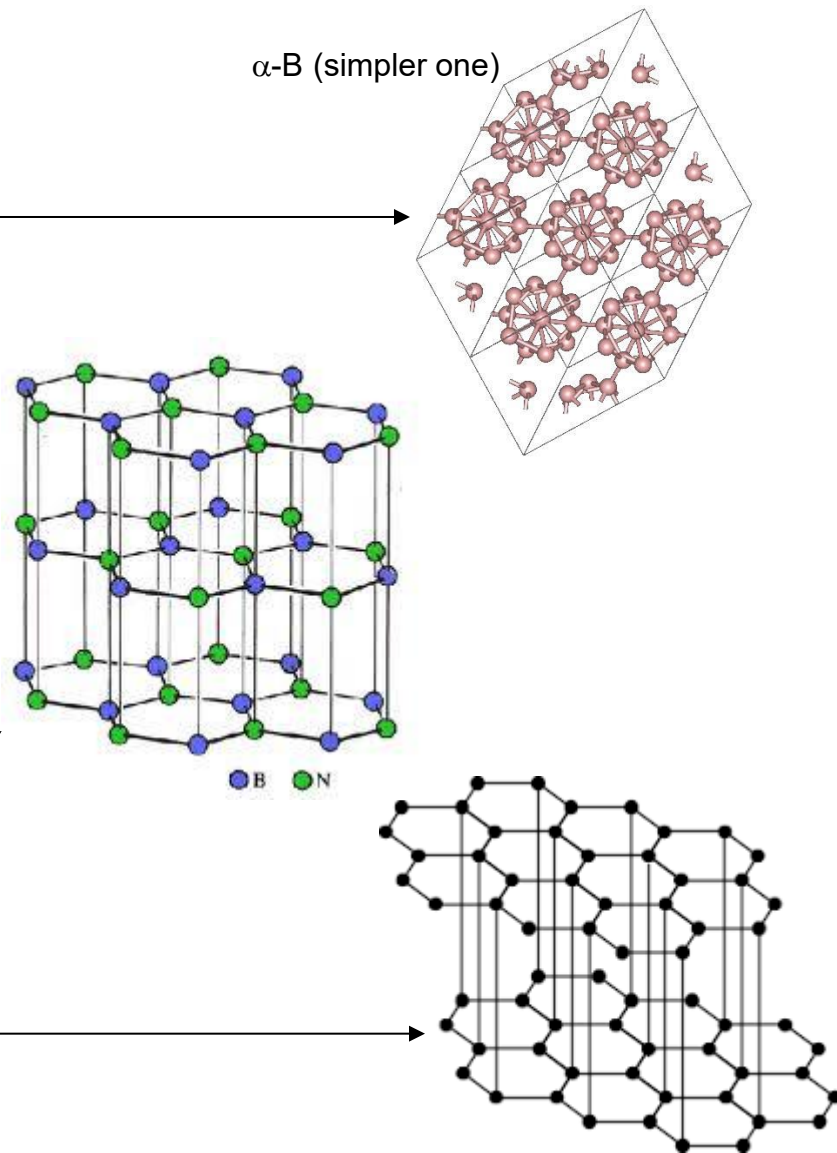
Mixed character of bonds

(summary of selected examples; further info above)

Boron (α a β): icosahedra B_{12}
where B has coordination 5
(but only 3 valence electrons)
- the bonds can be characterized
as very weak covalent; between
 B_{12} normal covalent bonds

h-BN: bonds between the planes
of hexagons are not only van der
Waals, but also ionic. Thus, BN
planes prefer to have B^+ a N^-
above each other (in the case
of graphite, C atoms are shifted
of its lattice constant)

α -B (simpler one)



Lonepairs

Not all valence electrons like to take place in bonding. While this is clear in the case of filled shells or orbitals (noble gases, aforementioned noble metals), it happens also in other cases.

Oxygen (H_2O , $\text{O}=\text{O}$, SiO_2 , ...):

- total 6 valence electrons
 - 4 electrons form 2 lonepairs
 - 2 bonding electrons
- including 2 electrons supplied by bonded atoms, there is the ideal number of 8 of them interacting with O (filled shell)

Nitrogen (NH_3 , $\text{N}\equiv\text{N}$, Si_3N_4 , ...):

- total 5 valence electrons
 - 2 electrons form 1 lonepair
 - 3 bonding electrons
- including 3 el. supplied by bonded atoms there are again 8

3) Vibrations and thermal properties

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Lattice vibrations

first of all a reminder of reciprocal space

In the real space the lattice is defined by vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ ($\mathbf{a}_{1-3}$ do not necessarily define "real" primitive crystal cell, but also e.g. its integer multiple - that's not the point now)

Let's define a lattice vector $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ where n_{1-3} are integers

In the reciprocal space the lattice is defined by vectors $\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3$ where $\mathbf{A}_1 = 2\pi \cdot \mathbf{a}_2 \times \mathbf{a}_3 / (\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)$, etc.

Let's define a reciprocal lattice vector

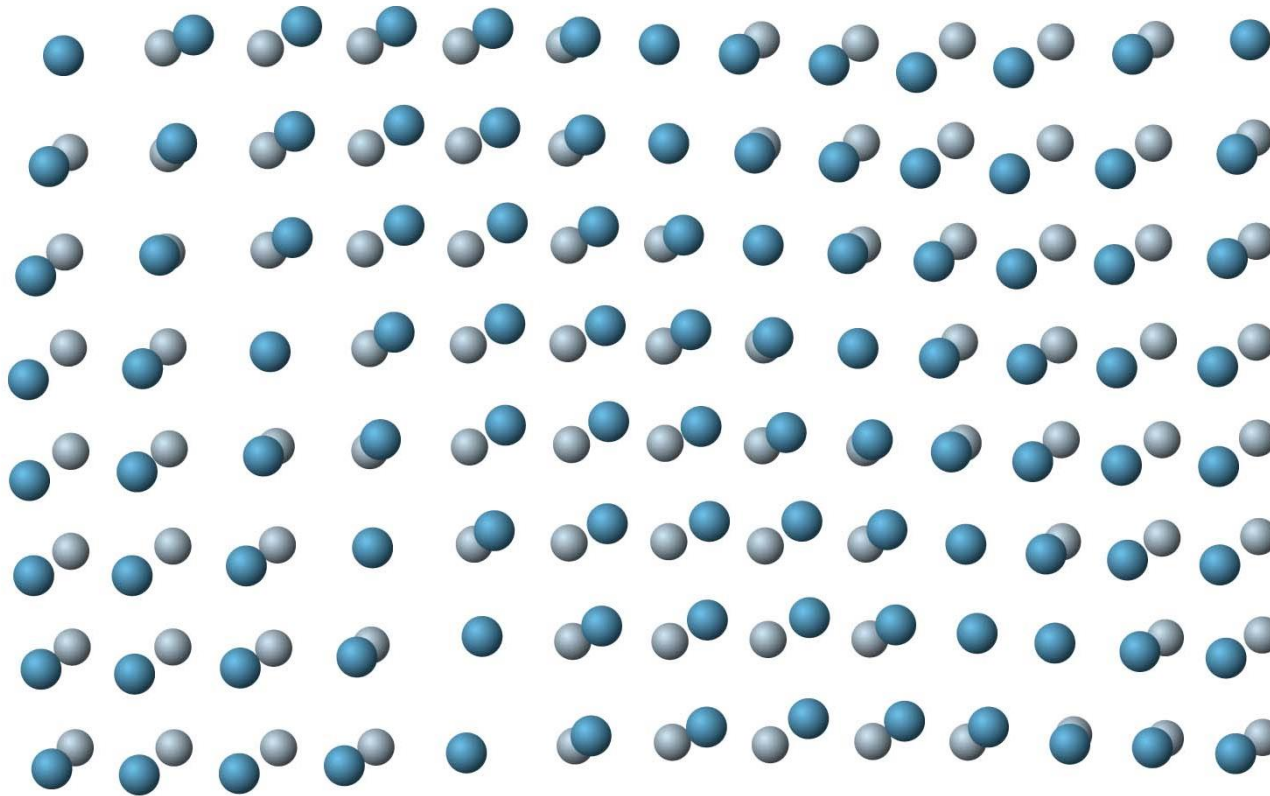
$$\mathbf{G} = m_1\mathbf{A}_1 + m_2\mathbf{A}_2 + m_3\mathbf{A}_3$$

It holds $\mathbf{G} \cdot \mathbf{R} = 2\pi(n_1 \cdot m_1 + n_2 \cdot m_2 + n_3 \cdot m_3) \Rightarrow e^{i\mathbf{G}\mathbf{R}} = 1$

Primitive reciprocal lattice cell (= Wigner-Seitz cell in the reciprocal space) is called first Brillouin zone

Phonon

Quasiparticle, representing a wave with (angular) frequency ω and wave vector $\mathbf{k}$ travelling through crystal



- Normal lattice positions for atoms
- Positions displaced because of vibrations

Phonon

Quasiparticle, representing a wave with (angular) frequency ω and wave vector $\mathbf{k}$ travelling through crystal

Phonon has an energy $\hbar\omega$ which is conserved (quantum of the energy $E_n = \hbar\omega(n + \frac{1}{2})$ of the corresponding vibrational mode - quantum harmonic oscillator)

Phonon behaves like it had a momentum $\mathbf{p} = \hbar\mathbf{k}$ (quasimomentum, crystal momentum)

which is conserved up to the reciprocal lattice vector $\mathbf{G}$

- for elastic scattering of photon (XRD in chapter 1)

it holds $\mathbf{k}_{\text{in}} + \mathbf{G} = \mathbf{k}_{\text{out}}$

- for inelastic scattering, when phonon takes/gives part of the momentum, it holds $\mathbf{k}_{\text{in}} + \mathbf{G} = \mathbf{k}_{\text{out}} + \mathbf{k}$

Special case $\mathbf{k} = 0$ corresponds to the movement of whole crystal (only here quasimomentum = real momentum)

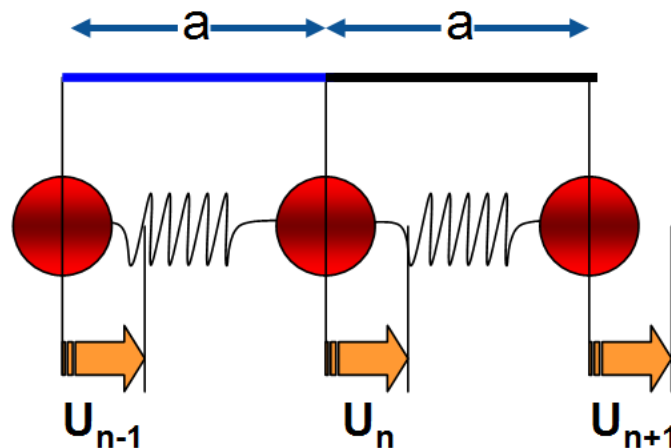
Lattice vibrations (1 element)

First a simplest idea:

- 1D chain of atoms
- all atoms are the same
- atoms are represented by balls with mass m connected by springs of stiffness $k_{\text{stiffness}}$ (don't confuse with wavenumber k)
- dependence of force on displacement is linear

Equation of motion

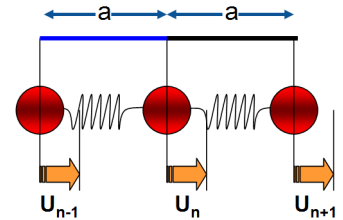
$$md^2u_n/dt^2 = -k_{\text{stiffness}}(u_n - u_{n-1}) - k_{\text{stiffness}}(u_n - u_{n+1})$$



Lattice vibrations (1 element)

Equation of motion

$$m d^2 u_n / dt^2 = -k_{\text{stiffness}} (u_n - u_{n-1}) - k_{\text{stiffness}} (u_n - u_{n+1})$$



Solution in the form of progressive wave

$$u_n = A \exp(i[kna - \omega t])$$

(total displacement is sum of all such displacements over all k)



$$-m \omega^2 u_n = -2k_{\text{stiffness}} u_n + k_{\text{stiffness}} u_n (e^{ika} + e^{-ika})$$

$$-m \omega^2 = -2k_{\text{stiffness}} + k_{\text{stiffness}} (2 \cos ka)$$

$$\omega^2 = 2k_{\text{stiffness}} / m \cdot (1 - \cos ka)$$

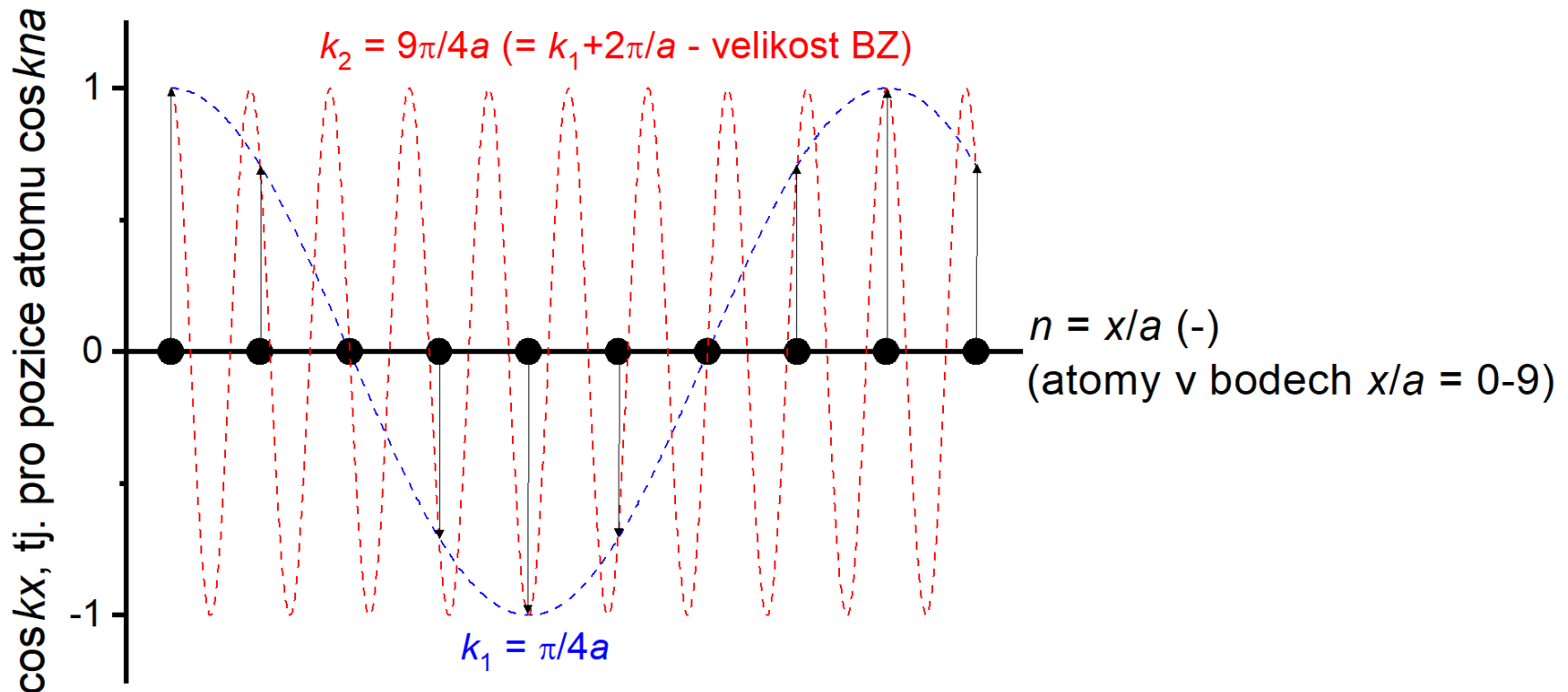
$$\omega^2 = 4k_{\text{stiffness}} / m \cdot \sin^2(ka/2)$$

Only the wavenumbers k in the first Brillouin zone, i.e. between $-\pi/a$ and $+\pi/a$, have unique meaning ($\Leftrightarrow$ it makes no sense to consider larger phase shift of neighbouring atoms than π)

Lattice vibrations (1 element)

$$u_n = A \exp(i[kna - \omega t]) \Rightarrow \omega^2 = 4k_{\text{stiffness}}/m \cdot \sin^2(ka/2)$$

Only the wavenumbers k in the first Brillouin zone, i.e. between $-\pi/a$ and $+\pi/a$, have unique meaning ($\Leftrightarrow$ it makes no sense to consider larger phase shift of neighbouring atoms than π)



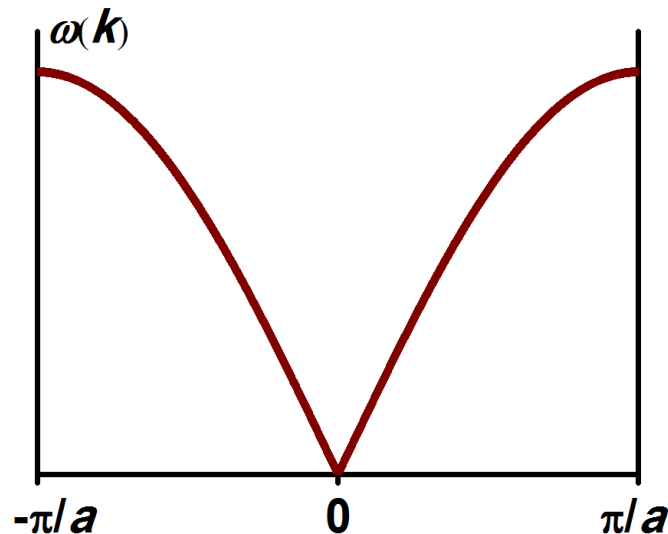
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Only the wavenumbers k in the first Brillouin zone, i.e. between $-\pi/a$ and $+\pi/a$, have unique meaning

Visualization of the dispersion in 1st Brillouin zone:

$$\omega_{\max} = 2\sqrt{(k_{\text{stiffness}}/m)}$$



Lattice vibrations (1 element)

$$u_n = A \exp(i[kna - \omega t]) \Rightarrow \omega^2 = 4k_{\text{stiffness}}/m \cdot \sin^2(ka/2)$$

Only the wavenumbers k in the first Brillouin zone, i.e. between $-\pi/a$ and $+\pi/a$, have unique meaning

$$\omega_{\text{max}} = 2\sqrt{(k_{\text{stiffness}}/m)}$$

Long waves (sound), i.e.

$$\lambda \gg a \Leftrightarrow ka \ll 1 \Leftrightarrow \omega^2 = 4k_{\text{tuhost}}/m \cdot (ka/2)^2 \Leftrightarrow \omega = \sqrt{(k_{\text{tuhost}}/m)} \cdot (ka)$$

$$\text{phase velocity} \quad \omega(k)/k = a\sqrt{(k_{\text{stiffness}}/m)}$$

$$\text{group velocity} \quad d\omega(k)/dk = a\sqrt{(k_{\text{stiffness}}/m)}$$

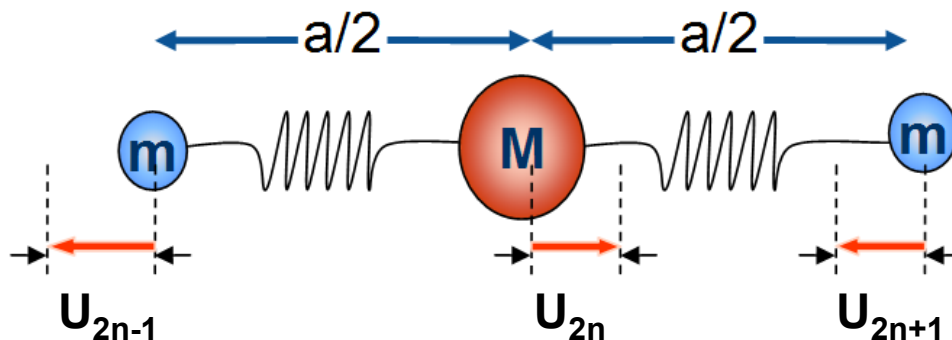
Lattice vibrations (2 elements)

Now slightly complicated idea:

- 2 different kinds of atoms with masses m and M
(all other simplifications remain)

Equations of motion

$$\begin{aligned} Md^2u_{2n}/dt^2 &= -k_{\text{stiffness}}(u_{2n} - u_{2n-1}) - k_{\text{stiffness}}(u_{2n} - u_{2n+1}) \\ md^2u_{2n+1}/dt^2 &= -k_{\text{stiffness}}(u_{2n+1} - u_{2n}) - k_{\text{stiffness}}(u_{2n+1} - u_{2n+2}) \end{aligned}$$



Lattice vibrations (2 elements)

Equations of motion

$$Md^2u_{2n}/dt^2 = -k_{\text{stiffness}}(u_{2n} - u_{2n-1}) - k_{\text{stiffness}}(u_{2n} - u_{2n+1})$$

$$md^2u_{2n+1}/dt^2 = -k_{\text{stiffness}}(u_{2n+1} - u_{2n}) - k_{\text{stiffness}}(u_{2n+1} - u_{2n+2})$$

Again, solution in the form of progressive waves

$$u_{2n} = A \exp(i[k\{2n\}\{a/2\} - \omega t])$$

$$u_{2n+1} = B \exp(i[k\{2n+1\}\{a/2\} - \omega t])$$



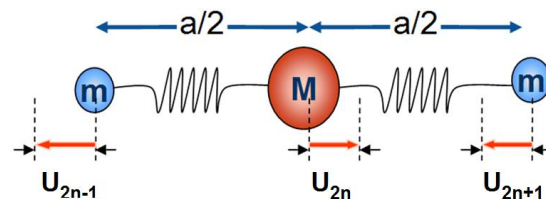
$$-M\omega^2 A = -2k_{\text{stiffness}}A + 2k_{\text{stiffness}}B \cos ka/2$$

$$-m\omega^2 B = -2k_{\text{stiffness}}B + 2k_{\text{stiffness}}A \cos ka/2$$



$$A \cdot (M\omega^2 - 2k_{\text{stiffness}}) + B \cdot 2k_{\text{stiffness}} \cos ka/2 = 0$$

$$A \cdot 2k_{\text{stiffness}} \cos ka/2 + B \cdot (M\omega^2 - 2k_{\text{stiffness}}) = 0$$



Lattice vibrations (2 elements)

$$A \cdot (M\omega^2 - 2k_{\text{stiffness}}) + B \cdot 2k_{\text{stiffness}} \cos ka/2 = 0$$

$$A \cdot 2k_{\text{stiffness}} \cos ka/2 + B \cdot (M\omega^2 - 2k_{\text{stiffness}}) = 0$$

Solution exists for zero determinant, i.e.

$$Mm\omega^4 - 2k_{\text{stiffness}}(M+m)\omega^2 + 4k^2 \sin^2(ka/2) = 0$$

equation for ω^2 is quadratic, i.e. two values of ω for each k

Lattice vibrations (2 elements)

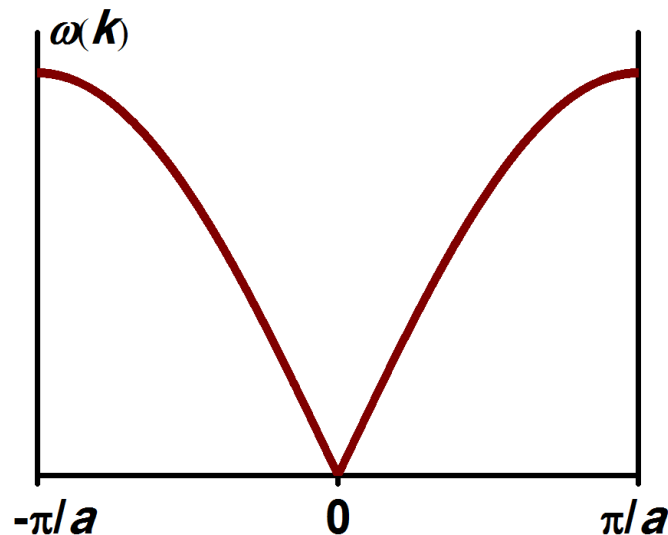
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equation for ω^2 is quadratic, i.e. two values of ω for each k

Visualization of the resulting dispersion in 1st Brillouin zone, for the above reason it has 2 branches (optical and acoustic)

not this figure anymore



Lattice vibrations (2 elements)

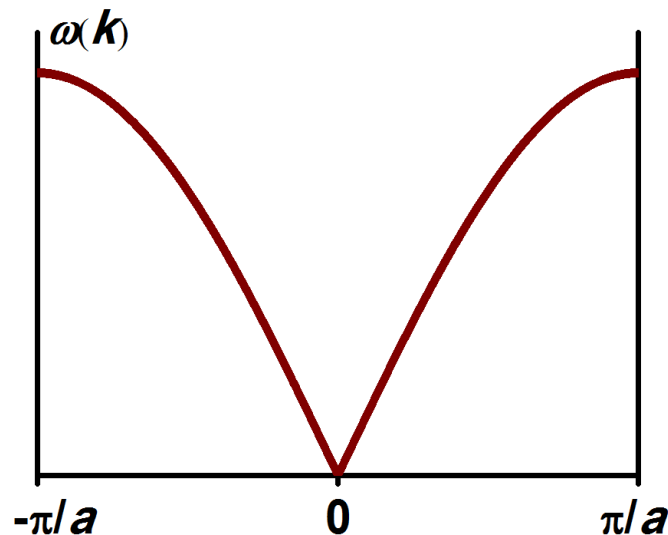
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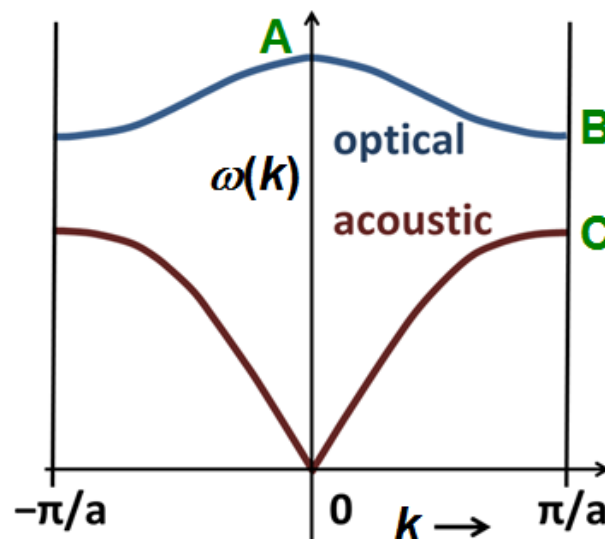
equation for ω^2 is quadratic, i.e. two values of ω for each k

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not this figure anymore



but this figure



Lattice vibrations (2 elements)

Visualization of the resulting dispersion in 1st Brillouin zone, for the above reason it has 2 branches (optical and acoustic)

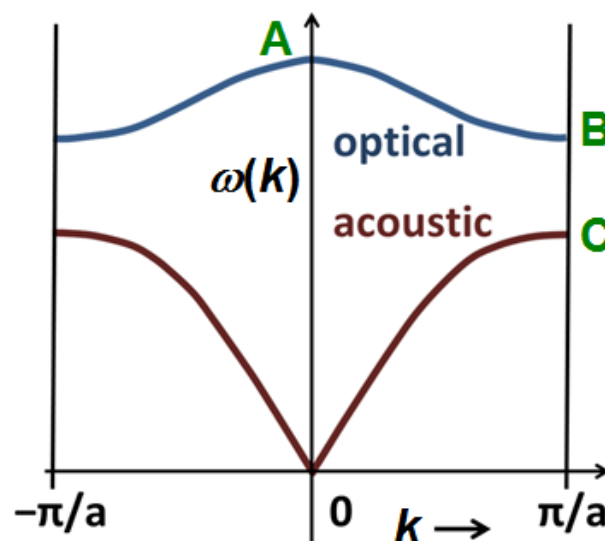
point A (fixed center of mass): $\omega_{\max} = \sqrt{(2k_{\text{stiffness}}[1/m+1/M])}$

point B: (only lighter atoms move): $\omega = \sqrt{(2k_{\text{stiffness}}/m)}$

point C: (only heavier atoms move): $\omega = \sqrt{(2k_{\text{stiffness}}/M)}$

Forbidden frequencies between

$\sqrt{(2k_{\text{stiffness}}/M)}$ a $\sqrt{(2k_{\text{stiffness}}/m)}$



Optical × acoustic branch

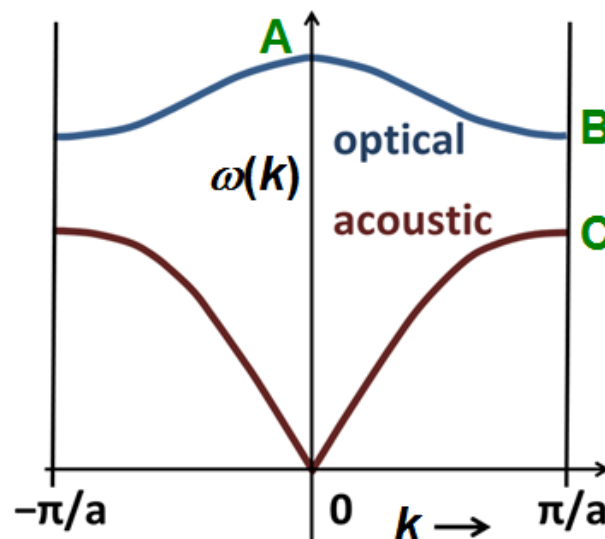
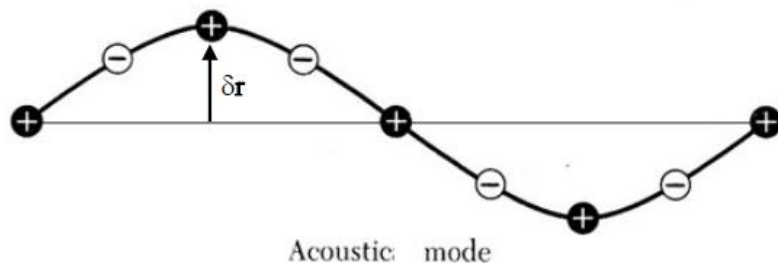
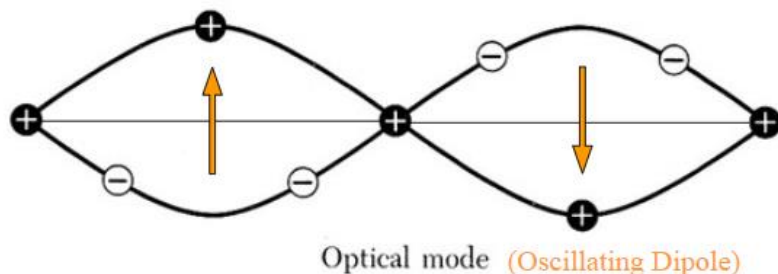
Interpretation of optical and acoustic branch, keeping in mind that atoms of different elements have different charges

Acoustic branch:

mech. signal is charge-independent $\Leftrightarrow$ atoms oscillate in phase

Optical branch:

EM signal is charge-dependent $\Leftrightarrow$ atoms have opposite phases

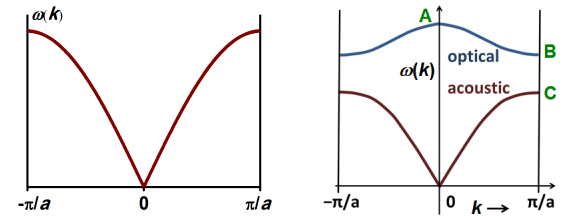


1 × 2 elements

Why are the figures qualitatively different?
Should not they overlap for $m=M$?

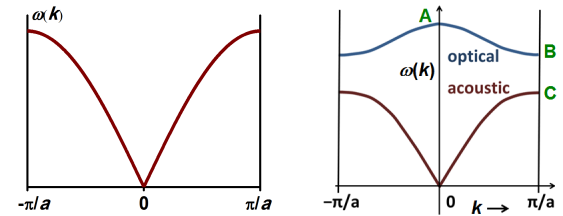
Although the maximum frequency

$2\sqrt{(k_{\text{stiffness}}/m)} = \sqrt{(2k_{\text{stiffness}}[1/m+1/M])}$ is the same for $m=M$, why is it achieved once at the edge and once in the middle of 1st BZ?



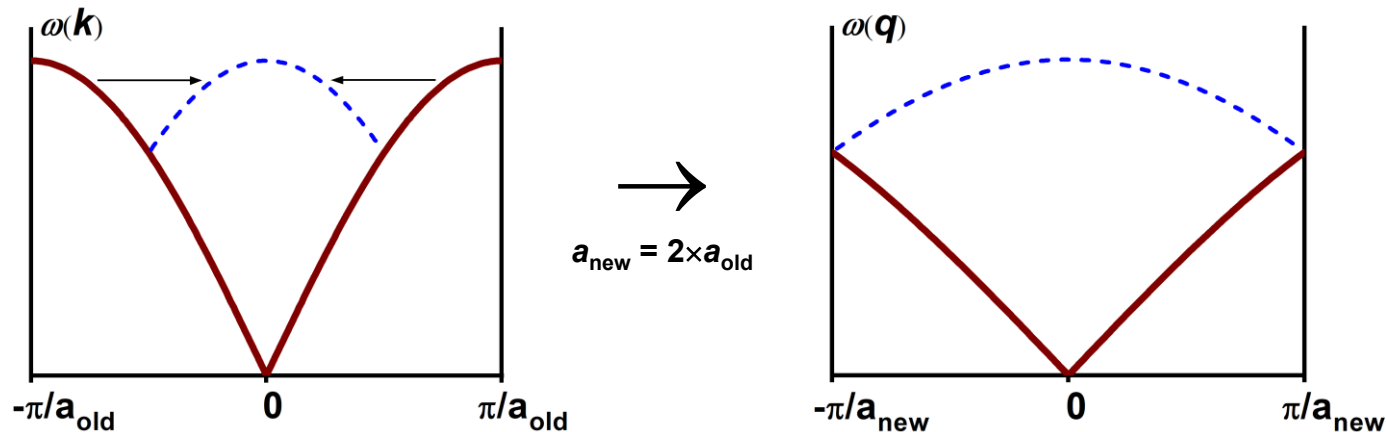
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Why are the figures qualitatively different?
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Although the maximum frequency $2\sqrt{(k_{\text{stiffness}}/m)} = \sqrt{(2k_{\text{stiffness}}[1/m+1/M])}$ is the same for $m=M$, why is it achieved once at the edge and once in the middle of 1st BZ?

Because for two-element chain the period (a) is doubled
⇒ Brillouin zone is halved ⇒ the curve flips inside

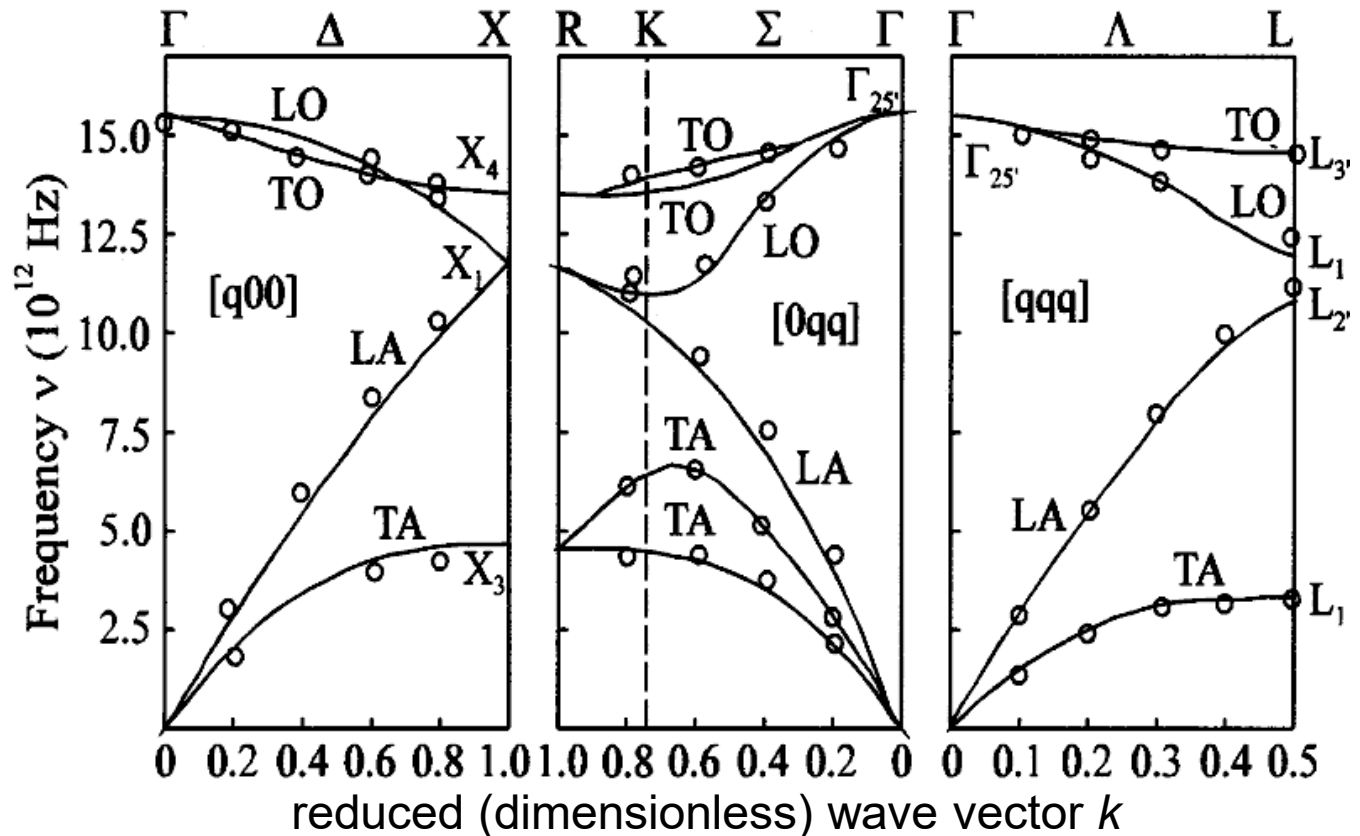


Lattice vibrations (more generally)

For 3D material with N atoms in primitive cell we have

- 3 acoustic branches (1 longitudinal, 2 transverse)
- $3(N-1)$ optical branches

Example for Si



Using that to study phase structure

For 3D material with N atoms in primitive cell we have

- 3 acoustic branches (1 longitudinal, 2 transverse)
- $3(N-1)$ optical branch

Vibrational frequencies are characteristics of a material
(of vibrational modes of a bond)

Measurement:

- **FTIR** = Fourier transform **infrared spectroscopy**
(Fourier transformation "only" speeds the measurement up
by allowing one to measure all wavelengths at once;
this is not the main point)
- **Raman spectroscopy**

FTIR

Energy of photon "flying around a bond" may or may not be invested into its vibrations. Electromagnetic field interacts with dipoles $\Rightarrow$ change of dipole moment is necessary.

FTIR

- source is infrared photon, which gets completely absorbed
- dipole moment is induced by change of atomic coordinates
- thus, we cannot analyze
 - vibrational modes with zero dipole moment
 - single-element materials ($\Rightarrow$ atoms have zero charge)
where the dipole moment is always zero (that's why various phases of C, C:H, Si, etc. are main applications of Raman)
- vibrational frequencies, if we distinguish longitudinal and transverse, allow us to calculate static dielectric constant (Lyddane-Sachs-Teller relationship; details in chapter 10)

Raman spectroscopy

Energy of photon "flying around a bond" may or may not be invested into its vibrations. Electromagnetic field interacts with dipoles $\Rightarrow$ change of dipole moment is necessary.

Raman spectroscopy

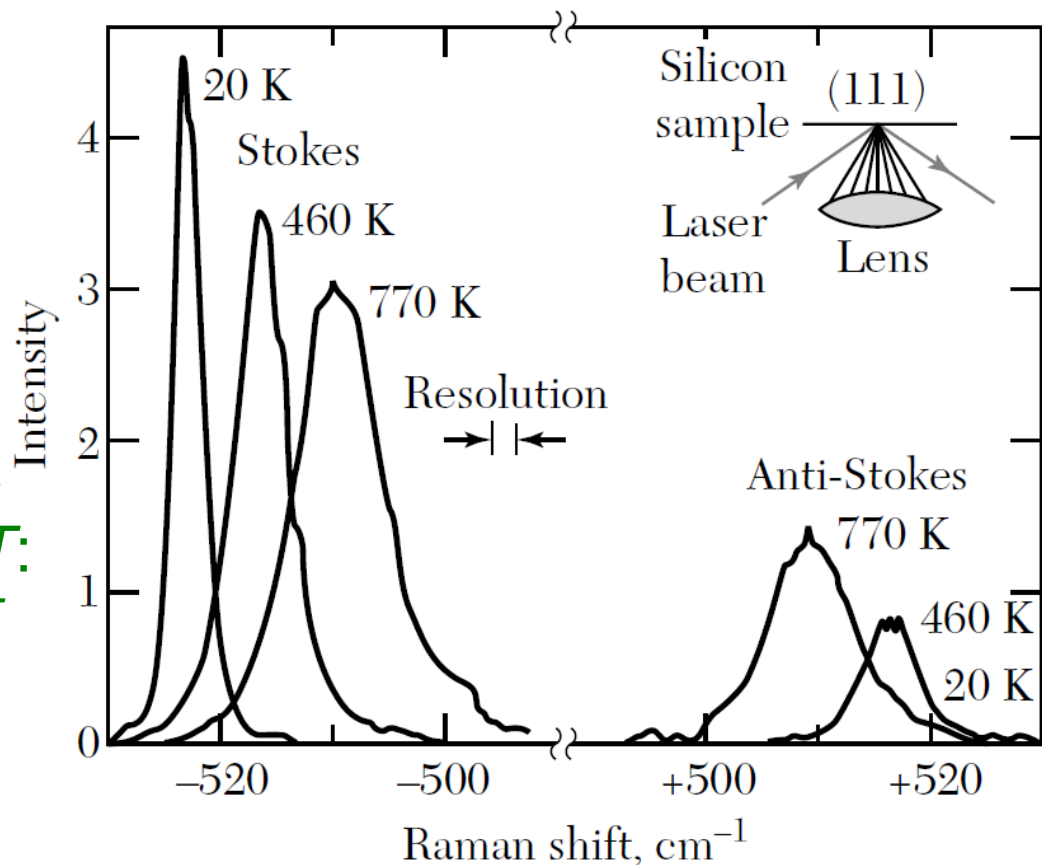
- source is energetic (visible, UV, ...) photon, which reflects
 - with original frequency (Rayleigh: most photons; filtered out)
 - with frequency lowered of IR frequency of bond (Stokes)
 - with frequency enhanced of IR frequency of bond (anti-S.)
- dipole moment induced by deformation of electron cloud
- thus, we cannot analyze
 - vibrational modes which do not change polarizability
 - material where no vibrations change polarizability
(all atoms are in a center of symmetry) - NaCl, MgO, etc.
 - metals, where the polarizability is infinite

Raman spectroscopy

- source is energetic (visible, UV, ...) photon, which reflects
 - with frequency lowered of IR frequency of bond (Stokes)
 - with frequency enhanced of IR frequency of bond (anti-S.)

Take the energy $h\nu$ from a bond is of course possible only when the energy is there, i.e. at sufficiently high temperature.

Thus, the ratio of intensities of both peaks depends on T :
 $\text{anti-Stokes/Stokes} = e^{-h\nu/k_B T}$



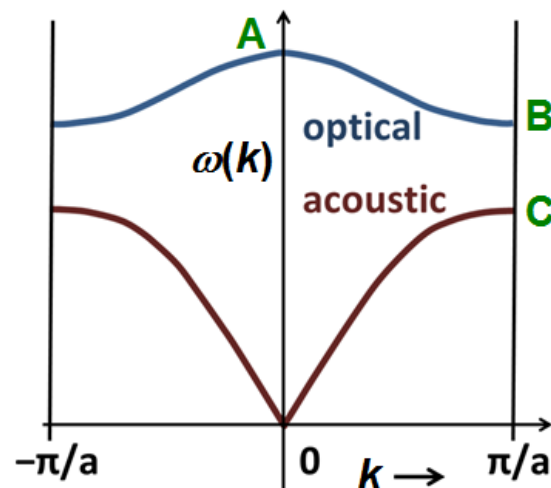
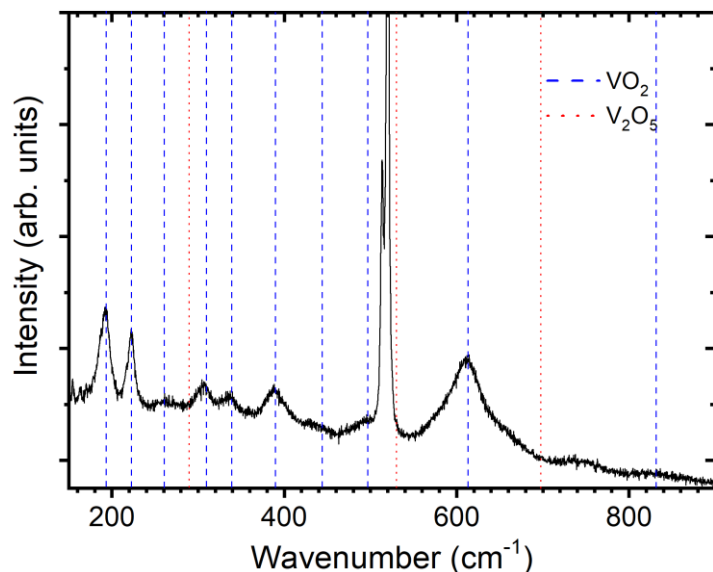
Lattice vibrations

(relationship to Raman and FTIR)

For 3D material we have 3 acoustic branches and especially many optical branches (depending on primitive cell)

Vibrational frequencies are characteristics of a material (of vibrational modes of a bond)

How does it come that we measure discrete frequencies, not packets of allowed frequencies along y-axis?



Lattice vibrations

(relationship to Raman and FTIR)

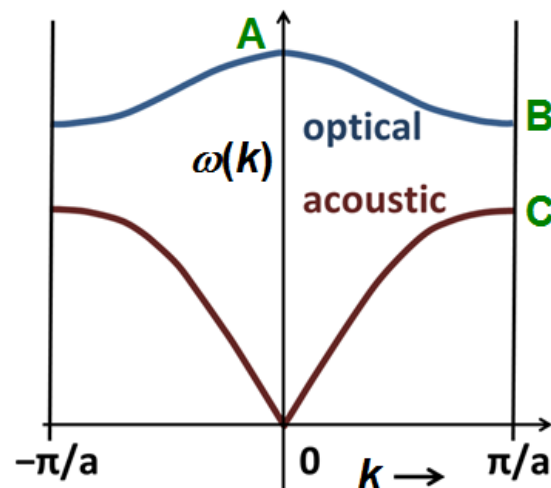
For 3D material we have 3 acoustic branches and especially many optical branches (depending on primitive cell)

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How does it come that we measure discrete frequencies, not packets of allowed frequencies along y-axis?

Because of momentum conservation, photons interact only with optical vibrations close to the middle of BZ

- Raman: $\mathbf{k} = \mathbf{k}_{\text{reflected_photon}} - \mathbf{k}_{\text{incident_photon}}$
 $\Rightarrow |\mathbf{k}| \leq 2|\mathbf{k}_{\text{photon}}| = 4\pi/\lambda \cong 10^{-3} 4\pi/a$
- FTIR: immediately $\mathbf{k} = \mathbf{k}_{\text{photon}}$



Lattice vibrations

(relationship to Raman and FTIR)

How does it come that we measure discrete frequencies, not packets of allowed frequencies along y-axis?

Because of momentum conservation, photons interact only with optical vibrations close to the middle of BZ

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 $\Rightarrow |\mathbf{k}| \leq 2|\mathbf{k}_{\text{photon}}| = 4\pi/\lambda \cong 10^{-3} 4\pi/a$

- FTIR: immediately $\mathbf{k} = \mathbf{k}_{\text{photon}}$

Acoustic vibrations, with frequency at the middle of 1st BZ going to zero, are relevant for Brillouin scattering (contrary to Raman scattering, the photon does not interact with a local bond but with a global low-frequency phonon $\Rightarrow$ info about el. prop.)

Heat capacity

first try: classically

N atoms have $3N$ degrees of freedom, their vibrations can be understood as a superposition of $3N$ waves

According to the equipartition theorem, there is energy $\frac{1}{2}k_B T$ per each quadratic term. There are two terms per each wave (kinetic + potential energy), i.e. total energy is $3Nk_B T$.

From here we get molar heat capacity (Dulong-Petit law)

$$C = dE/dT = 3N_A k_B = 3R = 24.94 \text{ Jmol}^{-1}\text{K}^{-1}$$

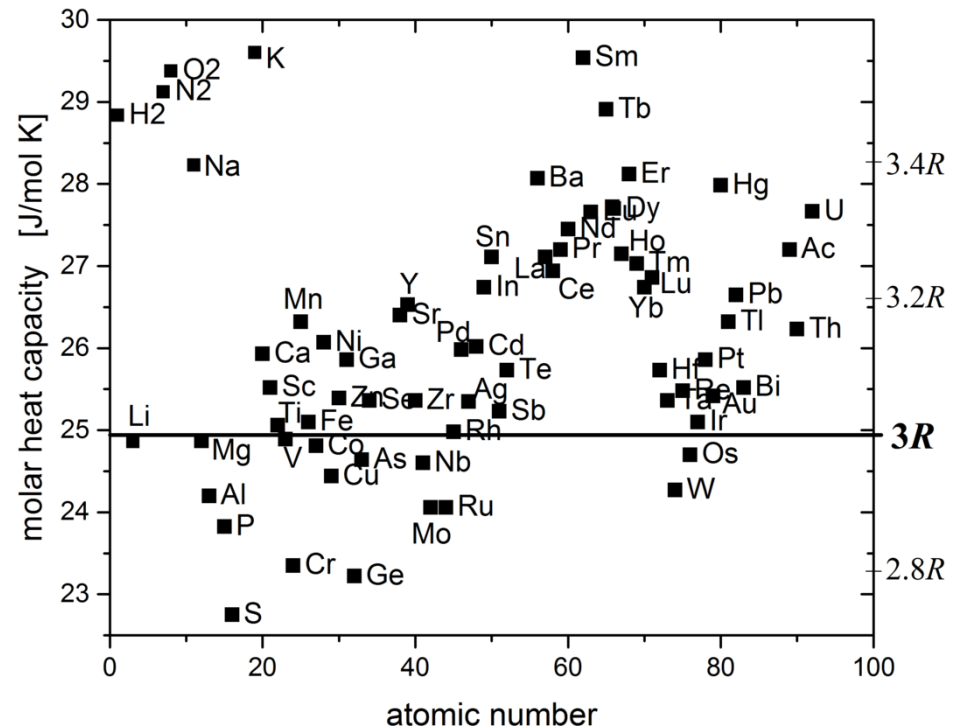
Heat capacity

first try: classically

Molar heat capacity (Dulong-Petit law)

$$C = dE/dT = 3N_A k_B = \mathbf{3R} = 24.94 \text{ Jmol}^{-1}\text{K}^{-1}$$

At room temperature
looks promising (25°C:
most elements **2.8-3.4 R**)



Heat capacity

first try: classically

Molar heat capacity (Dulong-Petit law)

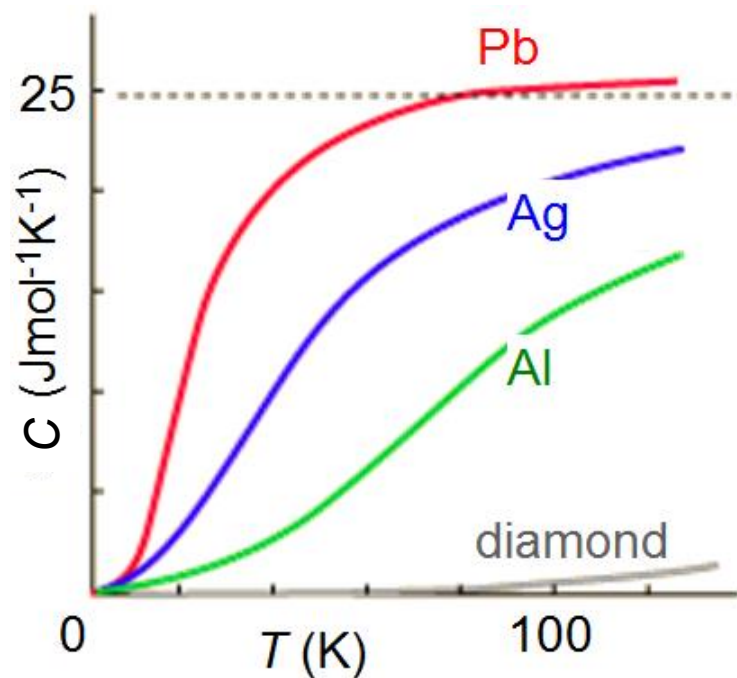
$$C = dE/dT = 3N_A k_B = \mathbf{3R} = 24.94 \text{ Jmol}^{-1}\text{K}^{-1}$$

At room temperature
looks promising (25°C:
most elements **2.8-3.4 R**)

But at low temperatures
the smile freezes:
C approaches zero



we need quantum description



Heat capacity

OK, quantum description

Classical oscillator:

$E = \frac{1}{2}k_B T$ (kinetic) + $\frac{1}{2}k_B T$ (potential) independently of frequency

Quantum harmonic oscillator:

$E_n = \hbar\omega(n + \frac{1}{2})$ (slide about phonons) depends on frequency

Mean value n is given by Planck relationship (14.12.1900):

$$\langle n \rangle = 1/[\exp(\hbar\omega/k_B T) - 1]$$

(for high T , $\langle n \rangle$ approaches $k_B T/\hbar\omega$ and E approaches $k_B T$)

The aim is to get heat capacity, i.e. energy differences.

Therefore the $\frac{1}{2}$ is not that important and is ignored below.

Heat capacity

OK, quantum description

Quantum harmonic oscillator:

$E_n = \hbar\omega(n + 1/2)$ depends on frequency

It is necessary to make clear what is the spectrum of frequencies

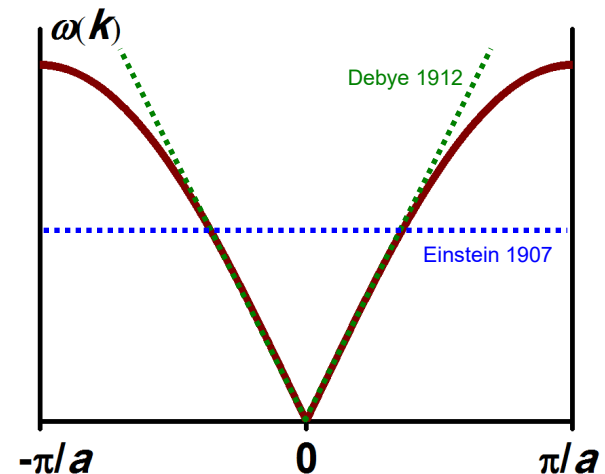
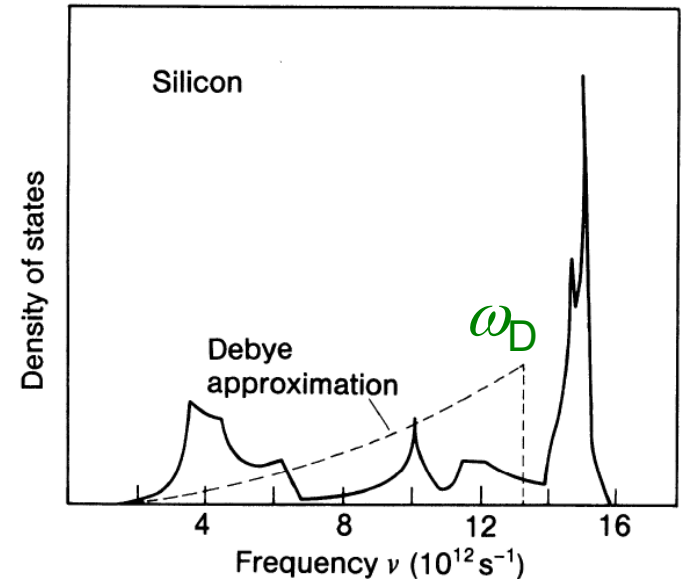
- real spectrum of frequencies: difficult to calculate
- Einstein 1907 (big simplification): single frequency (oscillators are quantum but independent - ignoring that they are in a cr. lattice; energy given by the relationship on previous slide): qualitatively $C \rightarrow 0$ for $T \rightarrow 0$, but quantitatively not so good
- Debye 1912 (only two smaller simplifications): real spectrum is replaced by a continuous one, from 0 to **Debye frequency** ω_D , and real dispersion relation $\omega(k)$ is replaced by a line (frequency-independent speed of sound): quantitatively better

Heat capacity

OK, quantum description

Debye 1912:
replacement by continuous spectrum
from 0 to **Debye frequency** ω_D

replacement of $\omega(k)$ by a line
(i.e. frequency-independent speed
of sound not only for the above case
 $\lambda \gg a$, but in general)



Heat capacity

OK, quantum description (Debye)

Assume N atoms (N cells with size a_0) in a cube of size L

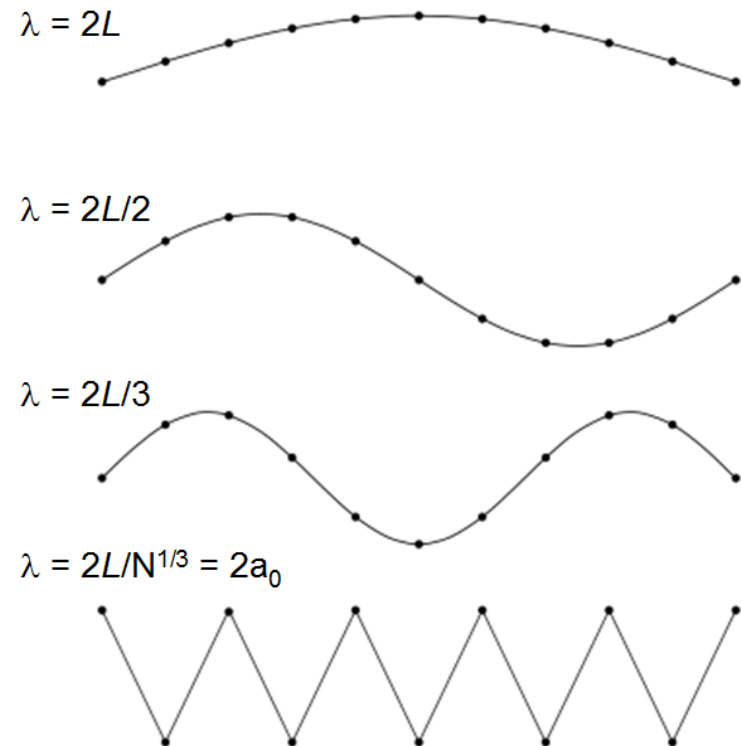
Assuming **standing waves**:

$$\lambda = 2L, 2L/2, 2L/3, \dots, 2L/N^{1/3} = 2a_0$$

in other words

$$k_{x,y,z} = \pi/L, 2\pi/L, 3\pi/L, \dots, N^{1/3}\pi/L = \pi/a_0$$

I.e. number of modes in 3D is N ,
after considering 1 longitudinal +
2 transverse polarizations total **$3N$**
(like in the classical calculation)



Heat capacity

OK, quantum description (Debye)

Consider N atoms (N cells of size a_0) in a cube of size L

Assuming **running** waves:

$$k_{x,y,z} = \pm 2\pi/L, \pm 4\pi/L, \pm 6\pi/L, \dots, \pm 2N^{1/3}\pi/L = \pi/a_0$$

note also the periodic boundary

$$\exp[i(k_x x + k_y y + k_z z)] = \exp[i(k_x [x+L] + k_y [y+L] + k_z [z+L])]$$

I.e. number of modes in 3D is N also from this point of view,
including 1 longitudinal + 2 transverse polarizations total **$3N$**
(doubled step is compensated by two signs of k)

Heat capacity

OK, quantum description (Debye)

According to previous slide $k_{x,y,z} = \pm 2\pi/L, \pm 4\pi/L, \pm 6\pi/L, \dots$

$\Rightarrow$ volume of k-space per one vibrational mode is $(2\pi/L)^3$

I.e. the number of modes N in a sphere in k-space of radius k is

$$N = 4/3 \cdot \pi \cdot k^3 / (2\pi/L)^3 = 4/3 \cdot \pi \cdot (\omega/c)^3 / (2\pi/L)^3 = V\omega^3 / 6\pi^2 c^3$$

where c is the speed of wave propagation, i.e. speed of sound

(similarly from the other assumption: mode of standing waves has eighth volume, but '+' instead of ' $\pm$ ' allow eighth of sphere)

From here we get density of states

$$D(\omega) = dN/d\omega = V\omega^2 / 2\pi^2 c^3$$

Consider 1 longitudinal + 2 transverse polarizations, and average the speed of sound over them:

$$D(\omega) = V\omega^2 / 2\pi^2 \cdot (1/c_l^3 + 2/c_t^3) = 3V\omega^2 / 2\pi^2 c_s^3$$

Heat capacity

OK, quantum description (Debye)

6 slides above: the mean energy of mode with frequency ω is $\hbar\omega\langle n \rangle = \hbar\omega / [\exp(\hbar\omega/k_B T) - 1]$

1 slide above: their density at each frequency from 0 to ω_D
 $D(\omega) = 3V\omega^2/2\pi^2c_s^3$

3N modes = $\int D(\omega) d\omega = V\omega_D^3/2\pi^2c_s^3 \Rightarrow \omega_D^3 = 6\pi^2c_s^3 \cdot N/V$

From here we get total energy

$$E = \int \varepsilon(\omega)\langle n \rangle(\omega)D(\omega)d\omega = \int_0^{\omega_D} \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1} 3V\omega^2/2\pi^2c_s^3 d\omega$$
$$= 3Vk_B^4 T^4 / 2\pi^2 c_s^3 \cdot \int_0^{x_D} \frac{x^3 dx}{\exp(x) - 1}, \quad \text{where } x_D = \hbar\omega_D/k_B T$$

Heat capacity

OK, quantum description (Debye)

Total energy

$$E = \int \varepsilon(\omega) \langle n \rangle(\omega) D(\omega) d\omega = \int_0^{\omega_D} \frac{\hbar \omega}{\exp(\hbar \omega / k_B T) - 1} 3V \omega^2 / 2\pi^2 c_s^3 d\omega$$

$$= 3V k_B^4 T^4 / 2\pi^2 c_s^3 \cdot \int_0^{x_D} \frac{x^3 dx}{\exp(x) - 1}, \quad \text{where } x_D = \hbar \omega_D / k_B T$$

In addition to Debye frequency ($\omega_D^3 = 6\pi^2 c_s^3 \cdot N/V$) introduce **Debye temperature $\Theta = \hbar \omega_D / k_B$** (i.e. $x_D = \Theta / T$):

$$E = 9Nk_B T \cdot (T/\Theta)^3 \cdot \int_0^{x_D} x^3 dx / (e^x - 1), \quad \text{per one mole } 9RT \cdot (T/\Theta)^3 \cdot \int_0^{x_D} x^3 dx / (e^x - 1)$$

$C = dE/dT$:

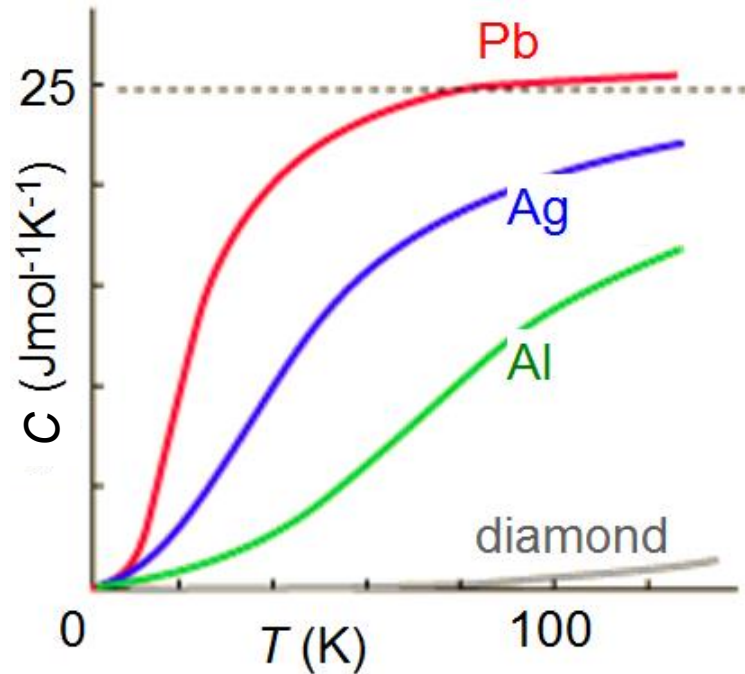
$$C = 9Nk_B (T/\Theta)^3 \cdot \int_0^{x_D} x^4 e^x dx / (e^x - 1)^2, \quad \text{per one mole } 9R(T/\Theta)^3 \cdot \int_0^{x_D} x^4 e^x dx / (e^x - 1)^2$$

Heat capacity

OK, quantum description (Debye)

Single curve (differing only in Θ) for all materials

Figure which we already know ...

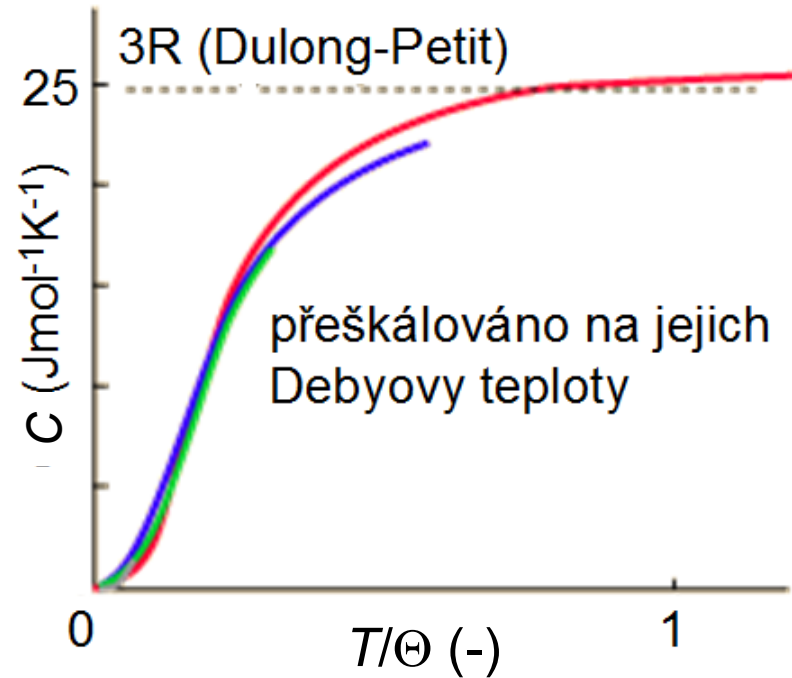
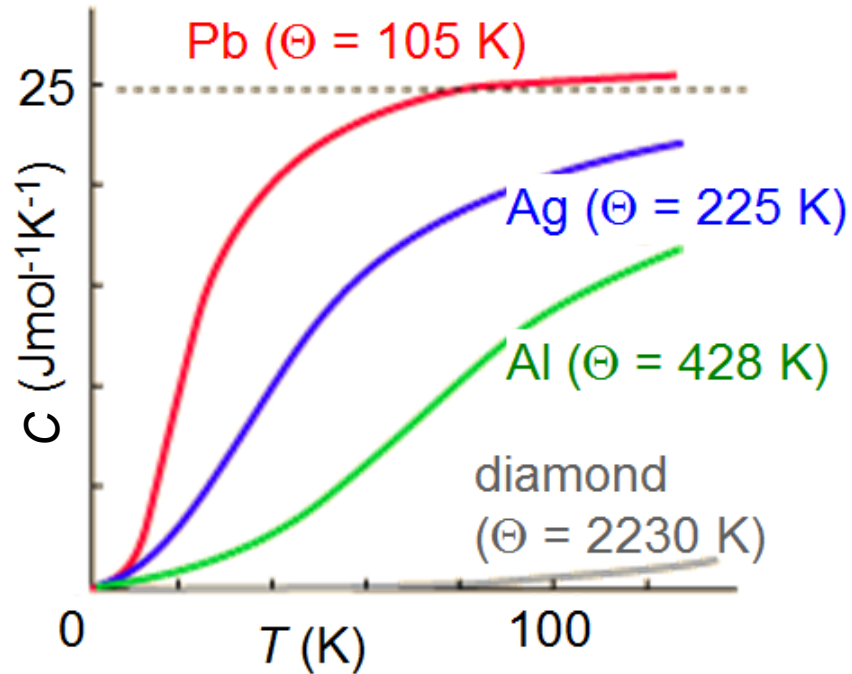


Heat capacity

OK, quantum description (Debye)

Single curve (differing only in Θ) for all materials

Figure which we already know ... is immediately understandable



Heat capacity asymptotes

3 slides above

$$E = 9Nk_B T \cdot (T/\Theta)^3 \cdot \int_0^{x_D} x^3 dx / (e^x - 1), \quad \text{per one mole} \quad 9RT \cdot (T/\Theta)^3 \cdot \int_0^{x_D} x^3 dx / (e^x - 1)$$

$$C = 9Nk_B (T/\Theta)^3 \cdot \int_0^{x_D} x^4 e^x dx / (e^x - 1)^2, \quad \text{per one mole} \quad 9R(T/\Theta)^3 \cdot \int_0^{x_D} x^4 e^x dx / (e^x - 1)^2$$

$T \ll \Theta$:

$x_D = \Theta/T$ approaches ∞ and the first integral $\pi^4/15 \Rightarrow$

$$E \approx 3\pi^4/5 \cdot Nk_B \Theta \cdot (T/\Theta)^4 \quad C \approx 12\pi^4/5 \cdot Nk_B \cdot (T/\Theta)^3$$

So much for crystalline materials, where it makes sense to discuss $3N$ harmonic modes etc. Non-negligible or even dominant linear term $C \sim T$ was observed for amorphous mater.

Heat capacity asymptotes

3 slides above

$$E = 9Nk_B T \cdot (T/\Theta)^3 \cdot \int_0^{x_D} x^3 dx / (e^x - 1), \quad \text{per one mole} \quad 9RT \cdot (T/\Theta)^3 \cdot \int_0^{x_D} x^3 dx / (e^x - 1)$$

$$C = 9Nk_B (T/\Theta)^3 \cdot \int_0^{x_D} x^4 e^x dx / (e^x - 1)^2, \quad \text{per one mole} \quad 9R(T/\Theta)^3 \cdot \int_0^{x_D} x^4 e^x dx / (e^x - 1)^2$$

$T \ll \Theta$:

$x_D = \Theta/T$ approaches ∞ and the first integral $\pi^4/15 \Rightarrow$

$$E \approx 3\pi^4/5 \cdot Nk_B \Theta \cdot (T/\Theta)^4 \quad C \approx 12\pi^4/5 \cdot Nk_B \cdot (T/\Theta)^3$$

$T \gg \Theta$:

$e^x - 1$ approaches x and the first integral $x_D^3/3 \Rightarrow$

$$E \approx 3Nk_B T (1 - \Theta/T) \quad C \approx 3Nk_B (1 - (\Theta/T)^2)$$

Heat capacity asymptotes

$T \ll \Theta$:

$$E \approx 3\pi^4/5 \cdot Nk_B \Theta \cdot (T/\Theta)^4 \quad C_V \approx 12\pi^4/5 \cdot Nk_B \cdot (T/\Theta)^3$$

The dependence $E \sim T^4$, i.e. $C \sim T^3$, is not only in excellent agreement with experiment, but also intuitive:

as a simplifying assumption, say that out of the aforementioned $3N$ modes, at a low temperature:

- modes with ω from 0 to ω_T are activated with classical en. $k_B T$
- modes with ω from ω_T to the maximum ω_D are not activated

$$\omega_T/\omega_D = T/\Theta$$

$$\Rightarrow \text{no. of activated modes } 3N(k_T/k_D)^3 = 3N(\omega_T/\omega_D)^3 = 3N(T/\Theta)^3$$

$$\Rightarrow \text{their energy } E = k_B T \cdot 3N(T/\Theta)^3 \sim T^4$$

$$\Rightarrow C = dE/dT = 12Nk_B(T/\Theta)^3 \sim T^3$$

Values of Debye temperature

First of all, the measured value of Debye temperature depends on ...

Values of Debye temperature

First of all, the measured value of Debye temperature depends on ... temperature! (Due to model approximations.)

Element	Debye Temperature			
	Click ▼ to see citations			
	Low Temperature Limit (at 0 K)		Room Temperature (at 298 K)	
Aluminum	433 K	▼	390 K	▼
Americium	121 K	▼		
Antimony	220 K	▼	200 K	▼
Argon	92.0 K	▼		
Arsenic	282 K	▼	275 K	▼
Barium	111 K	▼	116 K	▼
Beryllium	1481 K	▼	1031 K	▼
Bismuth	120 K	▼	116 K	▼
Boron	1480 K	▼	1362 K	▼
Cadmium	210 K	▼	221 K	▼
Calcium	229 K	▼	230 K	▼
Carbon	2230 K	▼	1550 K	▼
diamond	2250 K	▼		
graphite	413 K	▼		
Cerium	179 K	▼	138 K	▼
Cesium	40.5 K	▼	43 K	▼
Chromium	606 K	▼	424 K	▼
Cobalt	460 K	▼	386 K	▼
Copper	347 K	▼	310 K	▼
Curium	123 K	▼		
Dysprosium	183 K	▼	158 K	▼
Erbium	188 K	▼	163 K	▼
Europium	118 K	▼		
Francium	39 K	▼		
Gadolinium	182 K	▼	155 K	▼
Gallium	325 K	▼	240 K	▼
Germanium	373 K	▼	403 K	▼
Gold	162.3 K	▼	178 K	▼

[table from www.knowledgedoor.com]

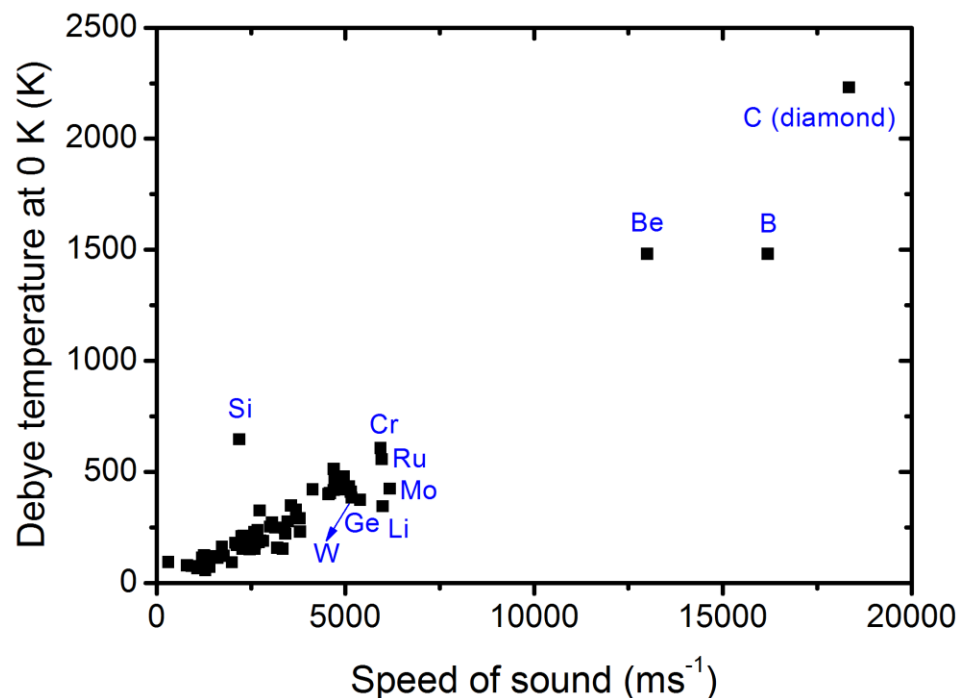
Values of Debye temperature

First of all, the measured value of Debye temperature depends on ... temperature! (Due to model approximations.)

Second, note $\omega_D^3 = 6\pi^2 c_s^3 \cdot N/V$, i.e. $\omega_D \sim c_s$, 9 slides above Relationships between speed of sound and mechanical properties are in chapter 9 below, spoiler $c_s^2 = (B+4/3G)/\rho$

High values

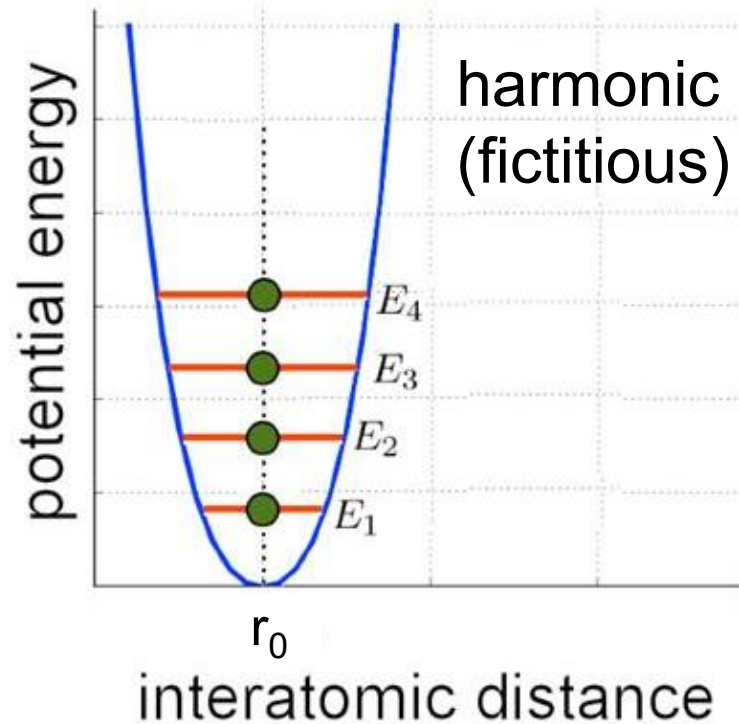
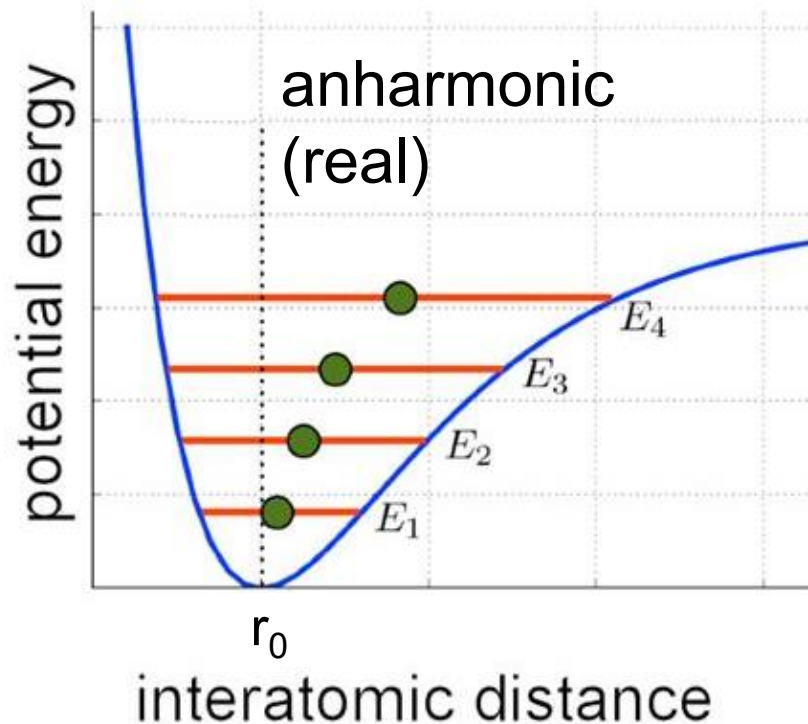
- thanks to high B and G , i.e.. tough covalent bonds, usual suspects: C, Si, Ge + Cr, Mo, W
- thanks to ρ light elements: Li, Be, B, again C



Thermal expansion

Potential representing interatomic interactions is not harmonic, note the asymmetry around the equilibrium (approaching infinity on the left, finite dissociation energy on the right)

Assume $E(r) = Ax^2 - Bx^3$ where $x = r - r_0$



Thermal expansion

Assume $E(r) = Ax^2 - Bx^3$ where $x = r - r_0$,
at given T vibrations between $x_0 - \Delta$ and $x_0 + \Delta$, looking for x_0

First simplifications

- physical: $E = k_B T$
- mathematical: the anharmonic term is a small correction only
($|Ax^2| \gg |Bx^3|$; $\Delta \gg x_0$)

$\Rightarrow k_B T = Ax^2 - Bx^3$ converts to $k_B T \approx Ax^2 \approx A\Delta^2$, i.e. $\Delta^2 = k_B T/A$

$\Rightarrow E(x_0 - \Delta) = E(x_0 + \Delta)$, i.e. $2Ax_0\Delta - 3Bx_0^2\Delta - B\Delta^3 = 0$,
converts to $2Ax_0\Delta - B\Delta^3 \approx 0$, after substitution $x_0 = k_B T.B/(2A^2)$

Thermal expansion coefficient $\alpha = (dx_0/dT)/r_0 = k_B B/(2A^2 r_0)$

Thermal expansion

Assume $E(r) = Ax^2 - Bx^3$ where $x = r - r_0$,
at given T vibrations between $x_0 - \Delta$ and $x_0 + \Delta$, looking for x_0

Next without simplification (standard statistical mechanics)

$$\Rightarrow \langle x \rangle = \int x \cdot \exp(-[Ax^2 - Bx^3]/k_B T) dx / \int \exp(-[Ax^2 - Bx^3]/k_B T) dx \\ = k_B T \cdot 3B / (4A^2) (1.5 \times \text{times more than above})$$

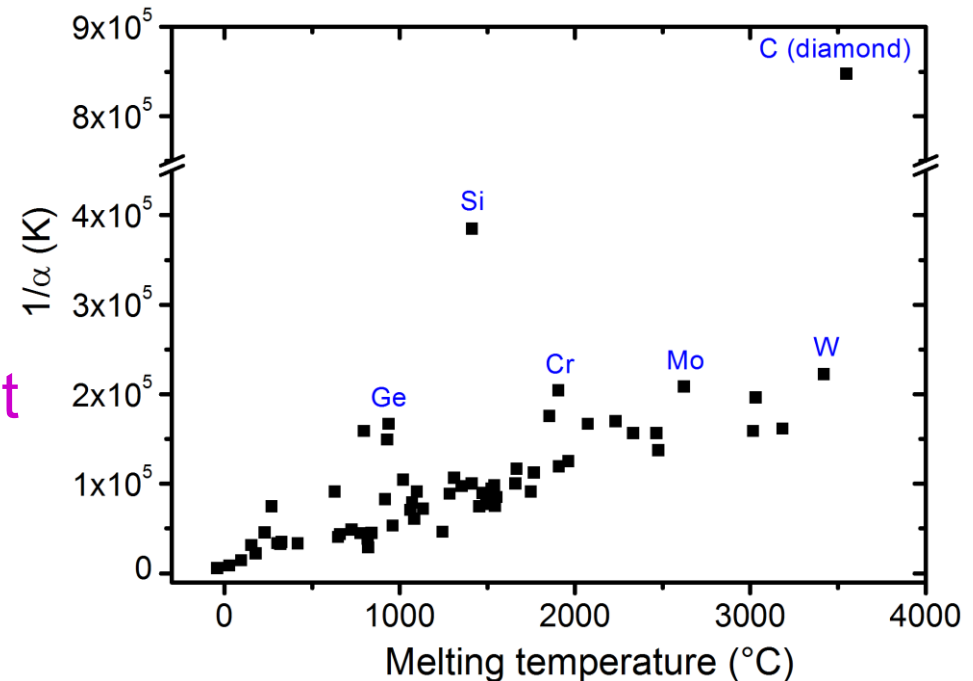
Thermal expansion coefficient $\alpha = (dx_0/dT)/r_0 = k_B 3B / (4A^2 r_0)$

Values of thermal exp. coefficient

Low values once again due to tough covalent bonds, usual suspects:
C, Si, Ge + Cr, Mo, W

Bonding energy (depth, but not width, of minimum) captured by melting temperature.

Most covalent C and Si are above the rest of dependence (even more than in the case of Θ): energy minima are not only deep, but also narrow.



(diamond usually recrystallizes to graphite before melting - i.e. the temperature shown is sublimation temperature of graphite, but this does not change diamond's low thermal expansion)

Values of thermal exp. coefficient

How does the thermal expansion α depend on temperature?

$$\alpha = 1/V \cdot (\partial V / \partial T)_P = 1/(3V) \cdot (\partial V / \partial T)_P = 1/(3B) \cdot (\partial P / \partial T)_V$$

- B is bulk modulus (chapter about mechanical properties below)
- pressure, P , represent energy density: its temperature dependence is given by the heat capacity discussed above



$$\alpha = 1/(3B) \cdot C_V$$

detailed calculation, not affecting the qualitative conclusions:

$$\alpha = 1/(3B) \cdot \gamma C_V \text{ where } \gamma \text{ is Grüneisen parameter}$$

The quantity which most changes with T is C_V , so

- $\alpha \sim T^3$ for $T \rightarrow 0$
- $\alpha \sim \text{const.}$ for $T \gg \Theta$

analogously to the asymptotes of heat capacity 9 slides above

Negative thermal expansion coef.

$\alpha < 0$ (in some temperature range)
non-intuitive, but possible

The structures of corresponding materials are not close packed, e.g. tetrahedrons and octagons (cation in the middle, anions in corners) only touch by their corners

Important role of disperse interactions (van der Waals interactions of temporary dipoles)

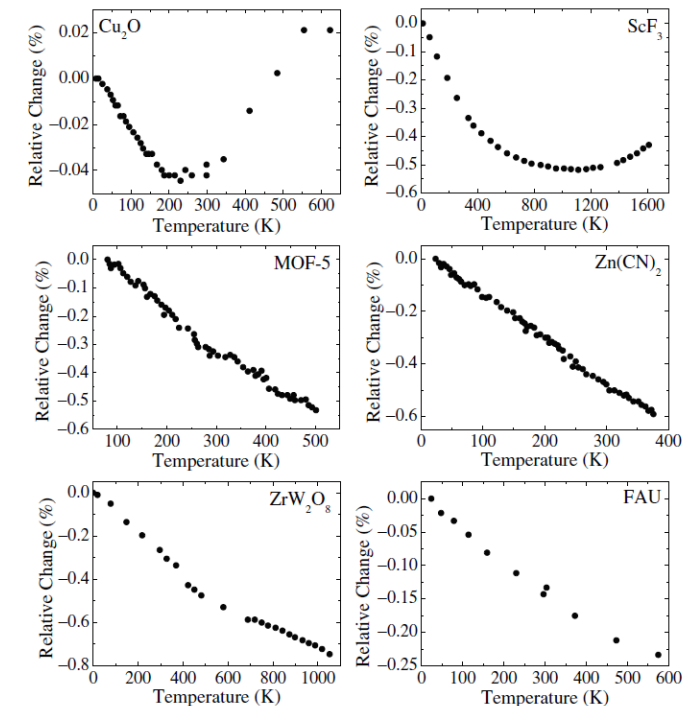
IOP Publishing
Rep. Prog. Phys. 79 (2016) 066503 (50pp)

Reports on Progress in Physics
doi:10.1088/0034-4885/79/6/066503

Review

Negative thermal expansion and associated anomalous physical properties: review of the lattice dynamics theoretical foundation

Martin T Dove¹ and Hong Fang^{2,3}



Importance of thermal expansion

In 1920, the candidates for Nobel prize were

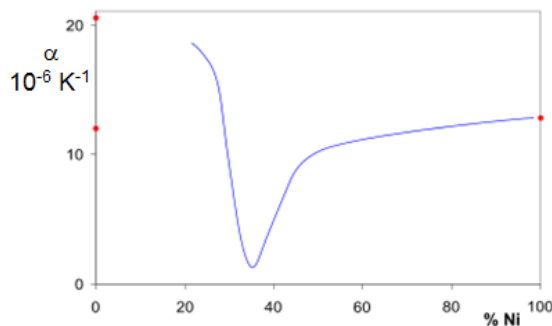
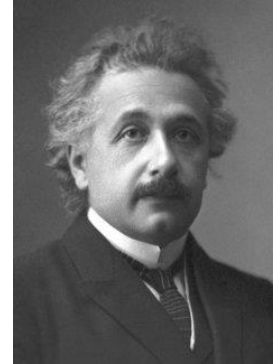
Albert Einstein

theory of relativity, photoeffect, Brown motion

and

Charles Edouard Guillaume

alloy $\text{Fe}_{64}\text{Ni}_{36}$, invar, which exhibits $\approx 10\times$
lower thermal expansion than usual steel
 $\Rightarrow$ stability of exact measuring instruments



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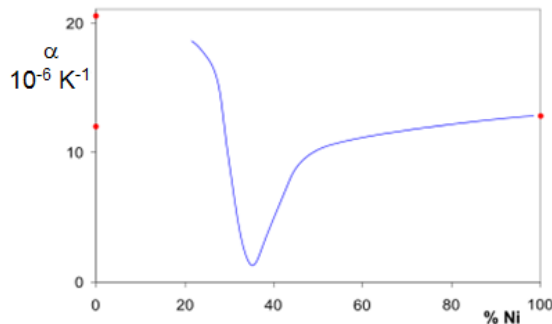
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alloy $\text{Fe}_{64}\text{Ni}_{36}$, invar, which exhibits $\approx 10\times$
lower thermal expansion than usual steel
 $\Rightarrow$ stability of exact measuring instruments

Guillaume got the prize (Einstein next year)



Importance of thermal expansion

May be also demonstrated more dramatically



Charles de Gaulle airport, Terminal E, 23.5.2004

differential thermal expansion was a major factor behind the collapse ... the head of the official investigation said this week.

Thermal conductivity

At this moment only the phonon contribution; electronic below

$$\lambda = 1/3 \cdot C_{\text{vol}} \cdot c_s \cdot l \quad \text{where}$$

$1/3$ says how many phonons affect the direction of ∇T

C_{vol} is heat capacity, this time **per volume**

c_s is mean velocity of phonons (sound)

l is mean free path of phonons (most important below)

l is limited by interactions (collisions) of phonons

1) with material's boundaries (boundary scattering)

2) with lattice defects (defect scattering)

3) with each other (phonon-phonon scattering)

Thermal conductivity

$$\lambda = 1/3 \cdot C_{\text{vol}} \cdot c_s \cdot l$$

1) boundary scattering

(like reflection of light on a boundary of two refractive indices)

Dominant process at low temperatures, when

- defect scattering is limited by long typical wavelengths of phonons (compared to distances between defects)
- phonon-phonon scattering is limited by low number of phonons

$$C_{\text{vol}} \sim T^3$$

$l \approx D$ (dimension) is independent of T



$$\lambda \sim T^3$$

Thermal conductivity

$$\lambda = 1/3 \cdot C_{\text{vol}} \cdot c_s \cdot l$$

2) defect scattering
(like light scattering)

Dominant process at medium temperatures, when

- typical phonon wavelengths become comparable to distances between defects
- phonon-phonon scattering is still limited by their number

$$C_{\text{vol}} \sim T^3$$

$l \approx D'$ (distance of defects) still independent of T

$\Downarrow$

$$\lambda \sim T^3$$

Thermal conductivity

$$\lambda = 1/3 \cdot C_{\text{vol}} \cdot c_s \cdot l$$

3) phonon-phonon scattering

Dominant process at high temperatures, mechanism below

$$C_{\text{vol}} \approx 3Nk_B/V \text{ independent of } T$$

$$l \sim 1/[\text{phonon_density}] \sim 1/T$$



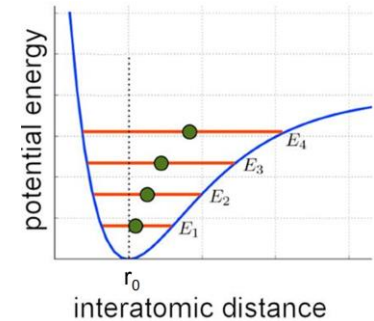
$$\lambda \sim 1/T$$

Why do phonons collide at all?

Because of the anharmonic dependence of interatomic force on interatomic distance

In a case of harmonic dependence

- dependence of force on displacement would be linear, i.e. sum of forces would lead to sum of displacements and vice versa without problem, individual phonons would not interfere (there would be no mechanism of their interaction)
- thus, thermal conductivity of a perfect crystal could be infinite

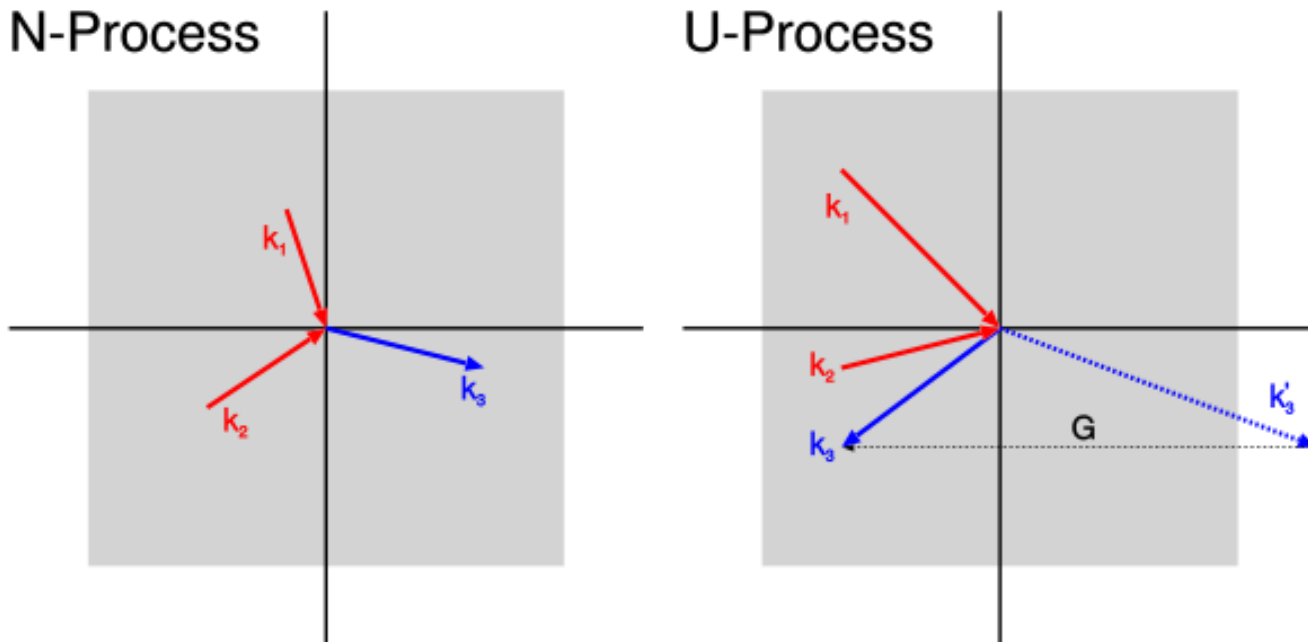


Why do the phonon collisions matter?

Because collisions preserve energy ($\omega_1 + \omega_2 = \omega_3$),
but not necessarily wave vector

Only vectors in the first Brillouin zone have unique meaning:

- $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3$, if $\mathbf{k}_3$ is in the first BZ (Normal process)
- $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{G}$, if $\mathbf{k}_3$ is not in the first BZ (Umklapp process)



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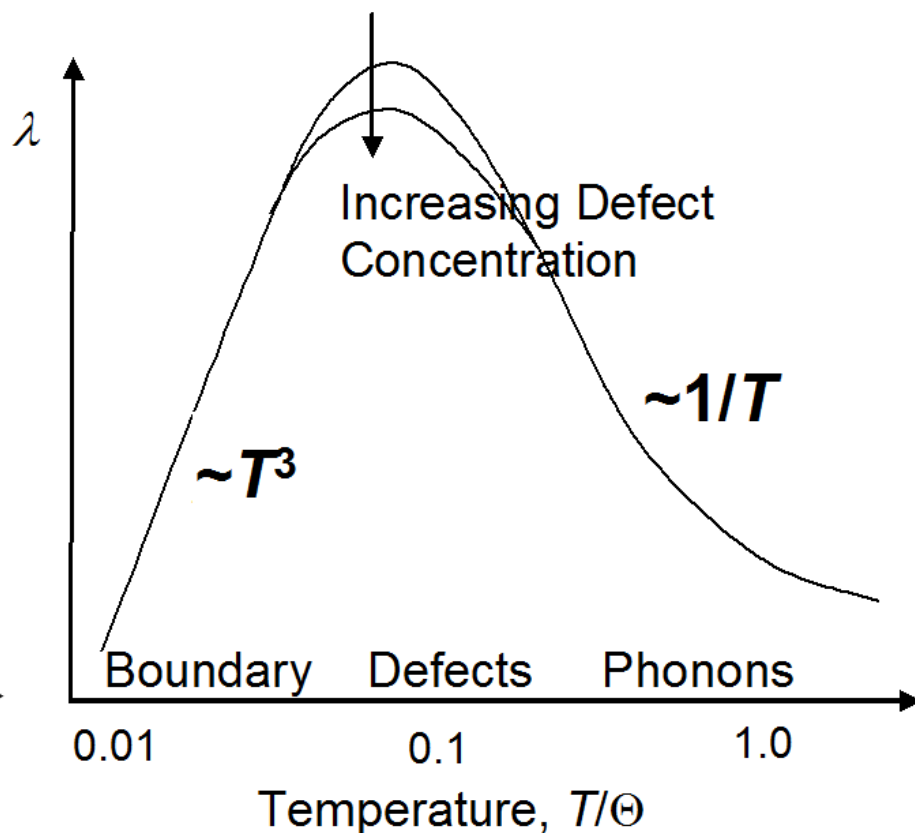
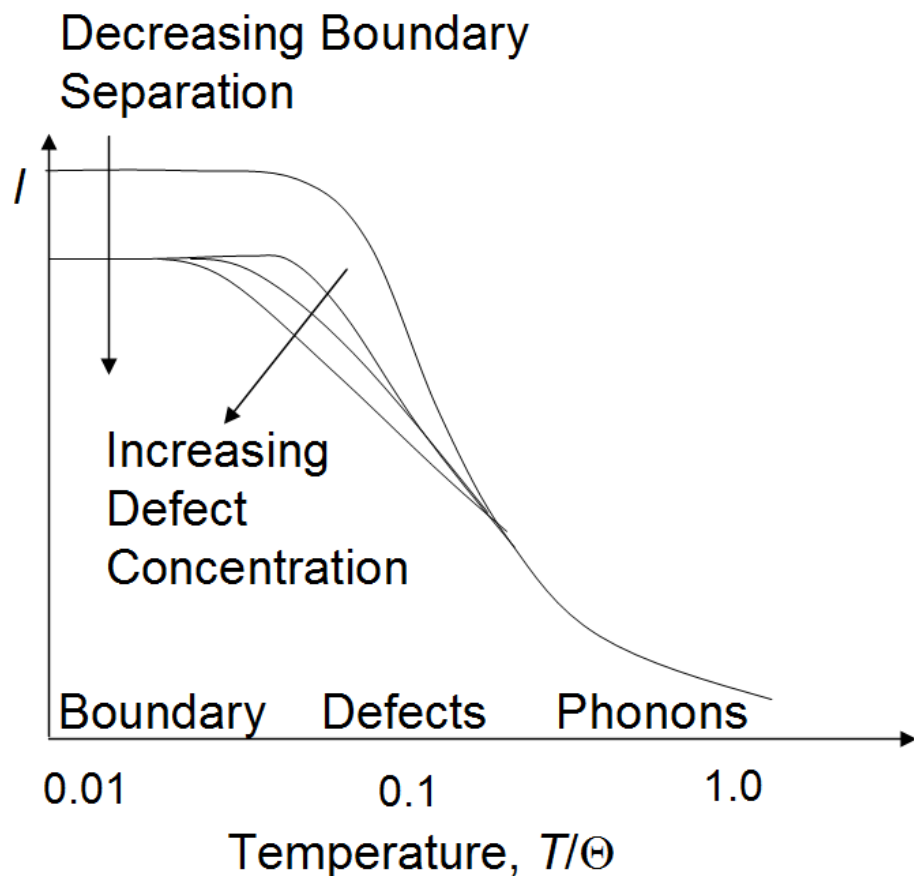
- $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3$, if $\mathbf{k}_3$ is in the first BZ (Normal process)
- $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{G}$, if $\mathbf{k}_3$ is not in the first BZ (Umklapp process)

Umklapp process changes not only the size but also the direction of $\mathbf{k}$, i.e. it obviously harms thermal conductivity

The probability that $\mathbf{k}_1 + \mathbf{k}_2$ is outside first BZ increases with the length of $\mathbf{k}_1$ and $\mathbf{k}_2 \Rightarrow$ umklapp process is dominant at high T (high density of not just phonons, but high-energy phonons)

Thermal cond. - graphical summary

$$\lambda = 1/3 \cdot C_{\text{vol}} \cdot c_s \cdot l \quad : \text{ graphical summary}$$



Values of thermal conductivity

typical values (note defect concentration) in $\text{Wm}^{-1}\text{K}^{-1}$ at RT

Molecular solids

- P 0.02
- S 0.17
- polystyrene 0.13
- acrylic glass 0.20
- polyethylene 0.50
- snow 0.05-0.25

Covalent and ionic bonds

- SiO_2 , glass 0.8-1.7
- Al_2O_3 26-40
- MgO 38
- Ge 42
- Si 84
- C(diamond) 650

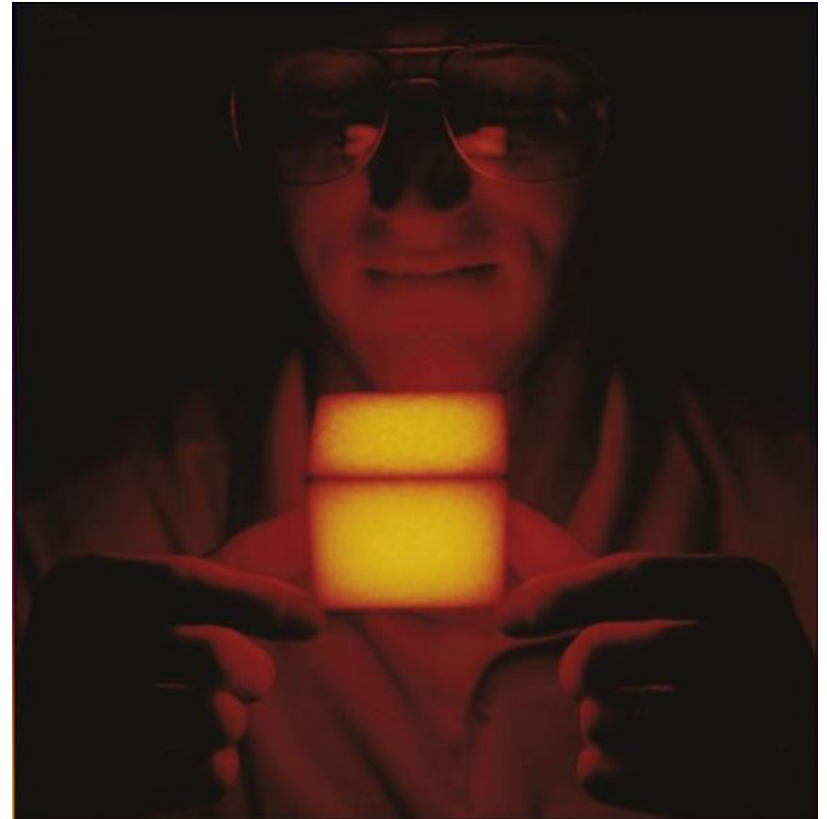
Metals (including electronic component discussed below)

- steel 16-54
- W 178
- Al 247
- Au 315

Temperature does not burn, heat does

Hot ($1250\text{ }^{\circ}\text{C}$) cube in the figure is of (fibers of) SiO_2 (part of the protective surface of space shuttles): according to previous slide only $0.8\text{-}1.7\text{ Wm}^{-1}\text{K}^{-1}$.

After cooling of its surface, the cube can be held in hands, because the heat moves from the interior to the surface very slowly.



[Lockheed Missiles & Space Company]

4) Classical calculations

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

brief version, see KFY/MPPL for details

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Modeling of solid materials

"Experiment" performed (fast, cheap) in a computer -
link between pure (analytical) theory and real experiment

Compared to both analytical theory and real experiment
still short history (several decades)

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 31, NUMBER 2

AUGUST, 1959

Studies in Molecular Dynamics. I. General Method*

B. J. ALDER AND T. E. WAINWRIGHT

Lawrence Radiation Laboratory, University of California, Livermore, California

(Received February 19, 1959)

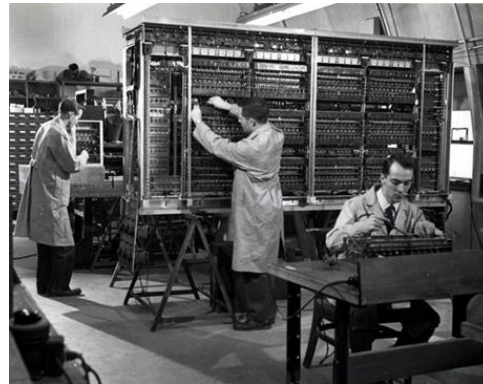
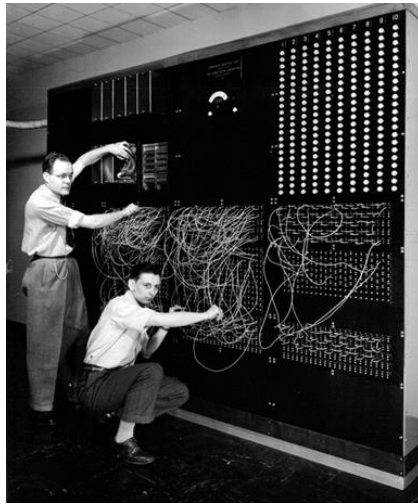
A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles. The study of this many-body problem is carried out by an electronic computer which solves numerically the simultaneous equations of motion. The limitations of this numerical scheme are enumerated and the important steps in making the program efficient on the computers are indicated. The applicability of this method to the solution of many problems in both equilibrium and nonequilibrium statistical mechanics is discussed.

Modeling of solid materials

"Experiment" performed (fast, cheap) in a computer -
link between pure (analytical) theory and real experiment

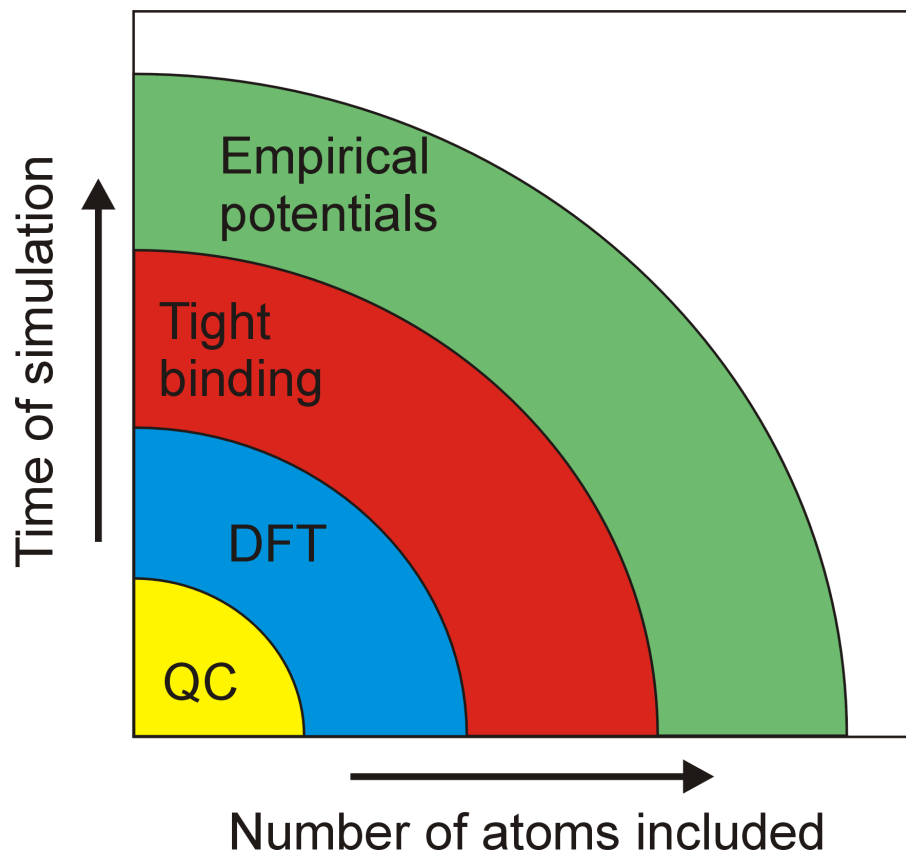
Compared to both analytical theory and real experiment
still short history (several decades)

The steeper development started



after sufficiently fast computers became available

Description of interatomic interactions



From fastest =
least accurate

- **Empirical potentials**
(chapter 4)
- **Tight binding**
(one of methods which are not very popular since introduction of DFT)
- **Density Functional Theory**
(chapter 8)
- **Quantum Chemistry**
(Hartree-Fock, post HF methods more precise & slower than DFT)

Empirical potential

Main simplifying assumption: atoms are (elastically colliding) balls. Sometimes neutral, sometimes charged.

Empirical potential (force field) includes

(1) Long range part = Coulombian term:

- present only when we consider charged atoms

(2) Short range part:

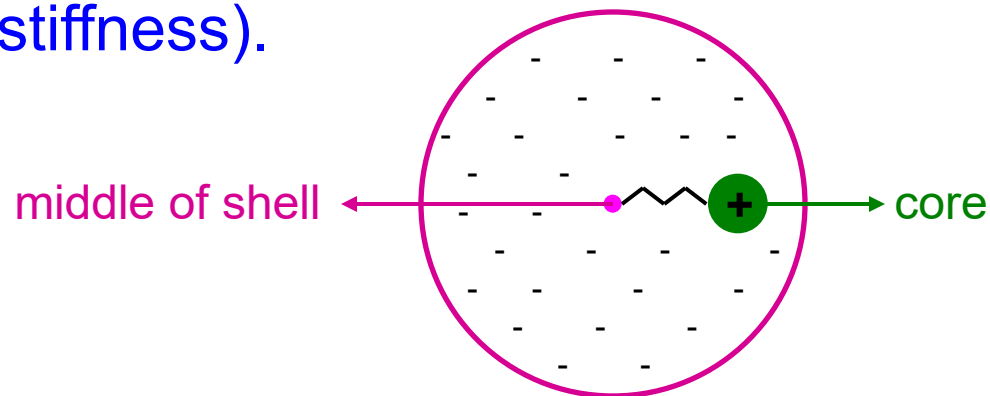
- present always
- sometimes "empirical potential" refers only to this part

Long range (Coulombian) part

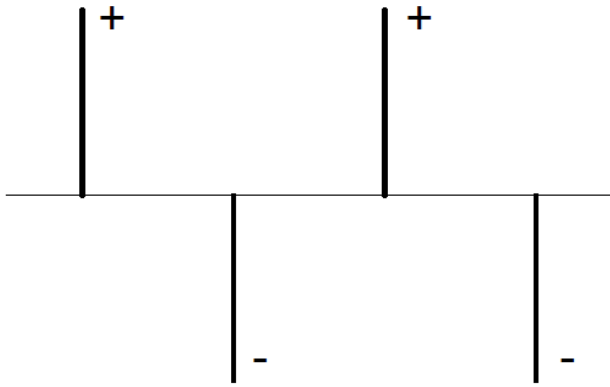
- (1) The system studied includes only one element
 - ⇒ atomic charges are zero
 - ⇒ Coulombian term does not make sense
- (2) The system studied includes more elements with similar electronegativities (covalent bonds)
 - ⇒ atomic charges are almost zero
 - ⇒ Coulombian term is not necessary
- (3) The system studied includes more elements with different electronegativities (ionic bonds)
 - ⇒ atomic charges between 0 and number of valence el. (e.g. for Al_2O_3 O^{-x} and $\text{Al}^{+1.5x}$, 'x' between 0 and 2)
- (4) The system studied includes more elements with very different electronegativities (very ionic bonds) ⇒ atomic charges corresponding to the number of valence electrons (e.g. for CaO O^{-2} and Ca^{+2})

Long range (Coulombian) part

- (5) If we want to do something very sophisticated (at the cost of much higher computational costs), e.g. using so called *reactive bond order potentials* (details later), there can be **variable charges** (each atom has different one, update after each update of coordinates).
- (6) Possibility to include polarizability of atoms (in parallel to all previous points): atom does not have to be one ball, but two balls (**core + middle of electronic shell**) connected by a spring. See above for total charge, but here we have two extra parameters for each element (shell charge and spring stiffness).



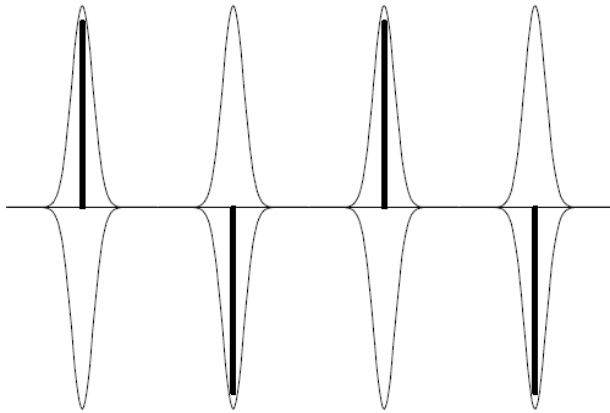
Ewald sum



Calculation of electrostatic interaction of **point charges** in a crystal (can be adapted to any system with periodical boundaries),

$1/2 \sum_{\mathbf{R}} \sum_i \sum_j q_i q_j / |\mathbf{r}_i - \mathbf{r}_j + \mathbf{R}|$ ($\mathbf{R}$ is lattice vector, $i \neq j$ for $\mathbf{R} = \mathbf{0}$),
converges very poorly

Ewald sum

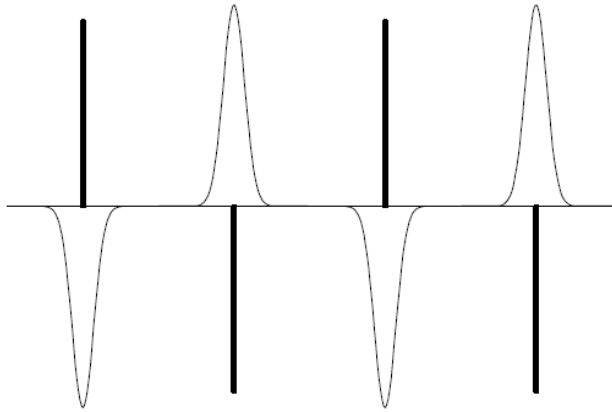


Calculation of electrostatic interaction of **point charges** in a crystal (can be adapted to any system with periodical boundaries),

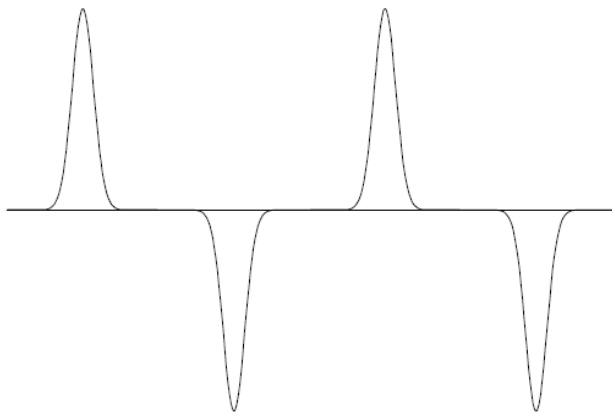
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converges very poorly

Typical solution (Ewald): add and subtract a cloud (e.g. Gaussian distribution; see the figure) of the same (in absolute value) charge to each **point** charge

Ewald sum



This part will be calculated in **real space**: equal charges of opposite signs shield each other ($\Rightarrow U \sim 1/r^2$ instead of $1/r$), which makes the convergence fast this time



This part will be calculated in **reciprocal space**: smooth periodic dependence there converts to a well converging Fourier series

Short range part

(1) **Two-body potentials** (Lennard-Jones, Buckingham, ...):

- energy depends on bond length only
- typically for ionic crystals

(2) **Multibody potentials** (Stillinger-Weber, Brenner, ...):

- energy depends also on the surroundings, specifically on coord. numbers of atoms, angle between bonds (3-body pot.), angle between bond and plane (4-body pot.)
- typically for covalently bonded materials

(2a) **Reactive potentials** (REBO, REAXFF):

- extremely sophisticated version of the stuff above

(3) **Embedded atom method** (EAM, MEAM):

- energy depends also on the surroundings, specifically on the contribution of each atom to an electronic cloud and on energy resulting from sitting in this cloud
- typically for metals

Short range part

(1) **Two-body potentials** (Lennard-Jones, Buckingham, ...):

- energy depends on bond length only
- typically for ionic crystals

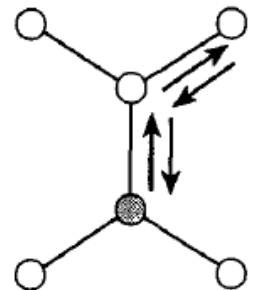
(2) **Multibody potentials** (Stillinger-Weber, Brenner, ...):

- energy depends also on the surroundings, specifically on coord. numbers of atoms, angle between bonds
(*3-body pot.*), angle between bond and plane (*4-body pot.*)

Just to illustrate that we cannot describe anything in any way: for some pairs of possible structures (e.g. fcc $\times$ bcc) it can be shown that the corresponding energy difference depends on fourth moment of the electronic density of states)

$\Rightarrow$ from quantum point of view counting with electron skipping along a path of length

$\Rightarrow$ from emp. pot. point of view requires considering neighbours of the bond studied (multibody pot.)



Two-body potentials

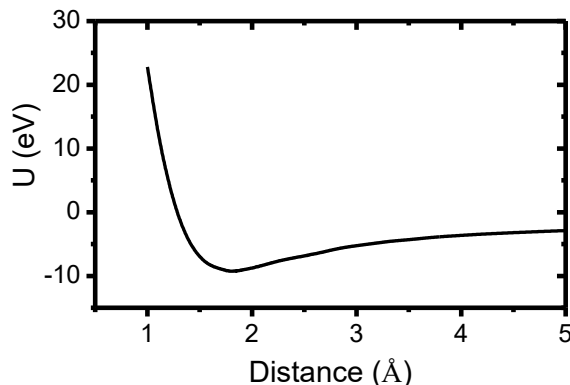
Simplest and most intuitive (but often insufficient) possibility: energy depends only on the bond length (interatomic distance)

$U(\mathbf{r}_i - \mathbf{r}_j)$, or shorter $U(r)$, for one bond

$1/2 \sum_{i,j \neq i} U(\mathbf{r}_i - \mathbf{r}_j)$ for whole system

Independently of specific formulas (listed below) it holds that the force ($-dU(r)/dr$) should be

- attractive for long distances
- repulsive for short distances



Example: Ti-N interaction
(sum of short-range and
Coulombian) in nc-TiSiN

[J. Houska et al, Surf. Coat. Technol. 203, 3348 (2009)]

Lennard-Jones (2-body)

Most often (albeit mostly due to a tradition) cited pair potential from pre-computer era

$$U = Ar^{-12} - Br^{-6} = \varepsilon[(r_m/r)^{12} - 2(r_m/r)^6]$$

where r_m is position of minimum and ε is energy therein

Br^{-6} : attractive term representing the van der Waals force between dipoles

Ar^{-12} : repulsive term, chosen in order to be easy to calculate in times of slow or none computers ($[r^{-6}]^2 = r^{-12}$)

In order to illustrate its limited usefulness: all single-element materials described by the LJ potential behave qualitatively in the same way (e.g. want to crystallize in the same structure), only have different lattice constant and cohesive energy.

In other words: there is only one LJ material, A and B only define the units of length and energy.

Buckingham (2-body)

Nowadays, the Buckingham potential is (for a reason) more often used to describe solids than the Lennard-Jones potential

$$U = Ae^{-r/\rho} - Cr^{-6} \text{ or } Ae^{-Br} - Cr^{-6}$$

Usually (contrary to LJ) including the Coulombian term

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1q_2/4\pi\epsilon_0r$$

advantages compared to LJ:

- more physical ($e^{-r/\rho}$ can be justified, r^{-12} not)
- more flexible due to one extra parameter (two extra parameters including the Coulombian term)

disadvantage compared to LJ:

- unphysical for $r \rightarrow 0$: $e^{-r/\rho}$, contrary to r^{-12} , does not diverge for $r \rightarrow 0$, therefore $U(0) = -\infty$, not ∞ like for LJ (not drama in praxis - atoms do not get that close)

Buckingham (2-body)

It is possible to find many fits of the same potential for the same material ... see e.g. the examples for TiO_2 below (some of them consider also polarizability - last 4 columns; some assume that the Ti-Ti interaction is purely Coulombian)

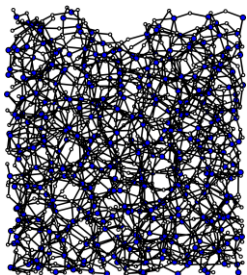
author	note	interaction	q1 (e)	q2 (e)	A (eV)	ρ (Å)	C (eV Å ⁶)	K1 (eV Å ⁻²)	shell charge1 (e)	K2 (eV Å ⁻²)	shell charge2 (e)
Collins 96	rigid O	O-O	-2	-2	95253.3	0.16117	0				
		Ti-O	4	-2	186862	0.227815	0				
le Roux 97	polarized O	O-O	-2	-2	95253.3	0.16117	0	53963.1	-2.71547	53963.1	-2.71547
		Ti-O	4	-2	186862	0.227815	0			53963.1	-2.71547
Grimes 94	full charge	O-O	-2	-2	9547.96	0.21916	32	54.8	-2.8	54.8	-2.8
		Ti-O	4	-2	2549.4	0.2989	0	181.2	-0.1	54.8	-2.8
	partial charge	O-O	-1.75	-1.75	2230386.3	0.1429	321	32.2	-2.23	32.2	-2.23
		Ti-O	3.5	-1.75	1889.4	0.2989	0	121.2	-0.1	32.2	-2.23
Postl 86	rutile	O-O	-2	-2	180079	0.3086	0				
	anatase	O-O	-2	-2	205058	0.3029	0				
	brookite 1	O-O	-2	-2	193175	0.3055	0				
	brookite 2	O-O	-2	-2	186146	0.3072	0				
	rutile	Ti-O	4	-2	416350	0.2639	0				
	anatase	Ti-O	4	-2	440826	0.2607	0				
	brookite	Ti-O	4	-2	430199	0.262	0				
Bush 94		O-O	-2	-2	25.41	0.6937	32.32	20.53	-2.513	20.53	-2.513
		Ti-O	4	-2	2088.107	0.2888	0	253.6	1.678	20.53	-2.513
Catlow 77		O-O	-2	-2	22764.3	0.149	112.2	86.4	-2.53	86.4	-2.53
& Lewis 85		Ti-O	4	-2	754.2	0.3879	0	37.3	2.89	86.4	-2.53
Matsui 91		Ti-Ti	2.196	2.196	31124.0	0.154	5.2476				
		O-O	-1.098	-1.098	11784.0	0.234	30.2262				
		Ti-O	2.196	-1.098	16960.0	0.194	12.5943				

Buckingham (2-body)

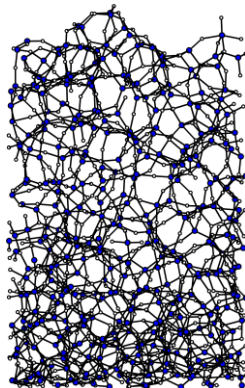
For all potentials considered here, the really existing crystalline phases constitute (local) energy minima

However, when modelling film growth, all of them do not lead to a correct result $\Rightarrow$ test them before using them!

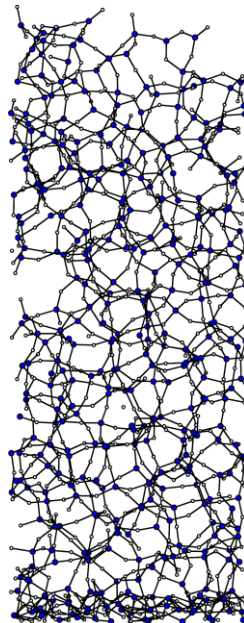
Matsui 91



Postl 86



Collins 96



Example: growth of α -TiO₂
(250 Ti + 500 O, always 1 eV)

Tersoff (3-body)

$$U_{ij} = f_C(r_{ij}) [f_R(r_{ij}) - \gamma_{ij} f_A(r_{ij})] \quad (i,j,k \text{ denotes atom; } I,J,K \text{ element})$$

where $f_R(r_{ij}) = A_{IJ} \exp(-a_{IJ} r_{ij})$

$$f_A(r_{ij}) = B_{IJ} \exp(-b_{IJ} r_{ij})$$

$$f_C(r_{ij}) = \begin{cases} 1 & \text{for } r_{ij} \leq R_{IJ} \\ 0.5 + 0.5 \cos[\pi(r_{ij} - R_{IJ}) / (S_{IJ} - R_{IJ})] & \text{for } R_{IJ} < r_{ij} \leq S_{IJ} \\ 0 & \text{for } r_{ij} > S_{IJ} \end{cases}$$

(in order to ensure smooth decrease to zero)

and, most importantly, $\gamma_{ij} = \chi_{IJ} (1 + \beta_I^{\eta_i} [\sum f_C(r_{ik}) \omega_{IK} g(\theta_{ijk})]^{\eta_i})^{-1/2 \eta_i}$

where $g(\theta_{ijk}) = 1 + c_I^2/d_I^2 - c_I^2/[d_I^2 + (h_I - \cos \theta_{ijk})^2]$

the promised dependence of the energy on the surroundings is hidden in the key function

$$\gamma = f(\chi_{IJ}, \beta_I, \beta_J, n_I, n_J, c_I, c_J, d_I, d_J, h_I, h_J, r_{ik}, r_{jk}, \theta_{jik} \text{ over all } k)$$

Tersoff (3-body)

$$U_{ij} = f_C(r_{ij}) [f_R(r_{ij}) - \gamma_{ij} f_A(r_{ij})] \quad (i,j,k \text{ denotes atom; } I,J,K \text{ element})$$

where $f_R(r_{ij}) = A_{IJ} \exp(-a_{IJ} r_{ij})$

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and, most importantly, $\gamma_{ij} = \chi_{IJ} (1 + \beta_I^{\eta_i} [\underbrace{\sum f_C(r_{ik}) \omega_{IK} g(\theta_{ijk})}_{\downarrow}]^{\eta_i})^{-1/2 \eta_i}$

generalized, non-integer, coordination
number (not including the bond studied)

Tersoff (3-body)

The number of fitted parameters becomes very high, e.g. 45 for three-element system (such as SiNH - see table)

†|

Atom	A	a	B	b	R	S	β	η	c	d	h
	eV	$\text{\AA}^{-1}$	eV	$\text{\AA}^{-1}$	$\text{\AA}$	$\text{\AA}$	-	-	-	-	-
N	6368.14	5.43673	511.76	2.7	1.8	2.1	5.2938e-3	1.33041	20312	25.5103	-0.56239
Si	1830.8	2.4799	471.18	1.7322	2.7	3.0	1.1e-6	0.78734	100390.0	16.217	-0.59825
H	86.712	3.7879	43.5310	1.98	0.8	1.0	4.0	1.0	0.0	1.0	1.0

(a)

Atom pair		χ	ω
		-	-
N	N	0.0	1.0
N	Si	0.65	1.0
N	H	0.76	1.0
Si	Si	1.0	1.0
Si	H	0.78	1.0
H	H	1.0	1.0

(b)

Different notation of the same quantities in different sources:

- $a_{IJ} = (a_I + a_J)/2$ (equivalent for b_{IJ})
- $A_{IJ} = (A_I A_J)^{0.5}$ (equivalents for B_{IJ} , R_{IJ} , S_{IJ})
- $a = \lambda = \lambda_1$, $b = \mu = \lambda_2$, $\eta = n$, $h = \cos \theta_0$
- $(S-R)/2 = D$, $(S+R)/2 = R'$

Reactive force field (illustration only)

$$E = E_{\text{bond}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{coa}} + E_{\text{tors}} + \\ E_{\text{conj}} + E_{\text{H}} + E_{\text{vdW}} + E_{\text{Coul}}$$

just to put an example (more versions, more notations)

E_{b} = bond energy

E_{lp} = lone-pair energy

E_{over} = overcoordination energy

E_{under} = undercoordination energy

E_{val} = valence angle energy

E_{pen} = double-bond valence angle penalty

E_{coa} = valence angle conjugation energy

E_{tors} = torsion energy

E_{conj} = conjugation energy

E_{H} = hydrogen bond energy

E_{vdW} = van der Waals energy

E_{Coul} = Coulombian energy (continuously updated charges)

There are hundreds (not tens anymore) fitted parameters

Embedded atom method

- Energy depends (in addition to a 2-body interaction) also on
- contribution of each atom to the electron cloud, and
 - energy resulting from the fact that atom is sitting in this cloud

Embedded atom method (EAM)

- for each pair of elements 1 dataset: 2-body interaction
- for each element two further datasets: electron cloud contributing function and embedding function
- i.e. total $N(N+1)/2 + 2N$ datasets

Modified EAM (MEAM)

- electron cloud contributing function depends on the angle (the cloud of electronic charge around atom core is not isotropic, but respects the crystal symmetry)

EAM - examples of exactness

Thermal expansion coefficient (10^{-6} K^{-1})

Element	EAM	Experiment
Cu	16.4	16.7
Ag	21.1	19.2
Au	12.9	14.1
Ni	14.1	12.7
Pd	10.9	11.5
Pt	7.8	8.95

Melting temperature (K)

Element	EAM	Experiment
Cu	1340	1358
Ag	1170	1234
Au	1090	1338
Ni	1740	1726
Pd	1390	1825
Pt	1480	2045

Activation energy for self-diffusion (eV)

Element	EAM	Experiment
Cu	2.02	2.07
Ag	1.74	1.78
Au	1.69	1.74
Ni	2.81	2.88
Pd	2.41	< 2.76
Pt	2.63	2.66

Software - classical calculations

The most difficult part is not to get a software which integrates equations of motion, but to get proper empirical potential



There are many codes, usually free

In the case of "exotic" empirical potentials it is necessary to choose code where this EP is implemented (there are even single-purpose specialized codes for some EPs)

Example 1: Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), www.lammps.org
- probably the most important one

Example 2: DL-POLY, www.ccp5.ac.uk/software
- out of specialities not implemented in LAMMPS
(for now) includes e.g. atom polarizability

Main simulation algorithms

(for given set of atoms and simulation cell)

Most of the algorithms below are relevant independently of the description of interactions (i.e. not only for empirical potentials)

- 1) Automatic geometry optimization, i.e. looking for the lowest-energy structure (not for a global minimum, but for a local minimum close to the initial geometry)
- 2) Energy calculation for several geometries (couple of local minima) - we are interested in energy differences
- 3) Observing the time evolution of a system, so-called molecular dynamics (term used also for solids)
- 4) Combinations of these (geometry optimization followed by MD, changing set of atoms when modelling film growth, etc.)

Using MD for film growth simulations

Exceptionally popular application of simulations - not only due to the objective usefulness, but also due to its intuitiveness / clarity also for pure experimentalists

Prerequisites on the theory side

- interaction potential (force field) including all present elements (including the substrate, if we want to simulate nucleation)
- code where the usage of this potential is implemented

Prerequisites on the experiment side

- know the film-forming atoms or radicals (which is not always clear in the case of CVD), if it is not the varied parameter
- know what does the film grow on, if simulating nucleation (atomic coordinates, not some word such as "cotton fibers")

Using MD for film growth simulations

(simulation algorithm)

Very intuitive - reproduces the experiment as exactly as possible

- 1) **Substrate** or previously nucleated crystal
(choose horizontal size, composition, structure, temperature T)
- 2) **New atoms** / molecules above the surface
(choose flux composition and particle energies E)
- 3) **Fixed-energy (NVE) run** (control only T of substrate)
(atomic collisions, bond breaking and forming, energy dissipation in the film bulk)
- 4) **Fixed-temperature (NVT) run**
(remove the remaining excess energy, reestablish T)
- 5) **Removal** of resputtered / desorbed particles and return to point 2 (typically thousands of cycles)

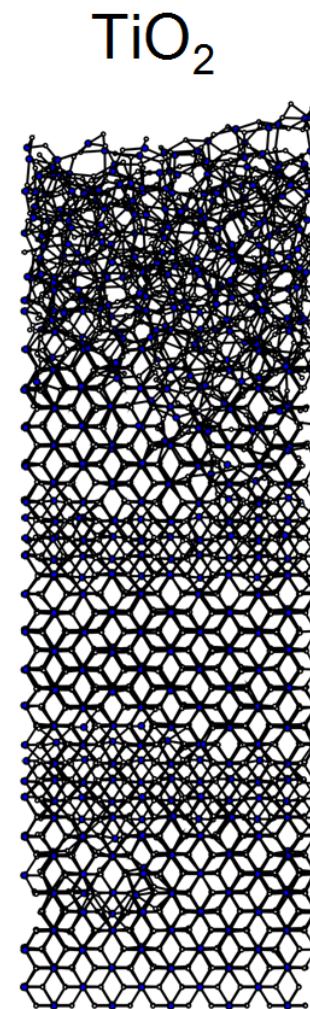
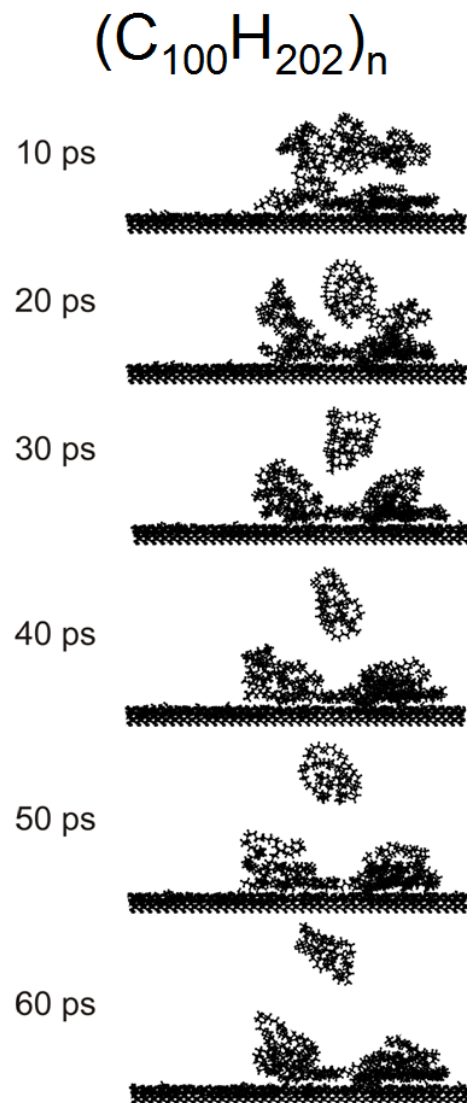
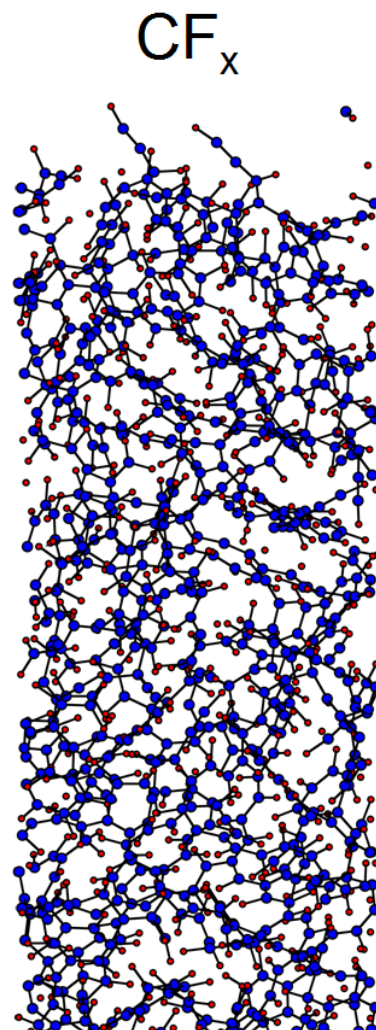
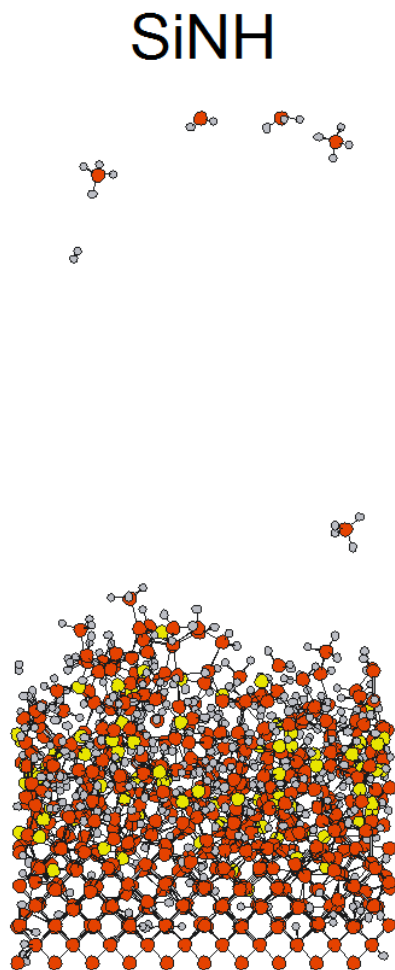
Using MD for film growth simulations

(summary of advantages)

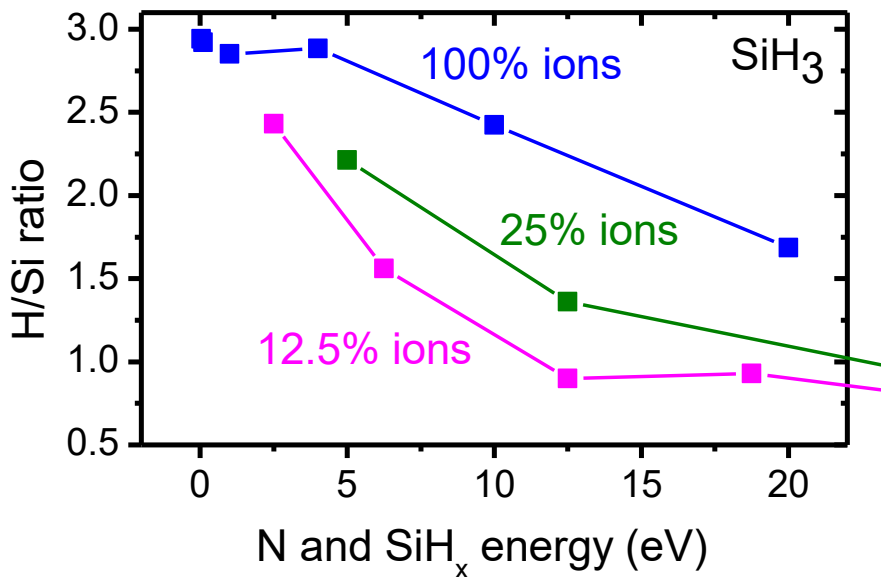
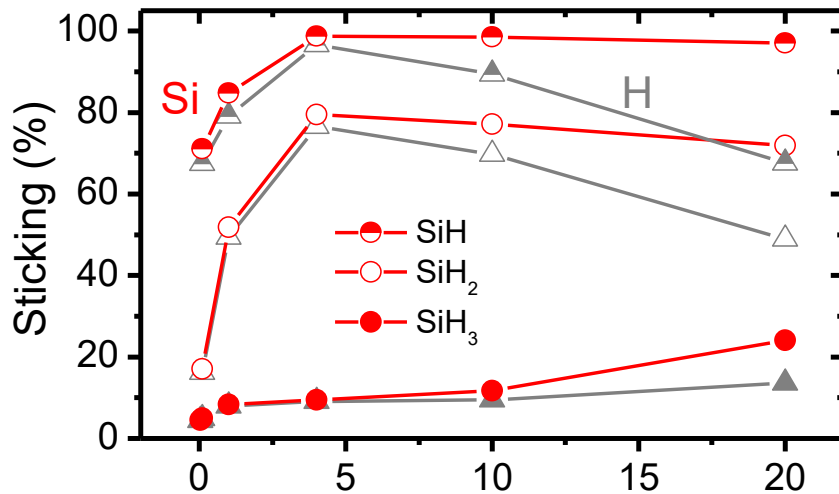
- 1) It is possible to disentangle (the conditions necessary for) crystal nucleation and crystal growth (if we skip the nucleation using a crystalline "substrate"). In the experiment, both processes take place in parallel.
- 2) It is possible to disentangle the effect of individual particles in the total particle flux (metal $\times$ oxygen, slow $\times$ fast, etc.) by modelling of individual impacts. All particles are arriving in parallel in the experiment.
- 3) It is easily possible to disentangle the effect of individual process parameters (e.g. temperature and energy of arriving particles).

Using MD for film growth simulations

(illustration of applicability to a wide range of materials)



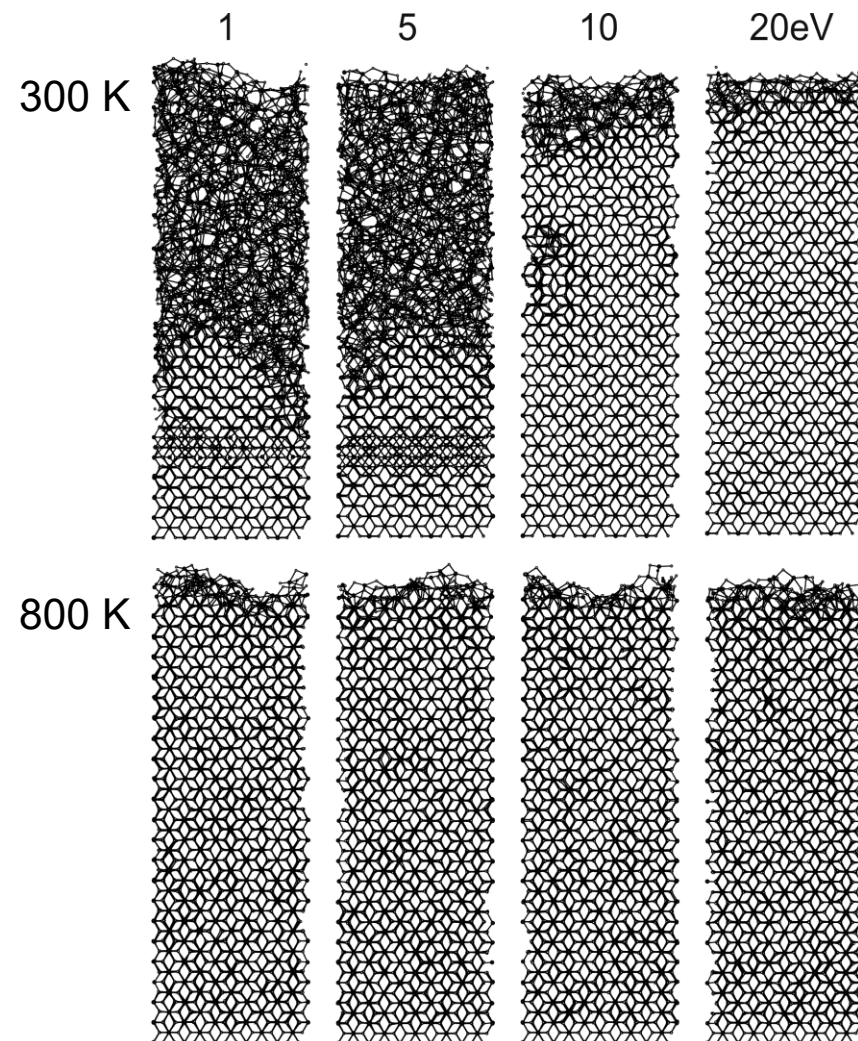
Example 1 - SiNH growth from $\text{SiH}_4 + \text{N}_2$



- Radicals SiH₃ have much higher concentration, but much lower sticking coef. than SiH₂ (and SiH) $\Rightarrow$ the relative importance of individual radicals differs from the plasma composition
- In a growth from SiH₃, H/Si is lower (H resputtering stronger)
 - for higher energy per particle
 - if the same total energy is distributed amongst less particles

Example 2 - TiO₂ growth

rutile (here) × anatase (next slide)



■ Experiment:

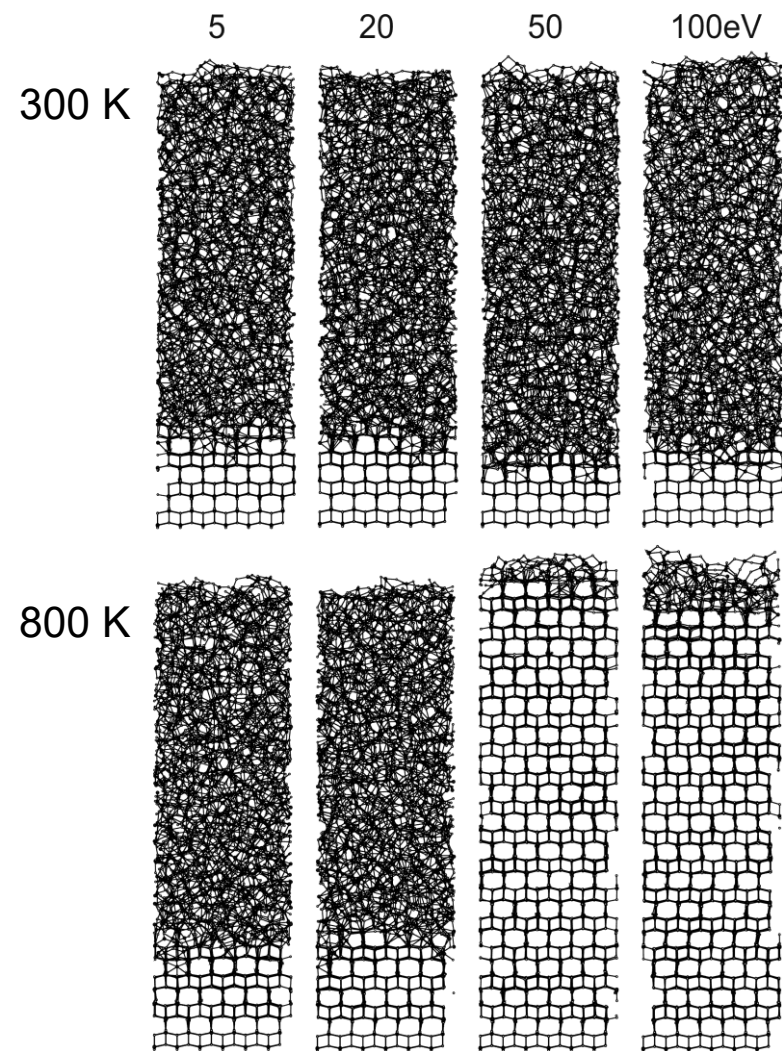
- deposition of rutile requires higher E and/or T

■ Simulation:

- higher E and/or T is necessary only for nucleation
- once the rutile nucleates, it actually grows in a wider range of conditions than anatase

Example 2 - TiO_2 growth

rutile (previous slide) $\times$ anatase (here)



■ Simulation:

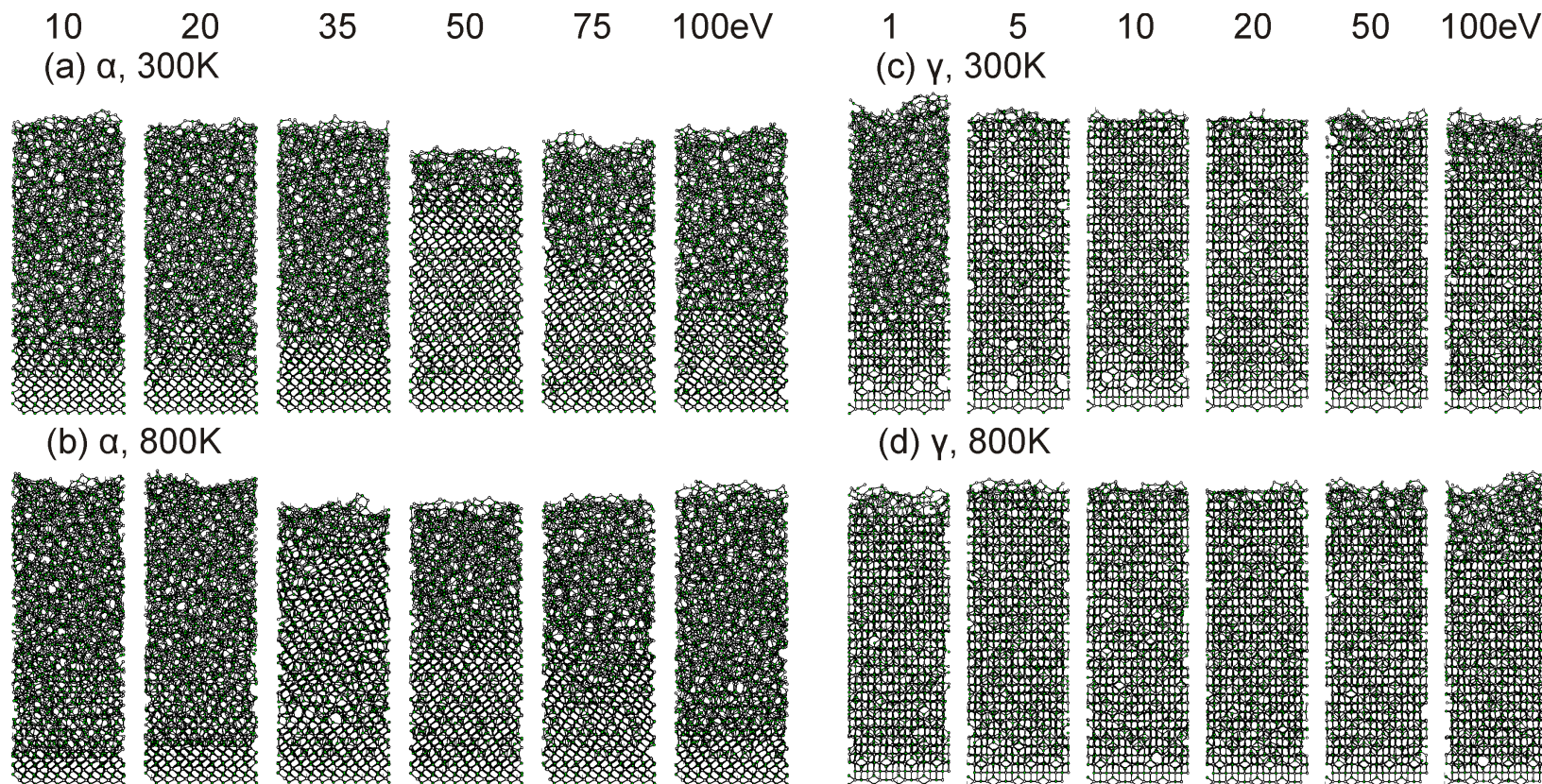
- amorphization for too low E and for too low T
- amorphization even for too high E (not shown here)



■ Qualitative difference

- presence of anatase is controlled by its growth
- presence of rutile is controlled by its nucleation

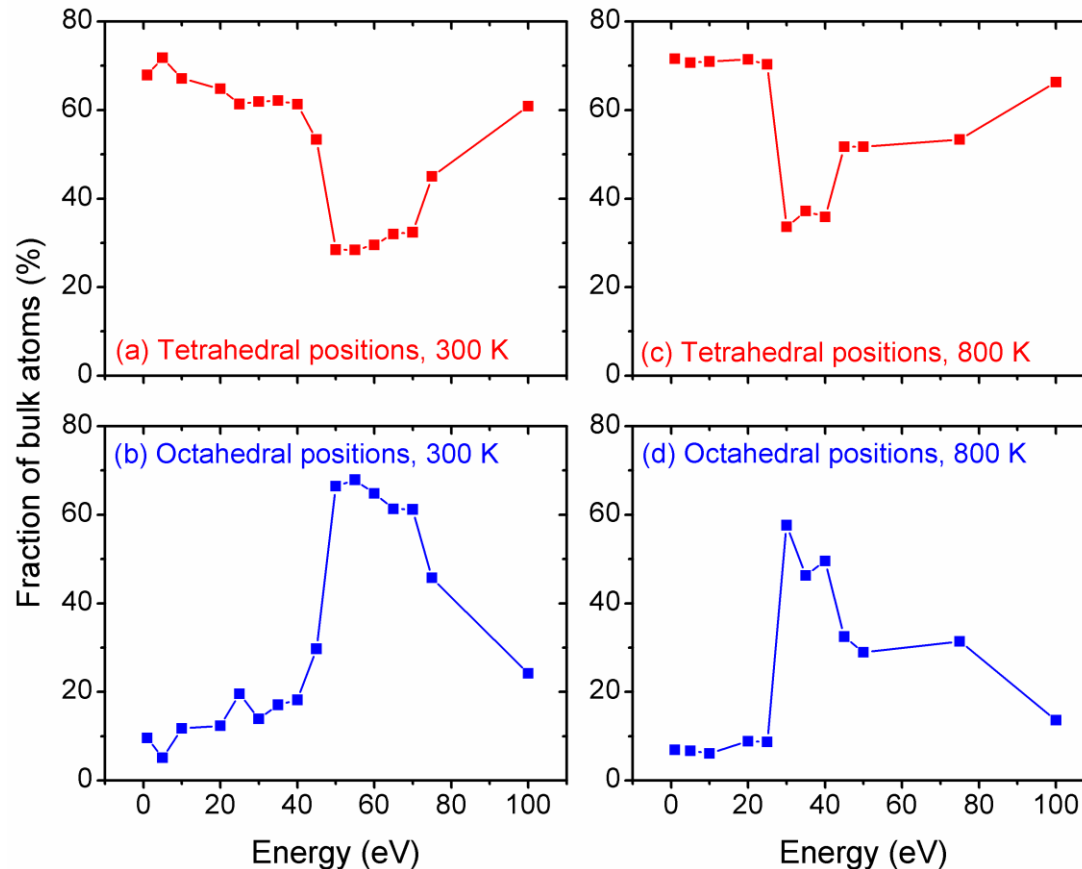
Example 3 - Al_2O_3 growth



- $\alpha\text{-Al}_2\text{O}_3$: energy window
 - 50 eV for 300 K
 - 35 eV for 800 K

- $\gamma\text{-Al}_2\text{O}_3$: growth for almost any energy

Example 3 - α - Al_2O_3 growth



- **Too low E :**

insufficient to
"punch" Al to
octahedral positions

- **Too high E :**

accumulation of ion-induced
defects, eventually leading
to amorphization

Software - visualization

Example of simple code: **XBS** (Balls + Sticks)

- 1) File with atomic coordinates (GEOMETRY.xyz)
is converted to the format understood by xbs (wann.bs)
- 2) At the end of file wann.bs, add requirements concerning
diameter and color of balls, diameter and color of bonds,
max. bond length (2.3 Å for Ti-O), scale, rotation step (*inc*)

```
# usage:
# awk -f awk.wann GEOMETRY.xyz

BEGIN { system("/bin/rm -f wann.bs") }

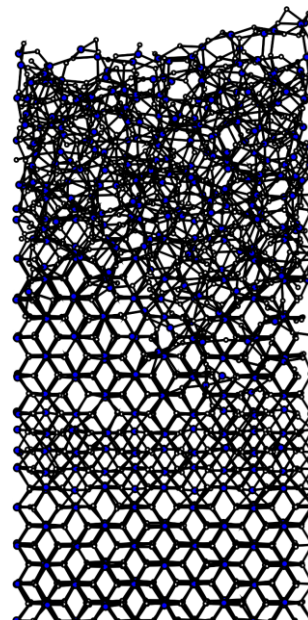
    { print "atom ",$1,$2,$3,$4 >> "wann.bs" }

END { print "spec Ti 0.25 grey "      >> "wann.bs"
      print "spec O 0.15 black"      >> "wann.bs"

      print "bonds O Ti 0",2.3,"0.02 grey" >> "wann.bs"

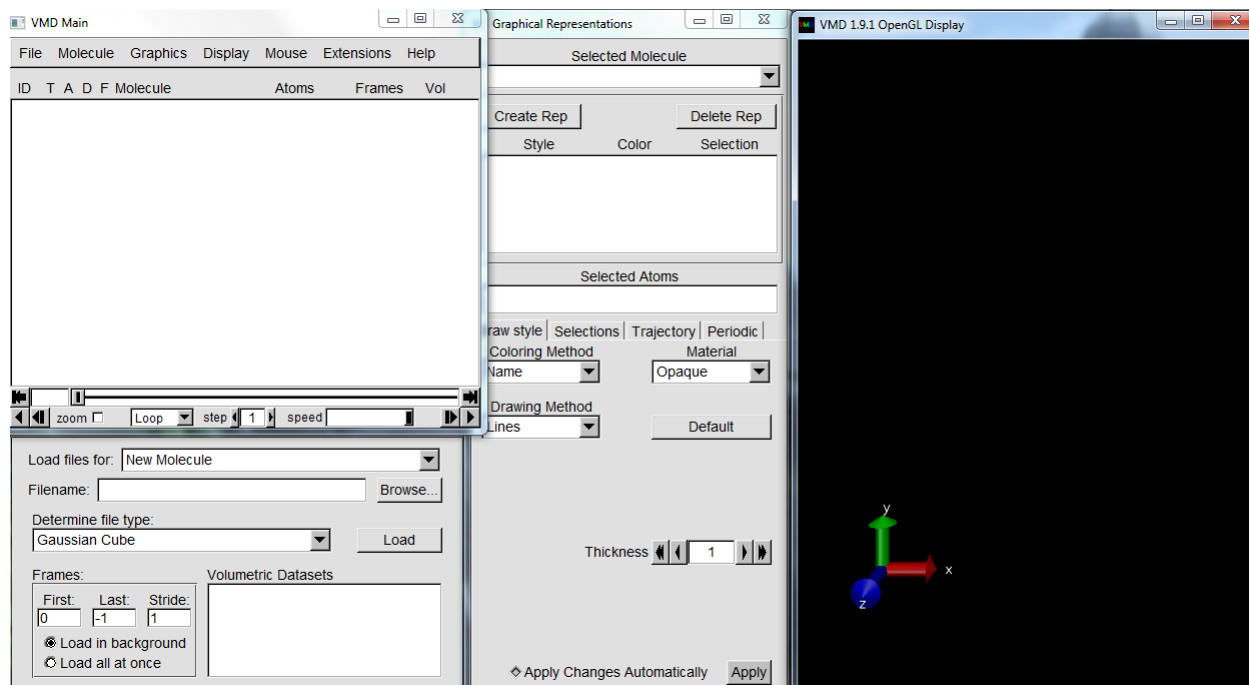
      print "inc 3"                    >> "wann.bs"
      print "scale 50"                  >> "wann.bs"
      system("xbsa wann")
    }
```

TiO₂



Software - visualization

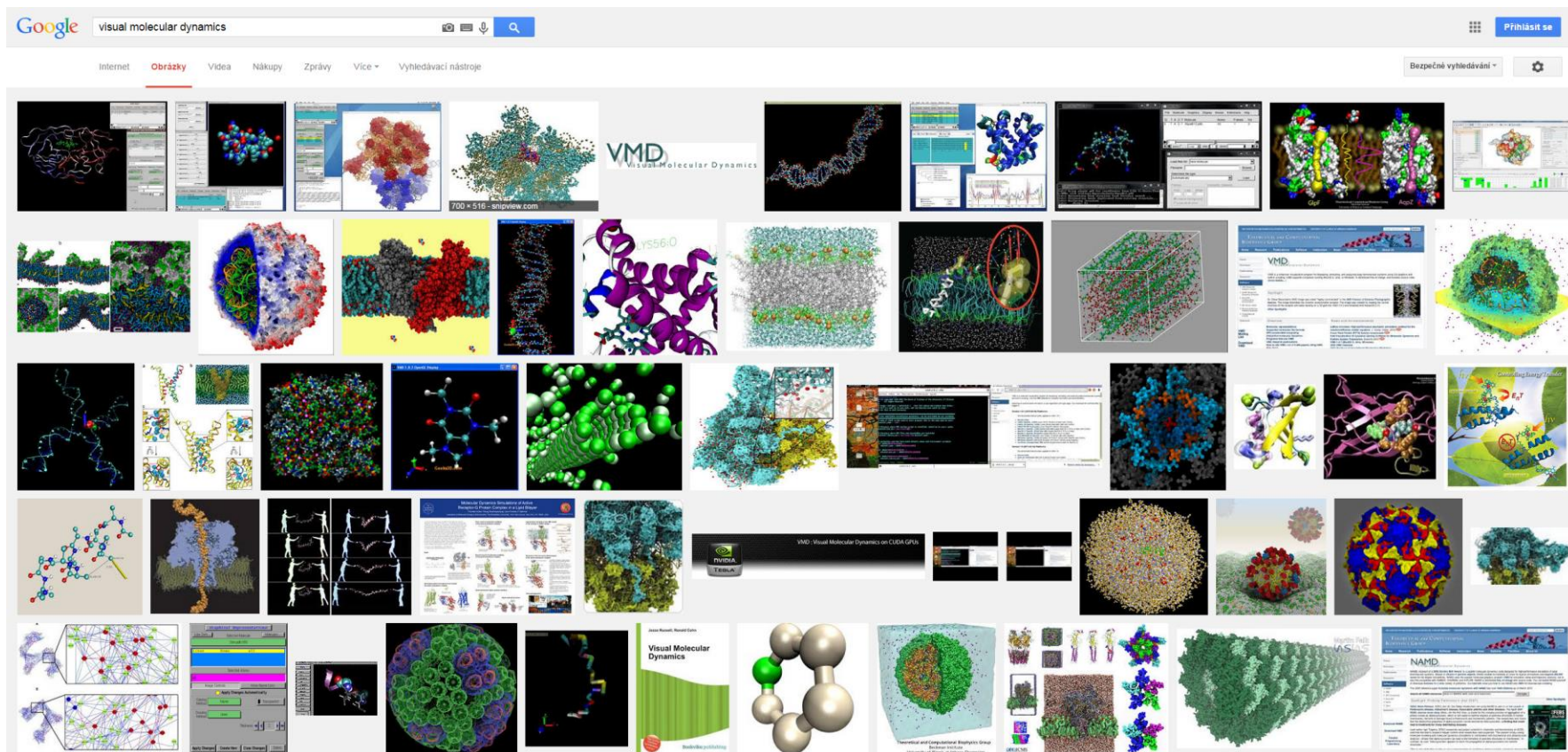
Example of mightier code: **VMD** (Visual Molecular Dyn.)



- Understands outputs of many simulation codes
- Balls and Sticks implemented too (less user friendly than XBS)
- A lot more is implemented, including the visualization of continuous quantities such as charge density

Software - visualization

Example of mightier code: **VMD** (Visual Molecular Dyn.)



5) Role of free electrons

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

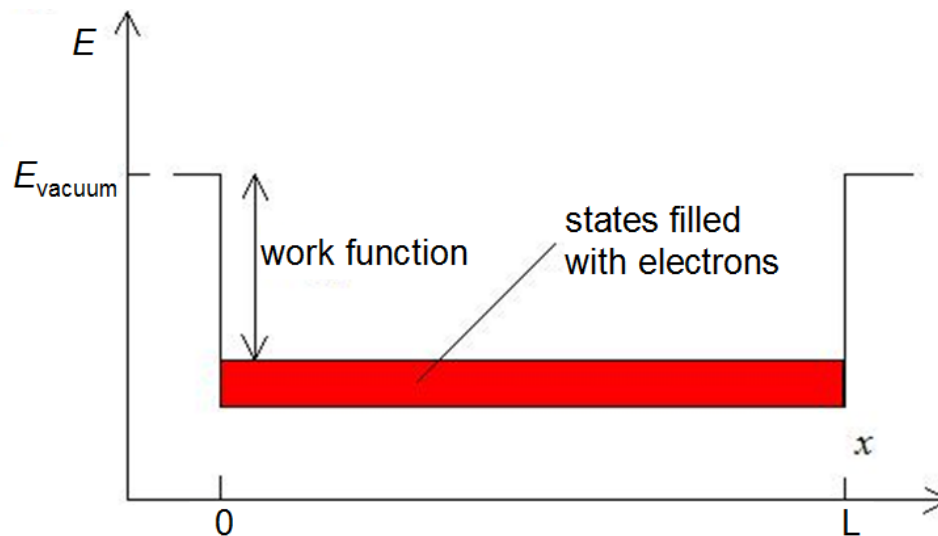
- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Free electron model

- For now only free electrons = electron gas in a potential hole
- regardless how they got there (band theory will come later)
 - regardless the cations around (smoothened hole bottom)

Responsibility for

- electrical conductivity (100%)
- thermal conductivity (90% etc., in parallel to phonons)
- heat capacity (1% etc., in parallel to phonons)



Free electron model

density of states

For now only free electrons = electron gas in a potential hole
- regardless how they got there (band theory will come later)
- regardless the cations around (smoothened hole bottom)

$$\Psi = 1/\sqrt{V} \cdot \exp(i[\mathbf{k} \cdot \mathbf{r} - \omega t])$$

where, like in the chapter 3 about phonons (running wave observing the boundary condition, directly for 3D)

$\mathbf{k} = 2\pi/L \cdot (n_x, n_y, n_z) \Rightarrow$ volume of 1 state in k-space is $(2\pi/L)^3$

states in a sphere of radius k : $2 \times 4\pi/3 \cdot k^3 / (2\pi/L)^3 = V/3\pi^2 \cdot k^3$

- phonons 3× due to 1 longitudinal + 2 transverse polarizations
- electrons 2× due to the spin

contrary to the chapter 3 about phonons: energy of one state

$$\varepsilon = \hbar^2/2m \cdot (k_x^2 + k_y^2 + k_z^2) = \hbar^2/2m \cdot k^2$$

Free electron model

density of states

states in a sphere of radius k : $2 \times 4\pi/3 \cdot k^3 / (2\pi/L)^3 = V/3\pi^2 \cdot k^3$

energy of one state: $\varepsilon = \hbar^2/2m \cdot (k_x^2 + k_y^2 + k_z^2) = \hbar^2/2m \cdot k^2$

both formulas combined $\Rightarrow$

states in a sphere of radius k : $N(\varepsilon) = V/3\pi^2 \cdot (2m\varepsilon/\hbar^2)^{3/2}$

density of states: $D(\varepsilon) = dN(\varepsilon)/d\varepsilon = V/2\pi^2 \cdot (2m/\hbar^2)^{3/2} \cdot \sqrt{\varepsilon} = 3/2 \cdot N/\varepsilon$

or per volume unit: $g(\varepsilon) = 1/2\pi^2 \cdot (2m/\hbar^2)^{3/2} \cdot \sqrt{\varepsilon} = 3/2 \cdot n/\varepsilon$

After substituting the density of electrons $n = N/V$:

Fermi wavenumber $k_F = (3\pi^2 \cdot n)^{1/3}$

Fermi momentum $p_F = \hbar k_F = \hbar \cdot (3\pi^2 \cdot n)^{1/3}$

Fermi velocity $v_F = \hbar k_F / m = (\hbar/m) \cdot (3\pi^2 \cdot n)^{1/3}$

Fermi energy $E_F = \hbar^2 k_F^2 / 2m = (\hbar^2/2m) \cdot (3\pi^2 \cdot n)^{2/3}$

mean energy $\langle \varepsilon \rangle = (\int \varepsilon) / n = 3/5 \cdot E_F$

Fermi temperature $T_F = E_F / k_B$

Free electron model

density of states

Typical values of quantities on previous slide for selected metals

prvek	z	n	k_F	v_F	E_F	T_F
		10^{28} m^{-3}	$\text{\AA}^{-1}$	10^6 ms^{-1}	eV	10^4 K
Li	1	4.70	1.11	1.29	4.72	5.48
Na	1	2.65	0.92	1.07	3.23	3.75
K	1	1.40	0.75	0.86	2.12	2.46
Cu	1	8.45	1.36	1.57	7.00	8.12
Ag	1	5.85	1.20	1.39	5.48	6.36
Be	2	24.2	1.93	2.23	14.14	16.41
Mg	2	8.60	1.37	1.58	7.13	8.27
Ca	2	4.60	1.11	1.28	4.68	5.43
Zn	2	13.1	1.57	1.82	9.39	10.9
Al	3	18.1	1.75	2.02	11.63	13.49
Ga	3	15.3	1.65	1.91	10.35	12.01
Pb	4	13.2	1.57	1.82	9.37	10.87
Sn	4	14.5	1.62	1.88	10.03	11.64

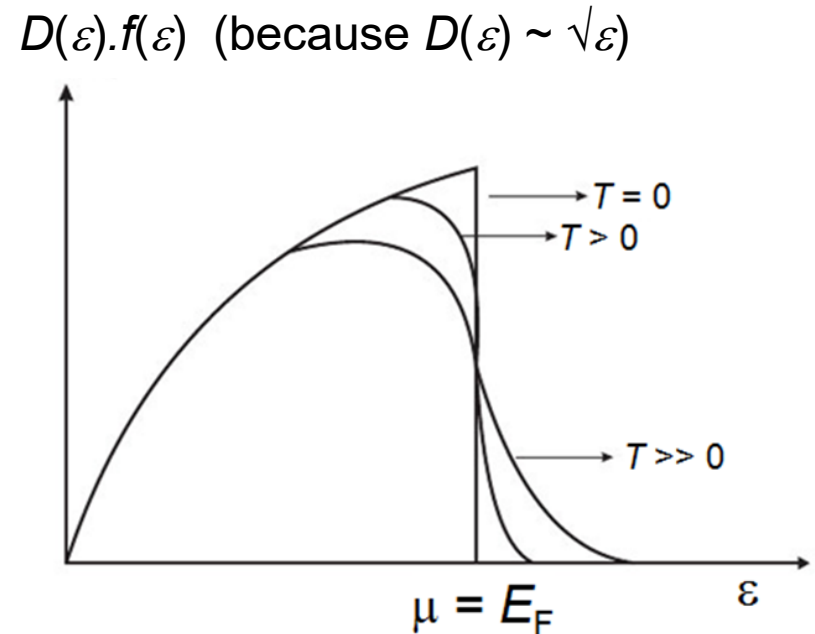
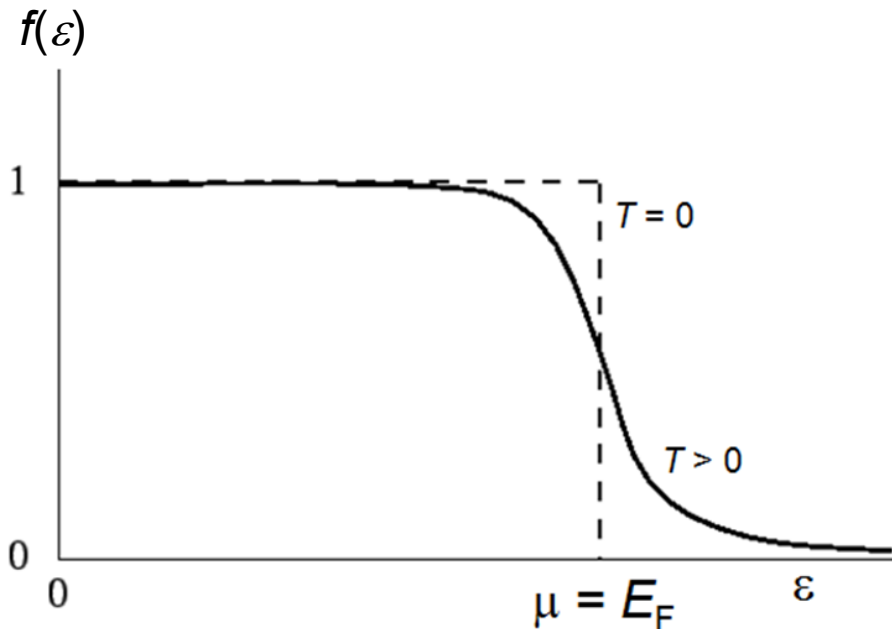
Free electron model

occupation of states

electrons are fermions, i.e.
respect Fermi-Dirac distribution

E_F (energy of state with occupation 0.5)
has the meaning of chemical potential μ

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1}$$



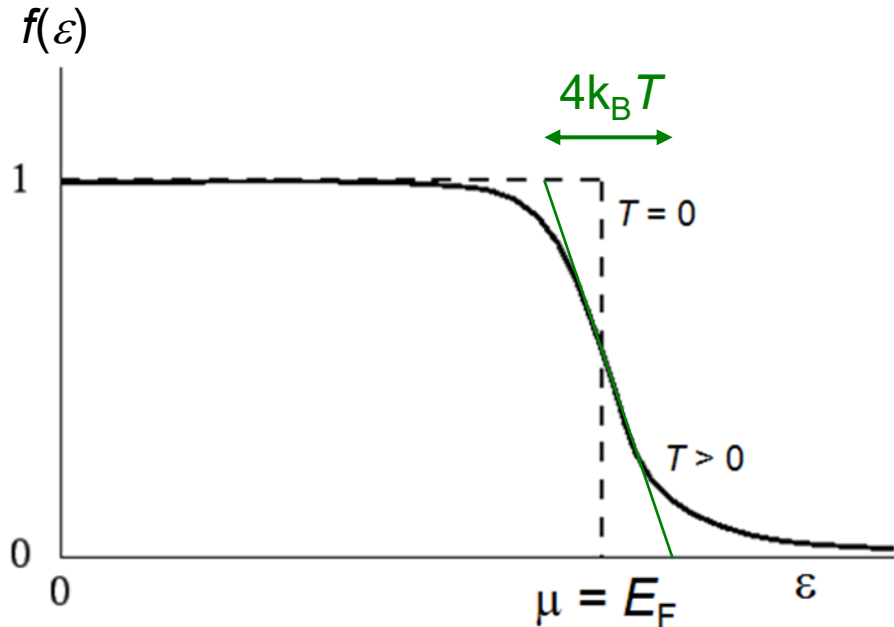
Free electron model

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$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1}$$



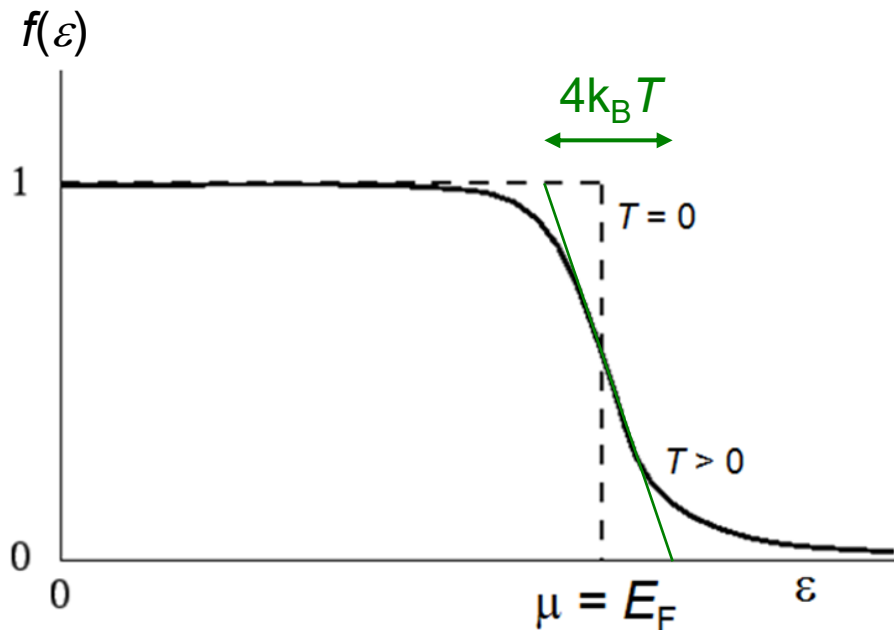
$$\left[\frac{df(\varepsilon)}{d\varepsilon} \right]_{\mu} = -1/4k_B T$$

width of the smearing of
occupations of states is
 $\approx 4k_B T$

Heat capacity of electrons

Classical free particles which do not know the Pauli pr. and F-D distribution: all of them get energy during heating $\Rightarrow C_{\text{free}} = 3/2.R$
Experimental heat capacity of electrons is of 2 orders lower!

Yes, conductive electrons are also free, but respect the Pauli principle and F-D distribution: only those which move from the top left triangle to the bottom right triangle get energy

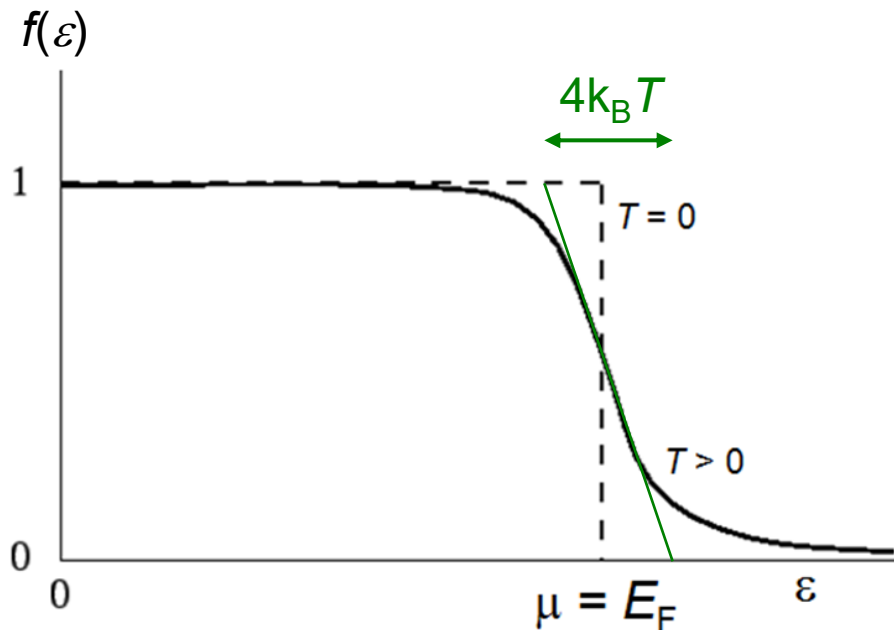


Heat capacity of electrons

4 slides above: $D(\varepsilon) = dN(\varepsilon)/d\varepsilon = V/2\pi^2 \cdot (2m/\hbar^2)^{3/2} \cdot \sqrt{\varepsilon} = 3/2 \cdot N/\varepsilon$

FD: area of triangles is $1/2 \cdot k_B T$, distance of centers is $4/3 \cdot k_B T$,
i.e. heating from 0 to T changes energy of $\Delta E \approx 2/3 \cdot k_B^2 T^2 \cdot D(E_F)$

Exact calculation: $\Delta E = \pi^2/6 \cdot k_B^2 T^2 \cdot D(E_F)$



Heat capacity of electrons

4 slides above: $D(\varepsilon) = dN(\varepsilon)/d\varepsilon = V/2\pi^2 \cdot (2m/\hbar^2)^{3/2} \cdot \sqrt{\varepsilon} = 3/2 \cdot N/\varepsilon$

FD: area of triangles is $1/2 \cdot k_B T$, distance of centers is $4/3 \cdot k_B T$,
i.e. heating from 0 to T changes energy of $\Delta E \approx 2/3 \cdot k_B^2 T^2 \cdot D(E_F)$

Exact calculation: $\Delta E = \pi^2/6 \cdot k_B^2 T^2 \cdot D(E_F)$

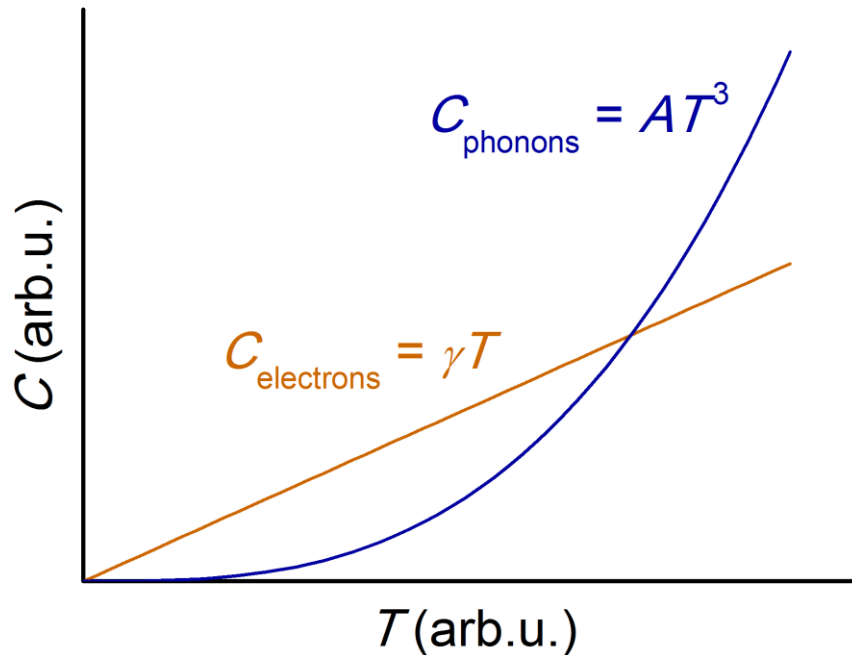
$C_{el} = \pi^2/3 \cdot k_B^2 T \cdot D(E_F) = \pi^2/2 \cdot k_B^2 N \cdot T/E_F = \pi^2/2 \cdot k_B N \cdot T/T_F$
or per volume unit $\pi^2/2 \cdot k_B n \cdot T/T_F$
or per one mol $\pi^2/2 \cdot R \cdot T/T_F$

$T_F \approx 10^4 - 10^5$ K $\Rightarrow$ for usual $T \approx 3 \times 10^2$ K is C_{el} only $\approx 1\%$ of the
aforementioned classical value $C_{free} = 3/2 \cdot R$, and only $\approx 1\%$
correction to the phonon component (chapter 3) $C_{ph} \approx 3R$

However, at low temperatures the electronic contribution ($\sim T$)
goes to zero slower than the phonon contribution ($\sim T^3$)

Heat capacity of electrons

However, at low temperatures the electronic contribution ($\sim T$) goes to zero slower than the phonon contribution ($\sim T^3$)



$$\gamma = \pi^2/2 \cdot R/T_F = \pi^2/2 \cdot R \cdot k_B \cdot (2m/\hbar^2) \cdot (3\pi^2 \cdot n)^{-2/3}$$

is Sommerfeld constant

Heat capacity of electrons

$$\gamma = \pi^2/2.R/T_F = \pi^2/2.R.k_B.(2m/\hbar^2).(3\pi^2.n)^{-2/3}$$

is Sommerfeld constant

Experimental values of γ (from measurements of $C_{el} = \gamma T$) and calculated values of γ (substituting n and electronic mass to the above equation) differ a lot. Why?

prvek	$\gamma_{\text{experiment}}$	$\gamma_{\text{calculated}}$
	mJ.mol ⁻¹ .K ⁻²	mJ.mol ⁻¹ .K ⁻²
Li	1.63	0.749
Na	1.38	1.094
K	2.08	1.668
Rb	2.41	1.911
Cs	3.20	2.238
Cu	0.695	0.505
Ag	0.646	0.645
Au	0.729	0.642

Heat capacity of electrons

$$\gamma = \pi^2/2 \cdot R/T_F = \pi^2/2 \cdot R \cdot k_B \cdot (2m/\hbar^2) \cdot (3\pi^2 \cdot n)^{-2/3} \sim m$$

is Sommerfeld constant

Experimental values of γ (from measurements of $C_{el} = \gamma T$) and calculated values of γ (substituting n and electronic mass to the above equation) differ a lot. Why?

Because m is not the mass of isolated electron m_e , but **effective mass** of electron in a crystal m^* (we just met it for the first time, but not for the last time)

prvek	$\gamma_{\text{experiment}}$ mJ.mol ⁻¹ .K ⁻²	$\gamma_{\text{calculated}}$ mJ.mol ⁻¹ .K ⁻²	m^*/m_e
Li	1.63	0.749	2.18
Na	1.38	1.094	1.26
K	2.08	1.668	1.25
Rb	2.41	1.911	1.26
Cs	3.20	2.238	1.43
Cu	0.695	0.505	1.38
Ag	0.646	0.645	1.00
Au	0.729	0.642	1.14

Heat capacity of electrons

Arnold Sommerfeld, pioneer of quantum physics:
84 nominations to NP in physics between 1917-1951
at least (contrary to Lewis, see above) did not commit suicide

Nobelprize.org
The Official Web Site of the Nobel Prize

Home | Nobel Prizes and Laureates | Nomination | Ceremonies | Alfred Nobel

Lists of Nobel Prizes and Laureates
Choose a list

Nomination Database

Arnold Sommerfeld

Lastname/org:	Sommerfeld
Firstname:	Arnold
Gender:	M
Year, Birth:	1868
Year, Death:	1951

Nominee in 84 nominations:

- Physics 1917 by Max von Laue
- Physics 1918 by Stefan Meyer
- Physics 1919 by Max von Laue
- Physics 1919 by Karl von Goebel
- Physics 1920 by Wilhelm Wien
- Physics 1922 by Stefan Meyer
- Physics 1922 by Karl Lindman
- Physics 1922 by August Schmauss



this is still not
absolute record:
Gaston Ramon
(diphtheria, tetanus)
155× for medicine

DC electrical conductivity

In 1D electrical field

$$m^* dv/dt = qE - m^* v/\tau$$

where m^* is effective mass and τ is effective time between momentum loss collisions (probability a of collision during time dt is dt/τ , by integration: τ is average time between collisions)

Stationary (average from a single particle viewpoint) velocity

$$v = q\tau/m^* \cdot E = \pm\mu \cdot E$$

where μ is mobility (defined as positive - therefore $\pm$; not to be confused with the aforementioned chemical potential)

DC electrical conductivity

why is there not $\frac{1}{2}$

In 1D electrical field $m^* dv/dt = qE - m^* v/\tau$

Average velocity $v = q\tau/m^* . E = \pm \mu . E$

In many sources (including the Drude paper) survives formula $v = q\tau/2m^* . E$. The formula is based on wrong interpretation of the fact that the velocity linearly increases between collisions from 0 to $v_{\max}$, so the average over this period is $v_{\max}/2$.

Refutation 1: collisions affect a random subset of electrons, i.e. electrons in this subset have the same mean velocity as all electrons (not its double)

DC electrical conductivity

why is there not $\frac{1}{2}$

In 1D electrical field $m^* dv/dt = qE - m^* v/\tau$

Average velocity $v = q\tau/m^* . E = \pm \mu . E$

In many sources (including the Drude paper) survives formula $v = q\tau/2m^* . E$. The formula is based on wrong interpretation of the fact that the velocity linearly increases between collisions from 0 to $v_{\max}$, so the average over this period is $v_{\max}/2$.

Refutation 2: for a random electron, τ is the mean time until the next collision, but also since the previous collision $\Rightarrow$ length of the period between collisions **which the electron is in** is 2τ (i.e. at its end it loses velocity $q2\tau/m^* . E$, so the mean is $q\tau/m^* . E$)

The aforementioned average length of a period between collisions is only τ ... isn't it a contradiction?

DC electrical conductivity

why is there not $\frac{1}{2}$

Refutation 2: for a random electron, τ is the mean time until the next collision, but also since the previous collision $\Rightarrow$ length of the period between collisions **which the electron is in** is 2τ (i.e. at its end it loses velocity $q2\tau/m^*.E$, so the mean is $q\tau/m^*.E$)

Average length of period between collisions is only τ , but longer periods have higher statistical weight, el. is more likely in them

Probability that electron will not collide during t : $e^{-t/\tau}$

Probability that after that it will collide during dt : dt/τ

Statistical weight (normalized to 1) of period long t : t/τ

Average length of a period between collisions: $\int t \cdot e^{-t/\tau} \cdot dt/\tau = \tau$

Average length of the period between collisions
which the electron is in right now: $\int t/\tau \cdot t \cdot e^{-t/\tau} \cdot dt/\tau = 2\tau$

DC electrical conductivity

back to the main topic

In 1D electrical field

$$m^* dv/dt = qE - m^* v/\tau$$

where m^* is effective mass and τ is effective time between col.)

Stationary (average from a single particle viewpoint) velocity

$$v = q\tau/m^* \cdot E = \pm \mu \cdot E$$

where μ is mobility (defined as positive - therefore $\pm$)

The density of free charge carriers n gives rise to a current

$$j = nqv = nq^2\tau/m^* \cdot E = \sigma \cdot E = 1/\rho \cdot E$$

Effective masses (in terms of m_e),
this time for semiconductors:
see the table from wikipedia

Group	Material	Electron	Hole
IV	Si (4K)	1.06	0.59
	Si (300K)	1.09	1.15
	Ge	0.55	0.37
III-V	GaAs	0.067	0.45
	InSb	0.013	0.6
II-VI	ZnO	0.29	1.21
	ZnSe	0.17	1.44

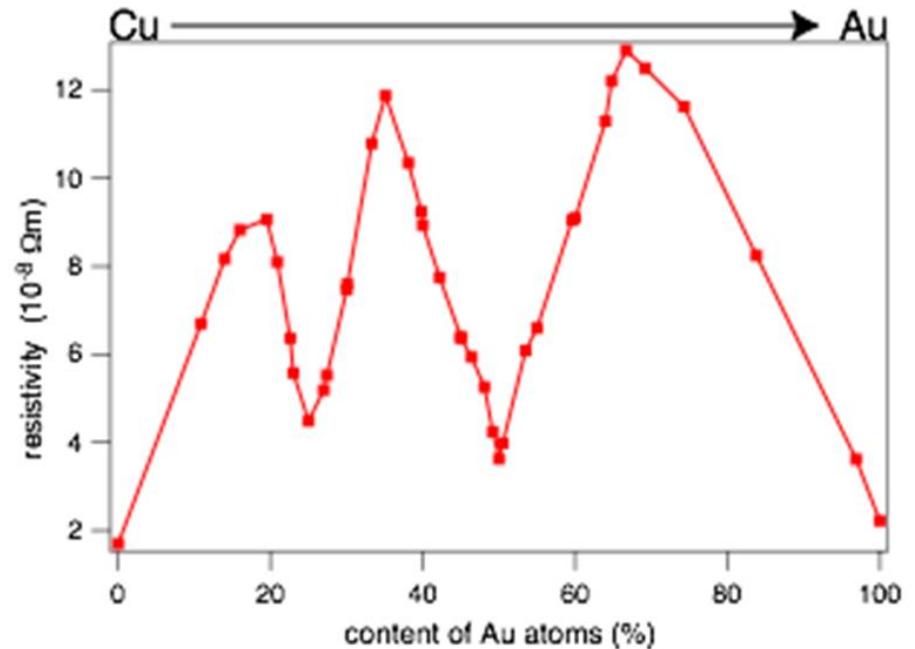
DC electrical conductivity

importance of material structure for mobility

$$\mathbf{v} = q\tau/m^* \cdot \mathbf{E} = \pm \mu \cdot \mathbf{E}$$

$$\mathbf{j} = nq\mathbf{v} = nq^2\tau/m^* \cdot \mathbf{E} = \sigma \cdot \mathbf{E} = 1/\rho \cdot \mathbf{E}$$

Example showing the importance of μ and τ :
resistivity of alloy $\text{Cu}_x\text{Au}_{1-x}$ is higher than those of Cu and Au, and has local minima for ordered crystalline phases ($\Rightarrow$ high mobility)
 Cu_3Au and CuAu



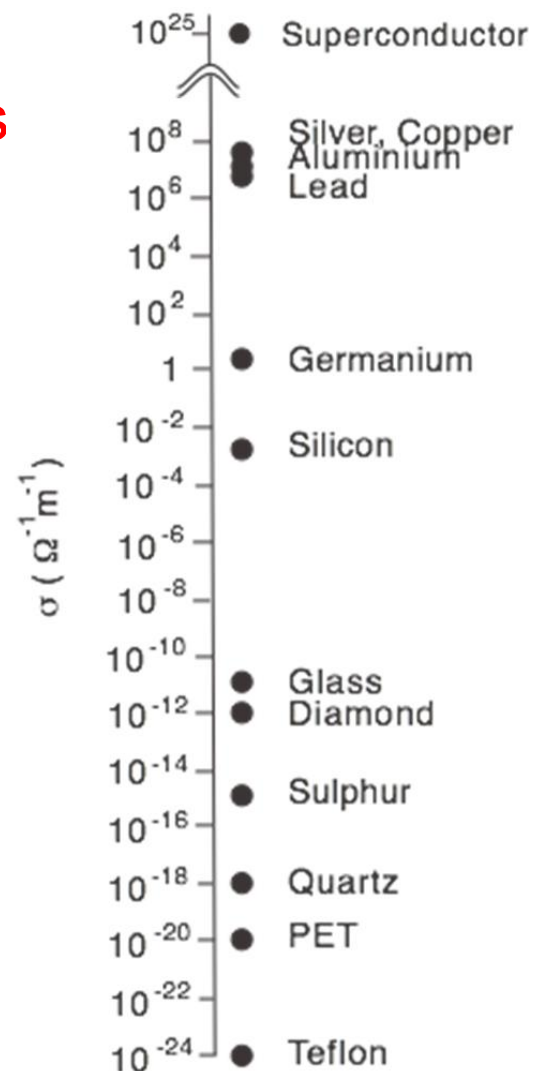
[C.H. Johansson and J.O. Linde, *Ann. Phys.* 25, 1 (1936)]

DC electrical conductivity

achievable values

Electrical conductivity / resistivity is the quantity which changes over most orders of magnitude for available materials

Thus, the mere order of magnitude is often a sufficiently interesting information



DC electrical conductivity

Ioffe-Regel limit

Can the resistivity of a metal be (e.g. due to many defects) arbitrarily high?

No: in the worst case (electron collides at any opportunity - "bad metals") mean free path corresponds to interatomic dist.

After substituting usual values we get the **Ioffe-Regel limit on the order of hundreds $\mu\Omega\text{cm}$ ($10^{-6} \Omega\text{m}$)**

Another viewpoint: $10^{-6} \Omega\text{m}$ is the order which separates metals and semicond. (resistivities increasing and decreasing with T)

Thermal conductivity of electrons

Thermal conductivity of phonons resulted from $\lambda_{ph} = 1/3 \cdot C_{vol} \cdot c_s \cdot l$

Thermal cond. of electrons will result from the same formula:

- for C_{vol} substitute $\pi^2/2 \cdot k_B^2 n \cdot T/E_F$
- for c_s substitute v_F
- for l substitute $v_F \cdot \tau$

after the substitutions $\lambda_{el} = 1/3 \cdot \pi^2/2 \cdot k_B^2 N \cdot v_F^2 \tau \cdot T/E_F$
 $E_F = 1/2 \cdot m^* v_F^2 \Rightarrow \lambda_{el} = 1/3 \cdot \pi^2 \cdot k_B^2 N \tau \cdot T/m^*$

Ratio of thermal and electrical cond.

1 slide above $\lambda_{el} = 1/3 \cdot \pi^2 \cdot k_B^2 n \tau \cdot T / m^*$

5 slides above $\sigma = ne^2 \tau / m^*$

The same carriers are responsible for (the electronic contribution to) both conductivities, so it is not surprising that n , τ and m^* cancel out when calculating their ratio:

Wiedemann-Franz law $\lambda_{el} = \text{const.} \cdot T \cdot \sigma$

where const. = Lorentz number = $1/3 \cdot \pi^2 \cdot (k_B/e)^2$

Ratio of thermal and electrical cond.

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where const. = Lorentz number = $1/3 \cdot \pi^2 \cdot (k_B/e)^2$

Materials with higher electrical conductivity [metals] therefore faster conduct heat away ...
so do not lick the rail



*screenshot from the movie
The Elementary School*

Ratio of thermal and electrical cond.

$$\text{Lorentz number} = 1/3 \cdot \pi^2 \cdot (k_B/e)^2 = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$$

Crosscheck for selected metals:

prvek	λ_{el}	$\lambda_{\text{el}}/T \cdot \sigma$
	$\text{Wm}^{-1}\text{K}^{-1}$	$10^{-8} \text{ W}\Omega\text{K}^{-2}$
Li	71	2.22
Mg	150	2.14
Na	138	2.12
Zn	113	2.28
K	100	2.23
Al	238	2.14
Cu	385	2.20
Fe	80	2.61
Ag	418	2.31
Pb	38	2.64

AC electrical conductivity

So we know the DC electrical conductivity

$$\sigma = nq^2\tau/m^* = ne^2\tau/m^*$$

Transition from **DC** (field $E = E_0$) to **AC** (field $E = E_0 e^{i\omega t}$)

↓ (after a new substitution for E to $m^* dv/dt = qE - m^* v/\tau$)

transition from $v_{dc} = q\tau/m^* \cdot E_0$ to $v_{ac} = q\tau/m^* (1 - i\omega\tau) \cdot E_0$

↓

transition from $\sigma_{dc} = ne^2\tau/m^*$ to $\sigma_{ac} = ne^2\tau/m^* (1 - i\omega\tau)$

- not that important for AC **electrical** current
(typical values of τ are fs to hundreds fs, i.e. $\omega\tau \ll 1$)
- however, the transition to the AC formula is important for interaction with EM fields of **optical** frequencies - see below

AC electrical conductivity

$$\sigma_{dc} = ne^2\tau/m^*, \quad \sigma_{ac} = ne^2\tau/m^*(1-i\omega\tau)$$

After substituting $j = \sigma_{ac}E$ to Maxwell equations we can derive the contribution of free charge carriers to the total permittivity:

$$\begin{aligned} \epsilon_{Drude} &= -\sigma_{dc} / [\epsilon_0(\tau\omega^2 + i\omega)] \\ &= -\hbar^2\sigma_{dc} / [\epsilon_0(\tau E^2 + i\hbar E)] && (E = \hbar\omega) \\ &= -\hbar^2 / [\rho_{dc}\epsilon_0(\tau E^2 + i\hbar E)] && (\rho_{dc} = m^*/ne^2\tau) \\ &= -\tau\omega_p^2 / [\tau\omega^2 + i\omega] && (\omega_p^2 = ne^2/m^*\epsilon_0) \\ &= -\hbar^2\sigma_{dc}/\epsilon_0 \cdot [(\tau E^2 - i\hbar E)/(\tau^2 E^4 + \hbar^2 E^2)] && ('i' \text{ in numerator}) \end{aligned}$$

Relation to permittivity and ext. coef.

$$\varepsilon_{\text{Drude}} = -\tau\omega_p^2/(\tau\omega^2+i\omega) = -\tau^2\omega_p^2\omega^2/(\tau^2\omega^4+\omega^2) + i\tau\omega_p^2\omega/(\tau^2\omega^4+\omega^2)$$

The term plasma frequency ($\omega_p^2 = ne^2/m^*\varepsilon_0$, see FYPL) is used in plasma physics as well as in solid state physics - the mechanism of photon absorption (mainly photons with $\omega < \omega_p$) by free charge carriers is the same in both cases

For an electron gas (if we approximate a metal by it), the real part of permittivity $\varepsilon_1 = 1 - \tau^2\omega_p^2\omega^2/(\tau^2\omega^4 + \omega^2) \cong 1 - \omega_p^2/\omega^2$ is equal to zero at the plasma frequency: one of methods how to quantify the free charge carrier concentration

Relation to permittivity and ext. coef.

$$\varepsilon_{\text{Drude}} = -\hbar^2 \sigma_{\text{dc}} / \varepsilon_0 \cdot [(\tau E^2 - i\hbar E) / (\tau^2 E^4 + \hbar^2 E^2)]$$

The key term for E below the band gap, where $\varepsilon = \varepsilon_{\infty} + \varepsilon_{\text{Drude}} = (n + ik)^2$. Negligible contribution to n , but source of non-zero k .

$\hbar = 0.658 \text{ eV}\cdot\text{fs}$, τ at least several fs $\Rightarrow$ in NIR (and above) the denominator is dominated by $\tau^2 E^4$ and for imag. part of ε it holds

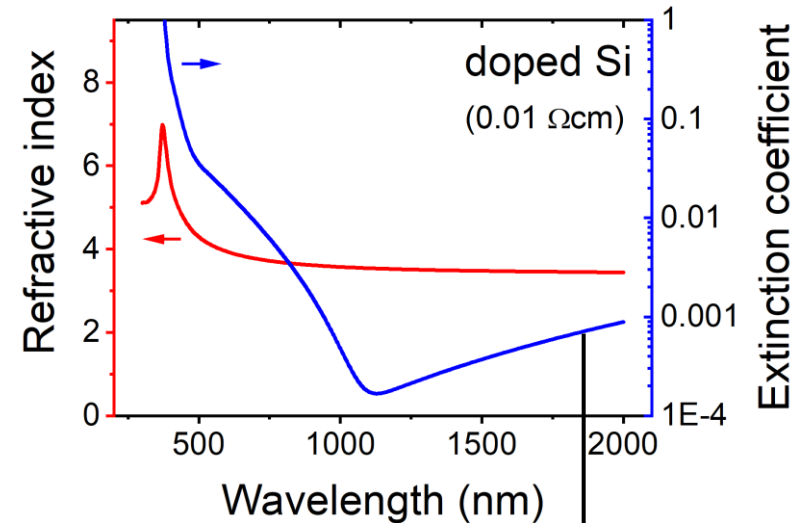
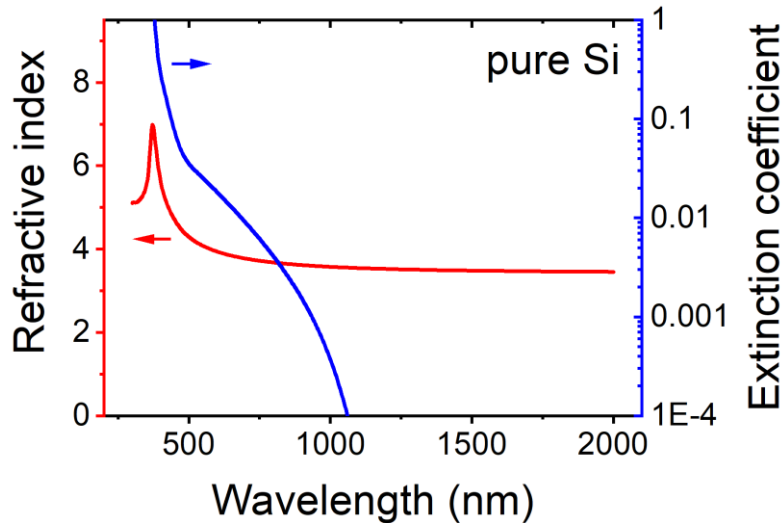
$$\varepsilon_2 = 2nk \cong \hbar^3 \sigma_{\text{dc}} / \varepsilon_0 \tau^2 E^3$$

in other words: at fixed electrical conductivity (fixed product $n\tau$) the material is more transparent (has lower k) at higher τ (in the first approximation even quadratic dependence)

yet other words: in the case of transparent conductive materials, it is better to have lower number of more mobile charge carriers: does not matter for the conductivity, better for the transparency

Relation to permittivity and ext. coef.

$$\varepsilon_2 = 2nk \cong \hbar^3 \sigma_{dc} / \varepsilon_0 \tau^2 E^3$$



Light absorption by free charge carriers in doped Si
($\Rightarrow$ higher σ_{dc} ; moreover usually lower τ) increases with increasing wavelength (decreasing energy: see $\varepsilon_2 \sim 1/E^3$)

Hall effect

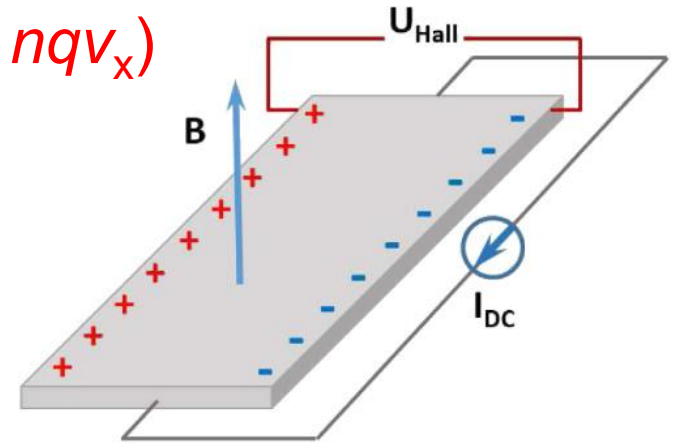
Stationary current in the direction x ($j_x = nqv_x$)

+

Magnetic induction in the direction z

↓

Voltage in the direction y



Equation of motion

$$m^* d\mathbf{v}/dt = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - m^* \mathbf{v}/\tau \quad (\text{in general})$$

$$m^* d\mathbf{v}/dt = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - m^* \mathbf{v}/\tau \quad (\text{for electrons: } q = -e)$$

$$\text{direction } x: \quad -eE_x - m^* v_x/\tau = 0$$

$$\text{direction } y: \quad -eE_y + ev_x B = 0$$

Hall effect

Stat. current in the direction x ($j_x = nqv_x$), below $q = -e$

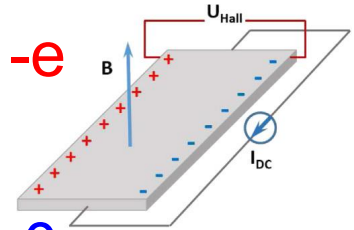
Equation of motion $m^*d\mathbf{v}/dt = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - m^*\mathbf{v}/\tau$

direction x :

$$-eE_x - m^*v_x/\tau = 0$$

direction y :

$$-eE_y + ev_xB = 0$$



- eq. in dir. $x \Rightarrow$ the above relationship for stationary velocity $v_x = -e\tau/m^*.E_x$ and current $j_x = ne^2\tau/m^*.E_x$
- eq. in dir. $y \Rightarrow$ transverse field $E_y = -e\tau/m^*.E_x.B = -1/ne.j_xB$

$$U_H = d_y.E_y = d_y.R_H.I/(d_y.d_z).B = R_H.I.B/d_z$$

where $R_H = -1/ne$ is Hall coefficient



measurements of the value of n

Hall effect

$$U_H = d_y \cdot E_y = d_y \cdot R_H \cdot I / (d_y \cdot d_z) \cdot B = R_H \cdot I \cdot B / d_z$$

where $R_H = -1/ne$ is Hall coefficient



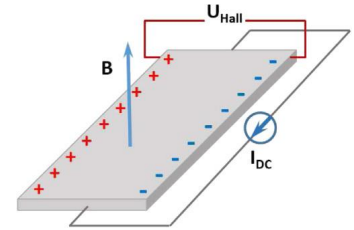
measurements of the value of n

$n > 0$ (within definition $q = -e$) $\Rightarrow$ charge carriers are electrons

$n < 0$ (within definition $q = -e$) $\Rightarrow$ charge carriers are holes

Be careful about the parallel presence of electrons and holes

- contribute to conductivity with the same sign
- contribute to Hall voltage with opposite signs

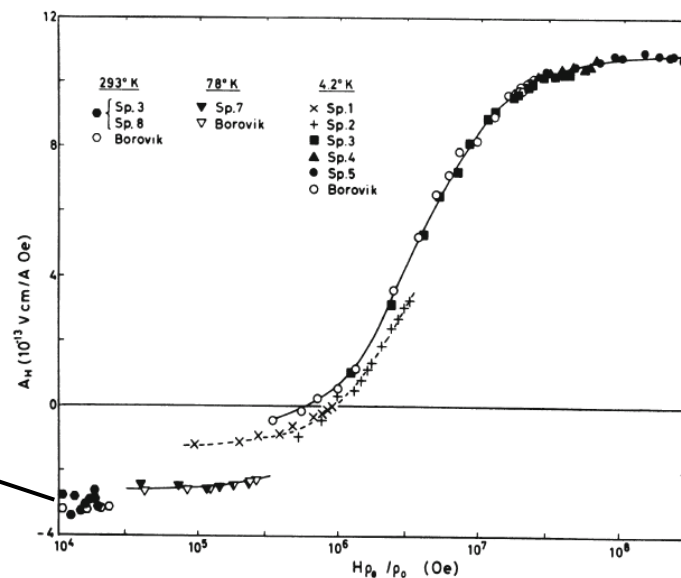


Hall effect

$R_H = -1/ne$ is Hall coefficient

In reality it is not that simple for some metals (not only semiconductors), starting with the sign of $m^* \Leftrightarrow$ sign of R_H .
 Role of band structure (see below for its relationship with m^*) which may look exotic, role of temperature, role of strength of B used to measure R_H (see the figure for Al: even varied sign)

element	$R_{H_experiment}$	R_{H_theory}
	$10^{-11} \text{ m}^3\text{C}^{-1}$	$10^{-11} \text{ m}^3\text{C}^{-1}$
Li	-17	-13.1
Na	-25	-25.5
Al	-3.5	-3.9
Cu	-5.5	-8.25
Ag	-9.0	-12.0
Zn	+3.3	-5.1
Be	+24.4	-2.5
Bi	$\approx 10^4$	-4.3



[book C.M. Hurd, *The Hall effect in metals and alloys*]

6) Band structure

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

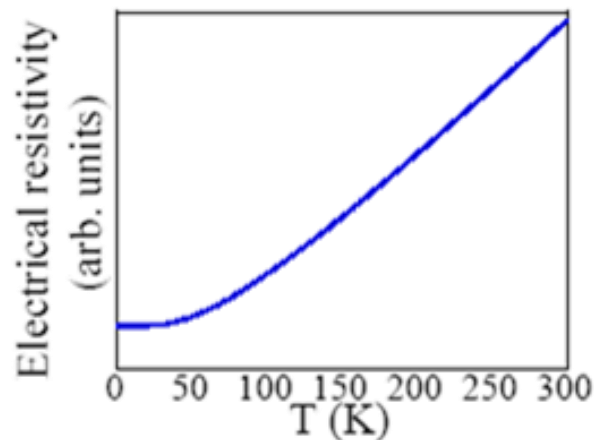
Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

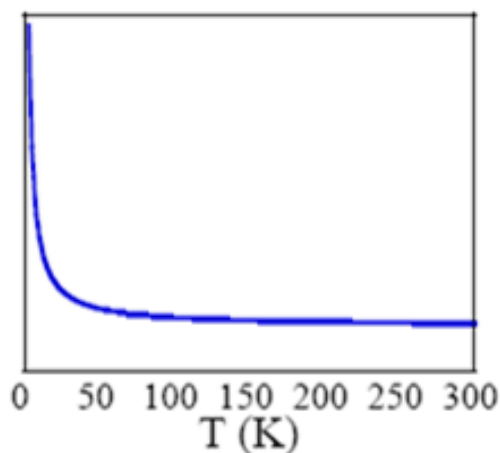
- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

To increase the motivation



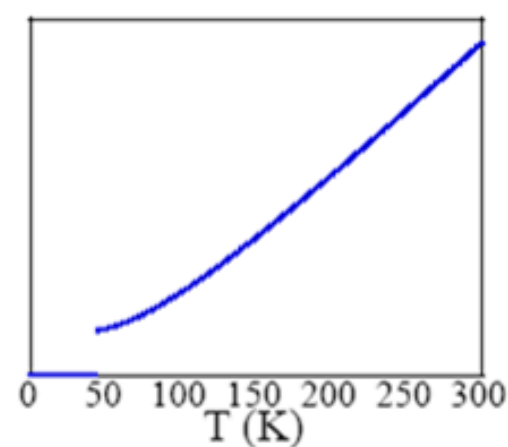
Metal

e.g. C (graphite)



Insulator

C (diamond)



Superconductor

C (doped C_{60})

Qualitatively different collective behaviors (different electronic structures), even though the element is the same. Similarly for other properties, e.g. thermal conductivity.

It is desirable to understand the physics in the background.

To increase the motivation

Vodivostní pás

Zakázaný pás

Valenční pás

Figure known (no only) from high school textbooks. At the high school no one told me what is on the horizontal axis

Starting points

Rigorous starting point is a single Schrödinger equation describing all present electrons and atoms cores at once: can be solved for atom H, but not for 10^{23} particles in a solid.

Separate description of cores (heavy, fixed, often in a periodic lattice) and of each electron (movement in a mean field formed by the other electrons) $\Rightarrow$ replacement of single many-particle Schr. equation by a system of single-particle Schr. equations

$$[-\hbar^2/2m \nabla^2 + V(\mathbf{r})]\psi_{n,k}(\mathbf{r}) + \text{mean field term} = E\psi_{n,k}(\mathbf{r})$$

Although these equations are also easier to write than to solve (details later - chapter 8, more details yet later - KFY/MPPL), they can be solved in principle.

Starting points

So we have a system of single-particle Schr. equations

$$[-\hbar^2/2m \nabla^2 + V(\mathbf{r})]\psi_{n,k}(\mathbf{r}) + \text{mean field term} = E\psi_{n,k}(\mathbf{r})$$

The notation $\psi_{n,k}(\mathbf{r})$ includes

- number of a (2-electron: forget magnetization for now) state n
- wave vector $\mathbf{k}$, wavenumber k : $k = 2\pi/\lambda = p/\hbar$

Note also the de Broglie wavelength $\lambda = h/p = 2\pi\hbar/p$

- for free electron it is more intuitive that it is a particle
 $\Rightarrow$ introduce de Broglie λ ($\Leftrightarrow k$) based on p ,
- for electron in crystal it is more intuitive that it is a wave (ψ)
 $\Rightarrow$ introduce "crystal momentum" p based on λ ($\Leftrightarrow k$),

the important thing is that the relationship
between k and p is the same

Reciprocal space

(one more reminder)

In the real space the lattice is defined by vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ ($\mathbf{a}_{1-3}$ do not necessarily define "real" primitive crystal cell, but also e.g. its integer multiple - that's not the point now)

Let's define a lattice vector $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ where n_{1-3} are integers

In the reciprocal space the lattice is defined by vectors $\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3$ where $\mathbf{A}_1 = 2\pi \cdot \mathbf{a}_2 \times \mathbf{a}_3 / (\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)$, etc.

Let's define a reciprocal lattice vector

$$\mathbf{G} = m_1\mathbf{A}_1 + m_2\mathbf{A}_2 + m_3\mathbf{A}_3$$

It holds $\mathbf{G} \cdot \mathbf{R} = 2\pi(n_1 \cdot m_1 + n_2 \cdot m_2 + n_3 \cdot m_3) \Rightarrow e^{i\mathbf{G} \cdot \mathbf{R}} = 1$

Primitive reciprocal lattice cell (= Wigner-Seitz cell in the reciprocal space) is called first Brillouin zone

Bloch theorem

Bloch theorem says that the wavefunction $\psi_{n,k}(\mathbf{r})$ in a periodic potential is periodic like this potential. At most, shift defined by a lattice vector can change the wavefunction phase.

$\psi_{n,k}(\mathbf{r})$ which fulfils this requirement is called Bloch wave

$$\psi_{n,k}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n,k}(\mathbf{r})$$

plane wave $e^{i\mathbf{k}\mathbf{r}}$ $\times$ periodic (like the potential) function $u_k(\mathbf{r})$

$u_k(\mathbf{r})$ has periodicity of the lattice, so it can be expressed using reciprocal lattice vectors $\mathbf{G}$: $u_{n,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,k}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}$

(recall $e^{i\mathbf{G}\mathbf{R}} = 1$, therefore indeed $u_{n,k}(\mathbf{r}) = u_{n,k}(\mathbf{r} + \mathbf{R})$)

$$\Rightarrow \psi_{n,k}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}} c_{n,k}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}} = \sum_{\mathbf{G}} c_{n,k}(\mathbf{G}) e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}$$

It is enough to choose the wave vector $\mathbf{k}$ inside the first Brillouin zone - we add reciprocal lattice vectors to it anyway (and OK, $\mathbf{k}$ will have infinite number of possible values anyway)

Bloch theorem

$$\psi_{n,k}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n,k}(\mathbf{r})$$

plane wave $e^{i\mathbf{k}\mathbf{r}}$ $\times$ periodic (like the potential) function $u_k(\mathbf{r})$

$u_k(\mathbf{r})$ has periodicity of the lattice, so it can be expressed using reciprocal lattice vectors $\mathbf{G}$: $u_{n,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,k}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}$

(recall $e^{i\mathbf{G}\mathbf{R}} = 1$, therefore indeed $u_{n,k}(\mathbf{r}) = u_{n,k}(\mathbf{r} + \mathbf{R})$)

$$\Rightarrow \psi_{n,k}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}} c_{n,k}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}} = \sum_{\mathbf{G}} c_{n,k}(\mathbf{G}) e^{i(\mathbf{k} + \mathbf{G})\mathbf{r}}$$

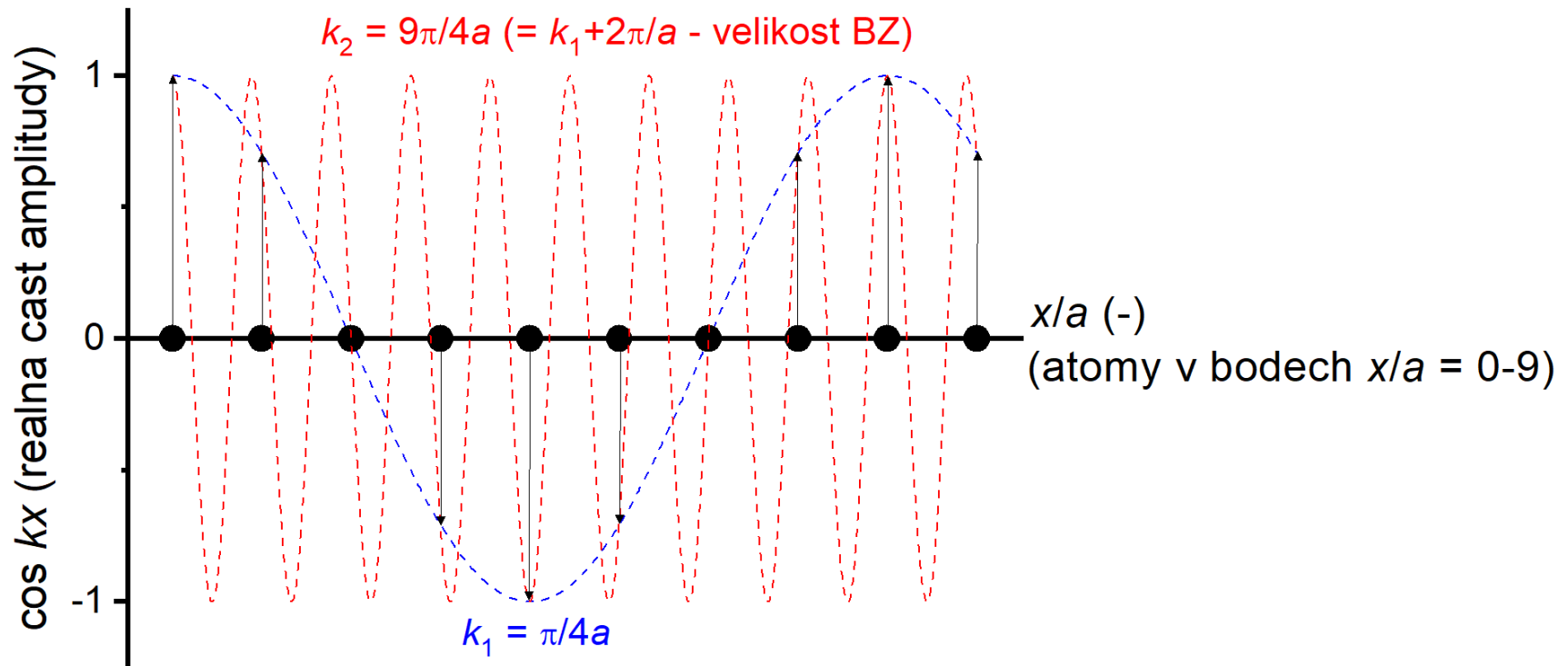
It is enough to choose the wave vector $\mathbf{k}$ inside the first Brillouin zone - we add reciprocal lattice vectors to it anyway (and OK, $\mathbf{k}$ will have infinite number of possible values anyway)

Twofold role of $\mathbf{k}$

- wave vector in the plane wave expansion (blue equation)
- subscript of function u , fully (within given band) defining ψ

Bloch theorem

"Particle-based" justification of the choice of k inside 1st BZ (similarly like in the case of phonons): imagine that electron is skipping from atom to atom, so the value of wavefunction is important only at points where some atom is (figure: $\Leftrightarrow x/a$ is integer) ... and these values do not change by adding $2\pi/a$ to k



Nearly free electron model

In the chapter 5 we considered **free electrons** (in a material = potential hole, but otherwise free: bottom of the hole was flat)

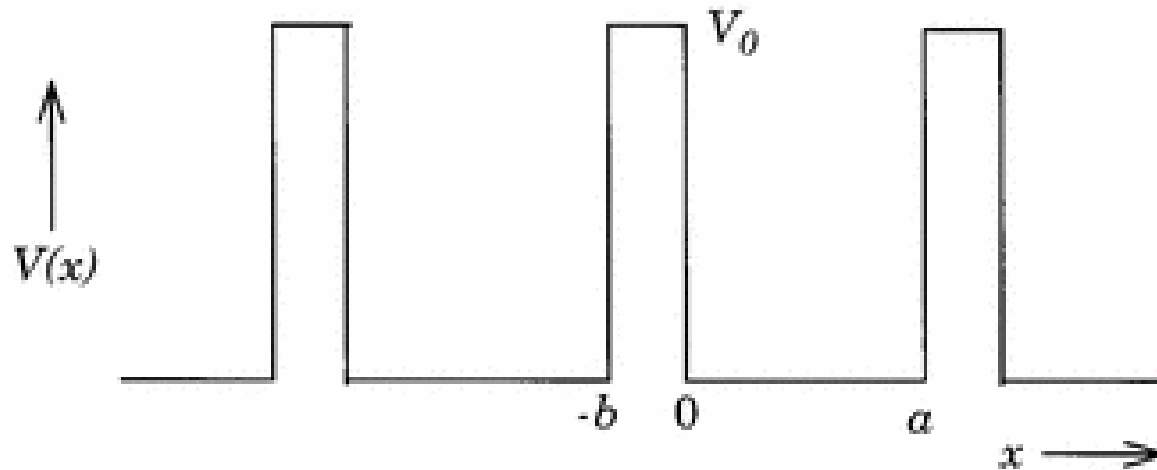
Now consider **nearly free electrons** (do not flat the hole bottom)

Also known as **Kroenig-Penney** model. It shows that the existence of a band structure is not surprising.

Nearly free electron model

1st approach: band structure obtained by a numerical solution of the system of equations 5 slides above

2nd approach: In parallel, there is an analytical solution for "nearly free electron" in a rectangular potential



(the calculations indicated below usually also include transition to delta functions as another simplification: $b \rightarrow 0$ and $V_0 \rightarrow \infty$ at preserved product $V_0 b$)

Nearly free electron model

Convert the Schrödinger equation from the general form
 $[-\hbar^2/2m \nabla^2 + U(\mathbf{r})]\psi_{n,k}(\mathbf{r}) + \text{mean field term} = E\psi_{n,k}(\mathbf{r})$ to form

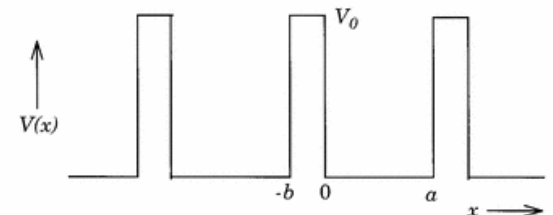
$$\begin{aligned} d^2\psi/dx^2 + 2mE/\hbar^2 \psi &= 0 && \text{from } 0 \text{ to } a \\ d^2\psi/dx^2 + 2m(E-V_0)/\hbar^2 \psi &= 0 && \text{from } a \text{ to } a+b \end{aligned}$$

↓

$$\begin{aligned} d^2\psi/dx^2 + \alpha^2 \psi &= 0 && \text{from } 0 \text{ to } a && \text{where } \alpha = 2mE/\hbar^2 \\ d^2\psi/dx^2 + \beta^2 \psi &= 0 && \text{from } a \text{ to } a+b && \text{where } \beta = 2m(E-V_0)/\hbar^2 \end{aligned}$$

Bloch theorem says $\psi(\mathbf{r}) = e^{ikr}u(\mathbf{r})$, here $\psi(x) = e^{ikx}u(x)$
 after substitution to the blue equations

$$\begin{aligned} d^2u/dx^2 + 2ikdu/dx + (\alpha^2 - k^2)u &= 0 && \text{from } 0 \text{ to } a \\ d^2u/dx^2 + 2ikdu/dx + (\beta^2 - k^2)u &= 0 && \text{from } a \text{ to } a+b \end{aligned}$$



Nearly free electron model

$$d^2u/dx^2 + 2ikdu/dx + (\alpha^2 - k^2)u = 0$$

od 0 do a

$$d^2u/dx^2 + 2ikdu/dx + (\beta^2 - k^2)u = 0$$

od a do $a+b$

solution of homogeneous linear differential eqs. of second order will have the form (note the roots of the characteristic equation)

$$u_1 = Ae^{i(\alpha-k)x} + A'e^{-i(\alpha+k)x}$$

from 0 to a

$$u_2 = Be^{i(\beta-k)x} + B'e^{-i(\beta+k)x}$$

from a to $a+b$

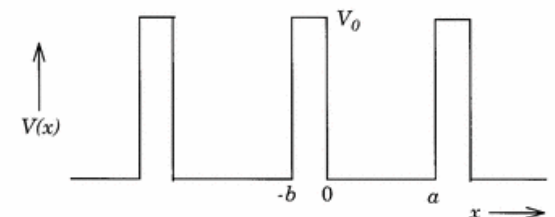
⇓ reminder $\psi(x) = e^{ikx}u(x)$

$$\psi_1 = Ae^{i\alpha x} + A'e^{-i\alpha x}$$

from 0 to a

$$\psi_2 = Be^{i\beta x} + B'e^{-i\beta x}$$

from a to $a+b$



Nearly free electron model

$$u_1 = Ae^{i(\alpha-k)x} + A'e^{-i(\alpha+k)x}$$

from 0 to a

$$u_2 = Be^{i(\beta-k)x} + B'e^{-i(\beta+k)x}$$

from a to $a+b$

$$\psi_1 = Ae^{i\alpha x} + A'e^{-i\alpha x}$$

from 0 to a

$$\psi_2 = Be^{i\beta x} + B'e^{-i\beta x}$$

from a to $a+b$

requirement of continuity, at least up to the first derivative

$$\psi_1(0^+) = \psi_2(0^-) \Rightarrow A + A' = B + B'$$

$$d\psi_1/dx(0^+) = d\psi_2/dx(0^-) \Rightarrow A\alpha - A'\alpha = B\beta - B'\beta$$

requirement of periodicity (with the period of the potential, i.e. $a+b$ - see the Bloch theorem), at least up to the first derivative

$$u_1(a) = u_2(-b)$$

$$\Rightarrow Ae^{i(\alpha-k)a} + A'e^{-i(\alpha+k)a} = Be^{-i(\beta-k)b} + B'e^{i(\beta+k)b}$$

$$du_1/dx(a) = du_2/dx(-b)$$

$$\Rightarrow A(\alpha-k)e^{i(\alpha-k)a} - (\alpha+k)A'e^{-i(\alpha+k)a} = B(\beta-k)e^{-i(\beta-k)b} - (\beta+k)B'e^{i(\beta+k)b}$$

Nearly free electron model

$$\begin{array}{rclcl}
 A & + & A' & - & B & - & B' & = & 0 \\
 A\alpha & - & A'\alpha & - & B\beta & + & B'\beta & = & 0 \\
 Ae^{i(\alpha-k)a} & + & A'e^{-i(\alpha+k)a} & - & Be^{-i(\beta-k)b} & - & B'e^{i(\beta+k)b} & = & 0 \\
 A(\alpha-k)e^{i(\alpha-k)a} - (\alpha+k)A'e^{-i(\alpha+k)a} - B(\beta-k)e^{-i(\beta-k)b} + B'(\beta+k)e^{i(\beta+k)b} & = & 0
 \end{array}$$

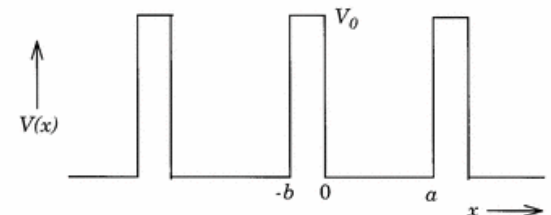
system of 4 linear equations without right-hand side, having non-zero solution ($\Leftrightarrow$ zero determinant, simplified by the aforementioned $b \rightarrow 0$ and $V_0 \rightarrow \infty$ at preserved $V_0 b$) if

$$P \sin(\alpha a) / \alpha a + \cos(\alpha a) = \cos(ka) \text{ where } P = mV_0 b a / \hbar^2$$

right-hand side is between -1 and 1, which the left-hand side fulfils only for some α , i.e. only some E (see $2mE/\hbar^2 = \alpha^2$)



some E values are forbidden

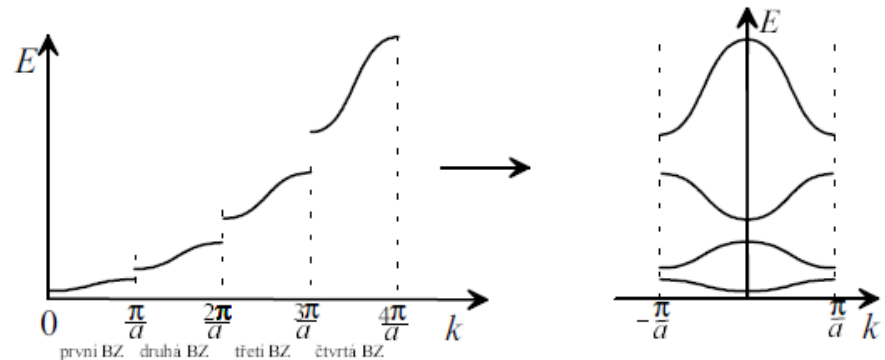
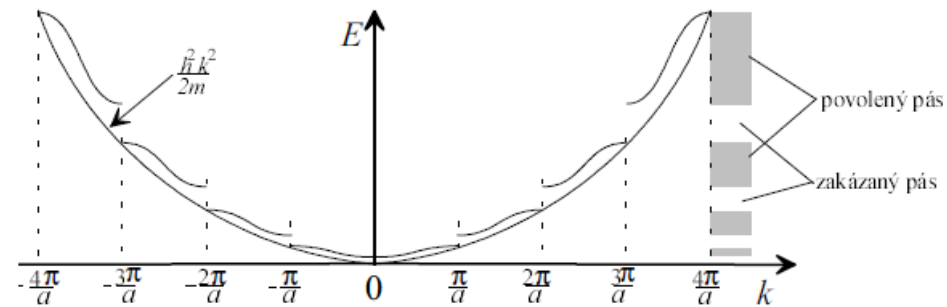


Nearly free electron model

right-hand side is between -1 and 1, which the left-hand side fulfils only for some α , i.e. only some E (see $2mE/\hbar^2 = \alpha^2$)

the function $E(k)$ is not discontinuous for any k , but for $k = n\pi/a \Leftrightarrow \cos(ka) = \pm 1$ (owing to the source of discontinuity [$\cos(ka)$ would be outside the range -1 to 1] this is not surprising)

all states can be described by wave vectors k inside 1st Brillouin zone (see above), i.e. all parts of the function $E(k)$ can be overturned there



Example of real band structure, direct × indirect band gap

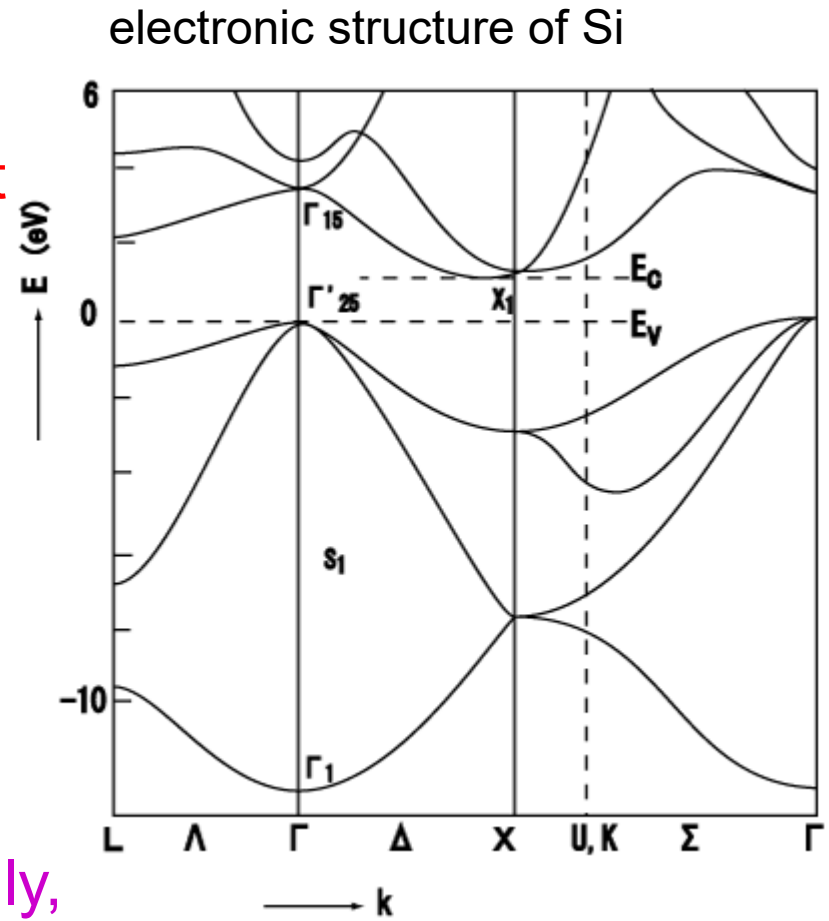
Top of valence and bottom of conduction band are sometimes at the same k , sometimes (Si) not



$E_C - E_V$ is the indirect Si band gap, well known 1.1 eV: (de)excitation accompanied by change of k

Direct Si band gap of 3.3 eV: (de)excitation "right up / right down" at a fixed k

Both gaps are measurable optically, only the indirect one also electrically



Example of real band structure, direct × indirect band gap

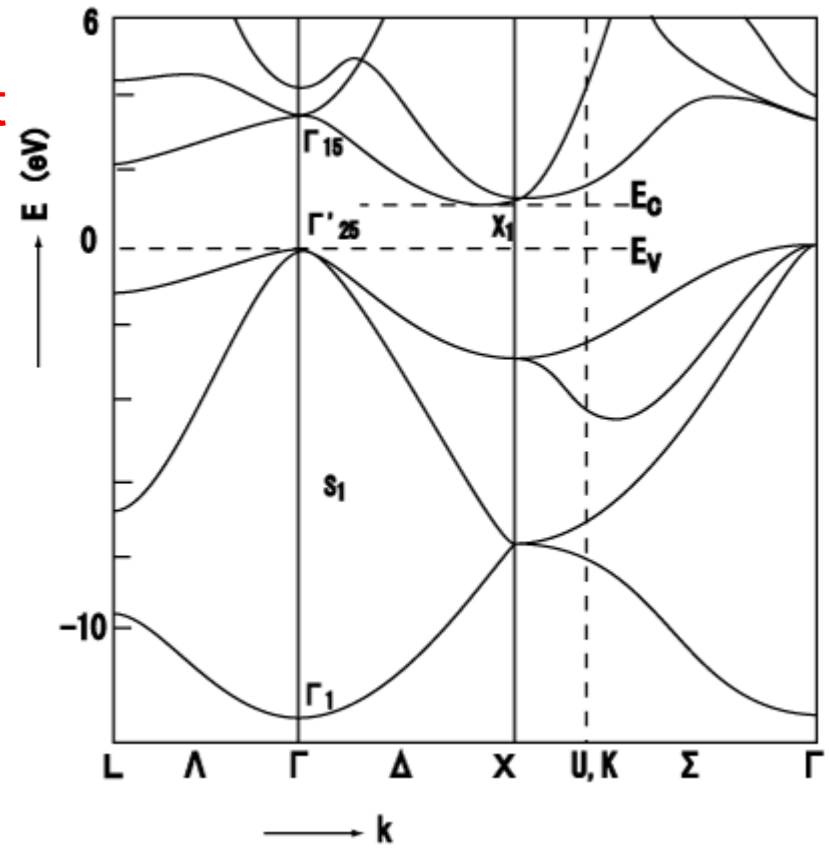
Top of valence and bottom of conduction band are sometimes at the same $\mathbf{k}$, sometimes (Si) not



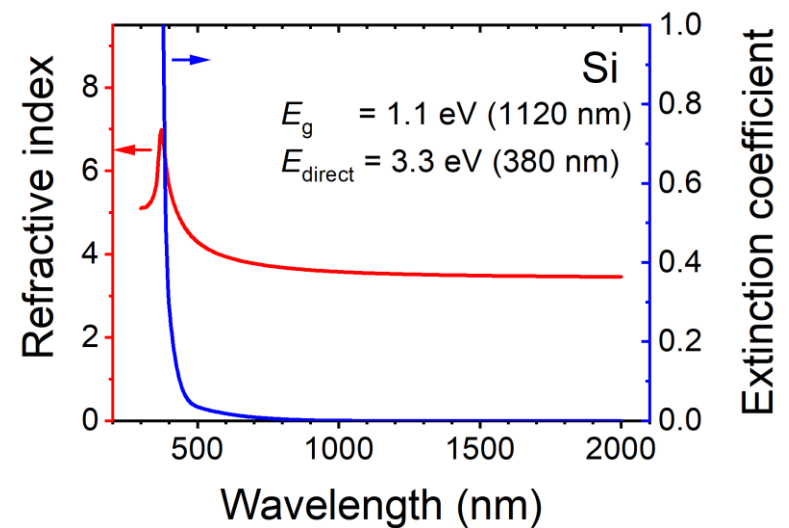
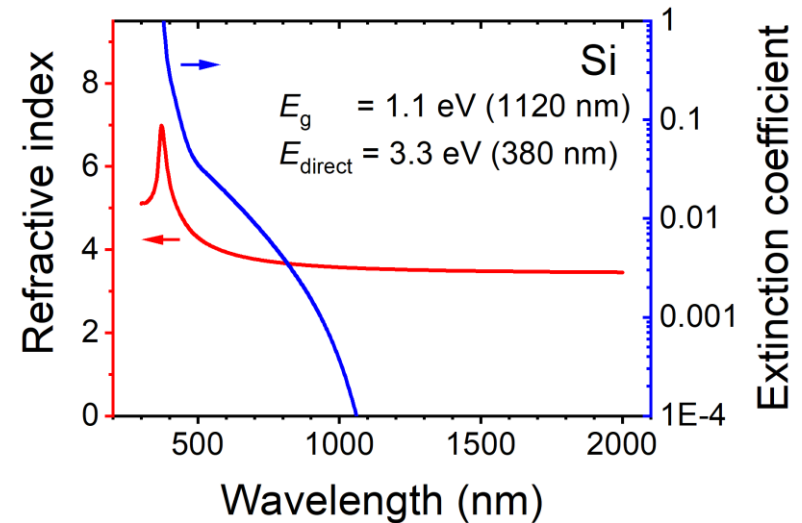
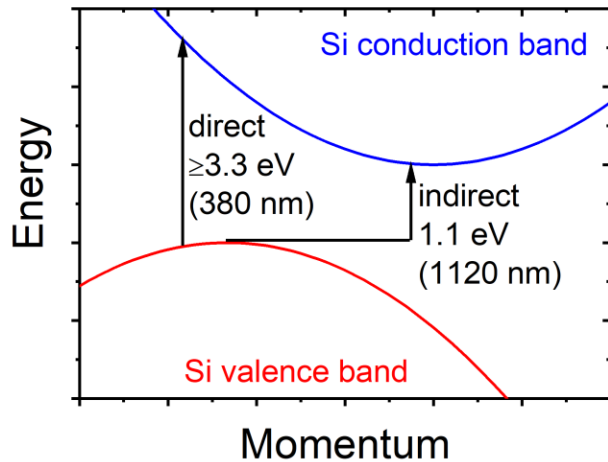
$E_C - E_V$ is the indirect Si band gap, well known 1.1 eV: (de)excitation accompanied by change of $\mathbf{k}$

In many - especially highly symmetrical - materials (including Si), the top of valence band is at the point Γ (gamma) $\mathbf{k} = [0,0,0]$. Generally not.

electronic structure of Si

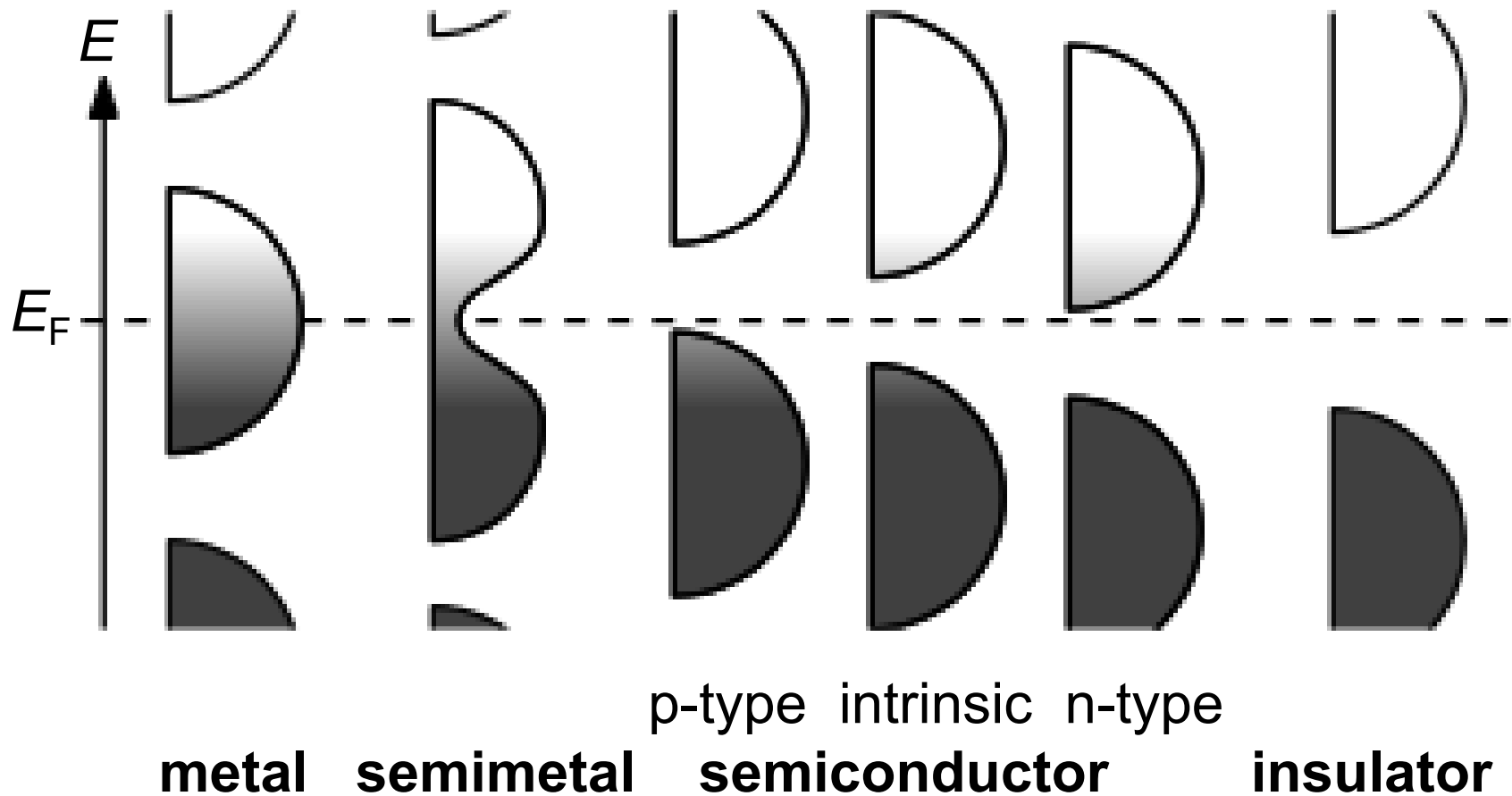


Example of real band structure, direct × indirect band gap



Extinction coefficient is >0 below **1100 nm**, but steeply increases below **400 nm** due to increasing probability of transitions - no change of momentum (phonon) required

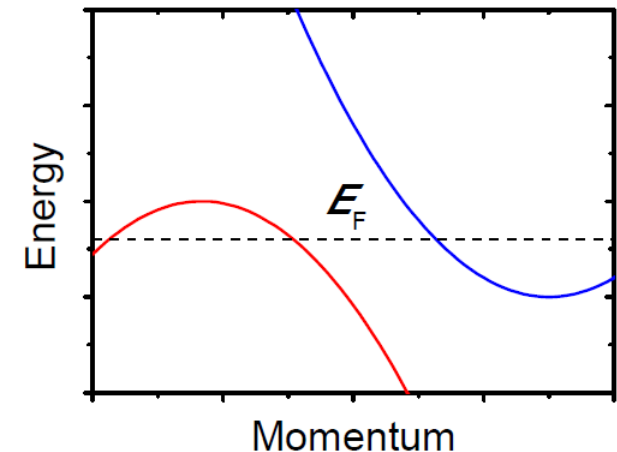
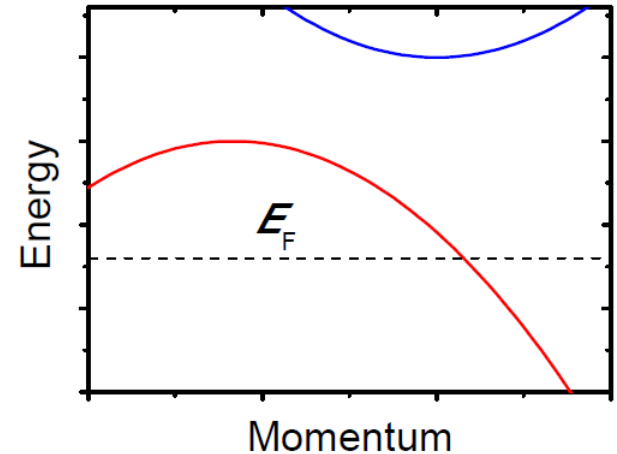
Possible band structures



Possible band structures

Metal: high density of states at E_F

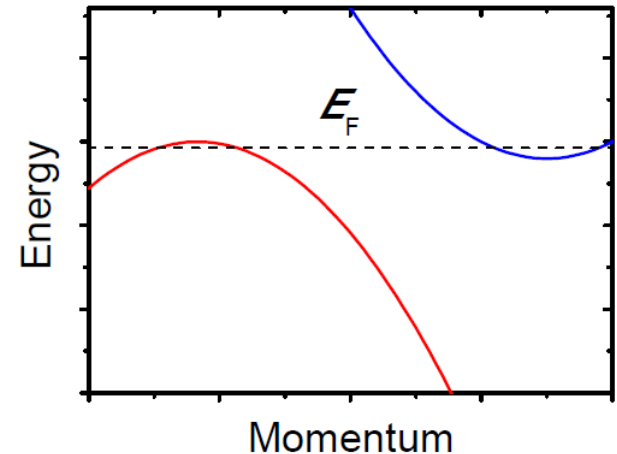
- either there is half-filled top non-empty band (there is a space for two electrons with opposite spins in each state):
consequence of odd number of electrons in primitive cell
- or there is even number of electrons in primitive cell, but the Fermi level intersects more overlapping ($\Rightarrow$ partially filled) bands



Possible band structures

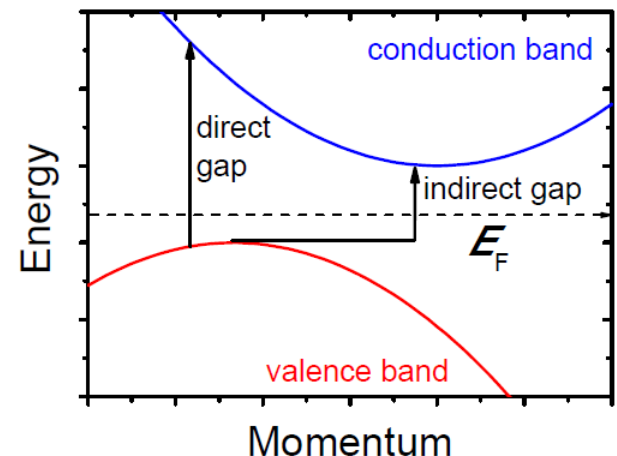
Semimetal: low - but nonzero - density of states at E_F

- even number of electron in primitive cell, Fermi level intersects more bands which do overlap but only just (in graphite they touch at a single point))



Semiconductor, insulator: no delocalized states at E_F

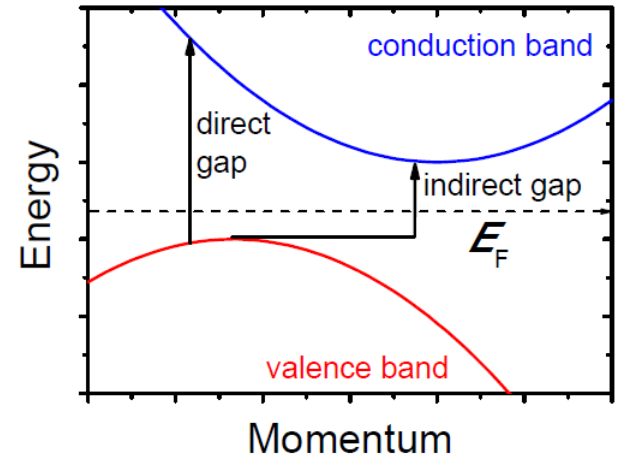
- Fermi level does not intersect any band (localized states sitting on dopants in [weakly] doped semiconductors are not taken as a part of valence / conductive band - they sit in the gap)



Possible band structures

Semiconductor, insulator: no delocalized states at E_F

- Fermi level does not intersect any band (localized states sitting on dopants in [weakly] doped semiconductors are not taken as a part of valence / conductive band - they sit in the gap)



Is the Fermi level uniquely defined at all in this case?

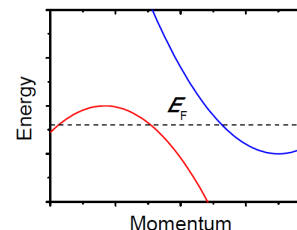
Yes: from the statistical point of view it has the meaning of a chemical potential (derivative of free enthalpy G by number of particles, i.e. electrons), and this potential is in the middle of band gap for intrinsic (undoped) semiconductor.

(It is not exactly true - see the next chapter 7 for details)

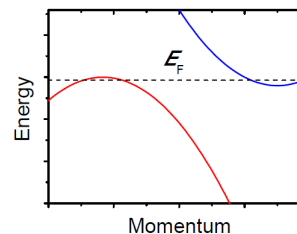
Possible band structures

Orders of magnitude of the free charge carrier concentrations

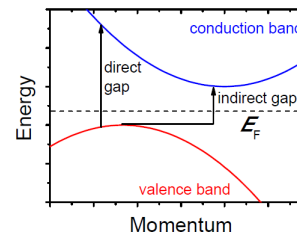
Cu (metal) $\sim 10^{23} \text{ cm}^{-3}$
further details 11-12 slides below



As (semimetal) $\sim 10^{20} \text{ cm}^{-3}$
Sb (semimetal) $\sim 10^{19} \text{ cm}^{-3}$
C (semimetal) $\sim 10^{18} \text{ cm}^{-3}$



Ge (semiconductor) $\sim 10^{13} \text{ cm}^{-3}$
Si (semiconductor) $\sim 10^{10} \text{ cm}^{-3}$
GaAs (semiconductor) $\sim 10^6 \text{ cm}^{-3}$

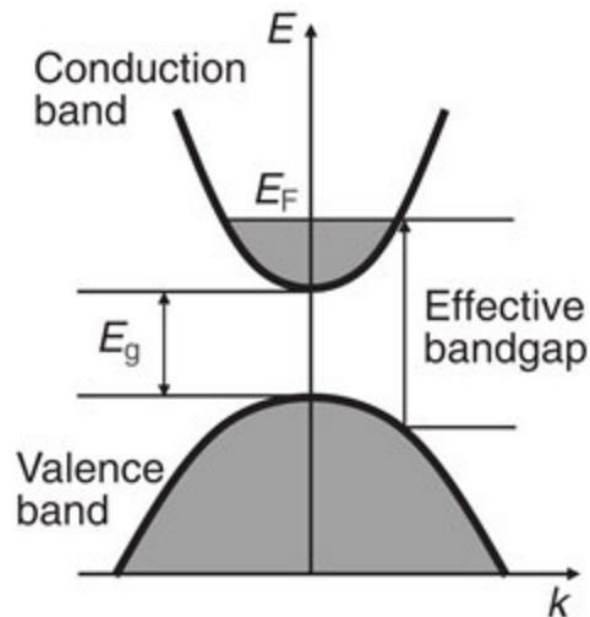
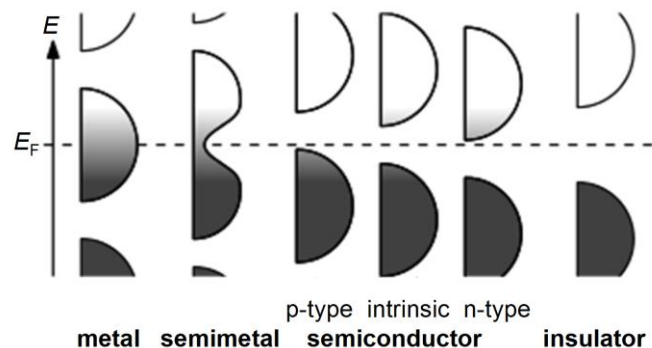


Other band gap than expected: Burstein-Moss effect

Reminder of figure above: in a (weakly) doped semiconductor, E_F moves from the middle of the band gap **to its edge**

In a heavily doped ("degenerated") semiconductor, E_F can move **behind the band gap edge**, e.g. inside the conduction band - electrons fill all states at its bottom (but their number is still insufficient to make the mat. metal)

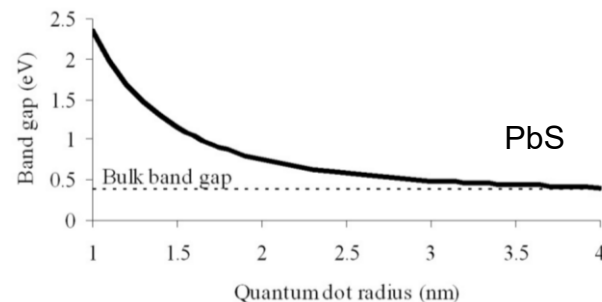
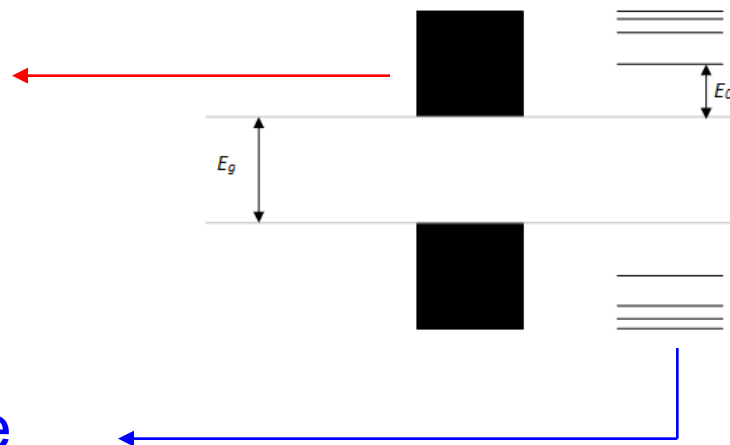
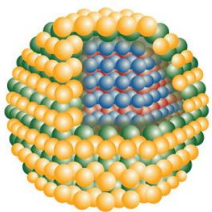
Thus, electron skipping from valence to conduction band registers higher band gap (higher distance to the lowest unoccupied state in conduction band)



Other band gap than expected: quantum confinement

The stuff above is valid for bulk materials: charge carriers (electron in metal, exciton = electron+hole in semiconductor) can move in a large space compared to their wavelength

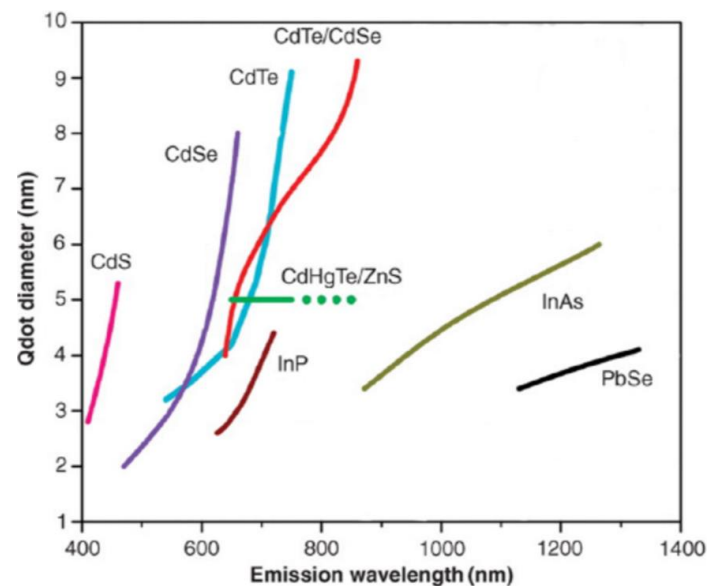
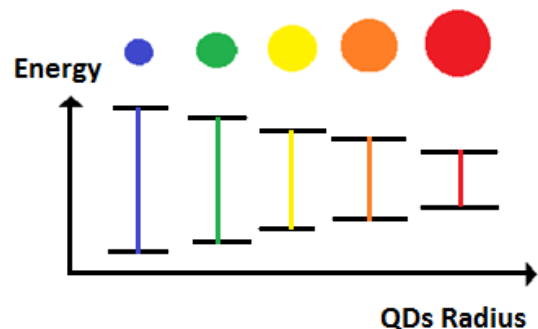
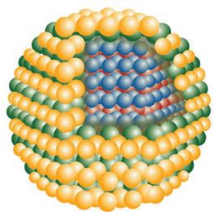
If materials dimension is comparable to this wavelength (**quantum dots**), the energy levels become discrete and the **band gap increases** (approx. quadratically with the dimension)



Other band gap than expected: quantum confinement

If materials dimension is comparable to this wavelength (**quantum dots**), the energy levels become discrete and the **band gap increases** (approx. quadratically with the dimension)

Electronic structure has sharp edges and is (by changing the dimension) smoothly tunable. Utilization in nanotechnologies, e.g. for setting the desired color ($\Rightarrow$ quantum dot displays)



Semimetal × half-metal × metalloid

What is the difference between these terms?

Semimetal × half-metal × metalloid

Semimetals (Sn, Sb, As, graphite, ...):

materials with a very low overlap of valence and conduction band $\Rightarrow$ with a low, but non-zero, density of states at $E_F \Rightarrow$ conductive, but lower density of charge carriers than in metals

Metalloids (B, Si, Ge, again Sb, again As, ...):

materials combining properties of metals (e.g. "metallic" appearance: band gap, if any, is narrower than energy of visible photons) and non-metals (e.g. brittleness: bonds are not predominantly metallic or lower-than-metallic conductivity)

Half-metals (CrO_2 , Fe_3O_4 , ...):

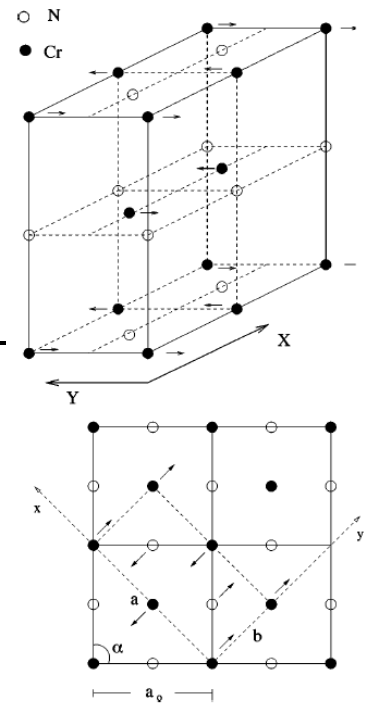
materials which have full valence band for spins of one orientation, and only partially full val. band for spins of the other orientation $\Rightarrow$ conductivity depends on spin (necessary condition are different numbers of spins $\uparrow$ and $\downarrow \Rightarrow$ magnetism)

Other conductivity than expected: Mott insulators

Materials for which a routinely calculated electronic structure does not contain band gap, i.e. they should conduct, but they don't. The reason is repulsion of electrons (their movement is correlated), which are forcing each other to stay at one place.

Necessary (not sufficient) condition:
Mott insulators are antiferromagnetic

Example: CrN (at low T there are the same spins in planes 110: two planes with spins up, two with spins down). Repulsion of electrons with same spins in neighbouring planes 110 also deforms the lattice: cubic changes to orthorhombic



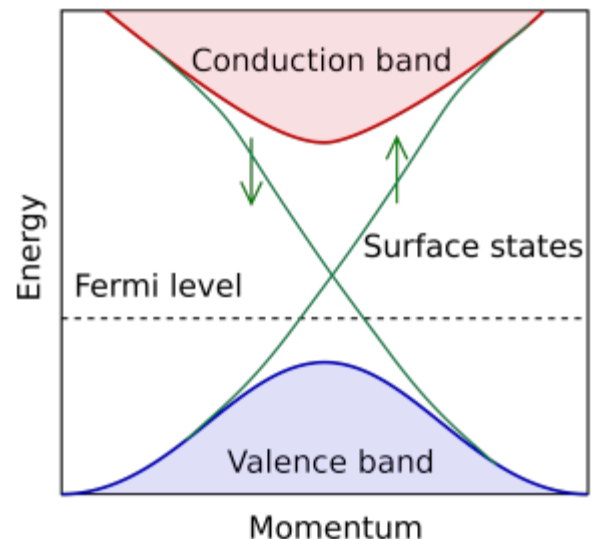
[A. Filipetti et al., Phys. Rev. B 59, 7043 (1999)]

Other conductivity than expected: topological insulators

Materials for which a routinely calculated electronic structure contains band gap, i.e. they should not conduct and indeed do not conduct in their volume, but they have additional states inside the gap on their surface $\Rightarrow$ conduct along the surface.

The states are not two-electron:
one band ($\Leftrightarrow$ conductive channel)
for spins up, one for spins down.

Example: Bi_2Se_3 , Bi_2Te_3 , Bi_2Sb_2



Role of E_F distance from vacuum

The band gap width tells us the excitation energy, but not

- ionization energy = electron affinity (distance of the bottom of cond. band, where electrons are emitted from, from vacuum)
- work function (distance of the Fermi level from vacuum),

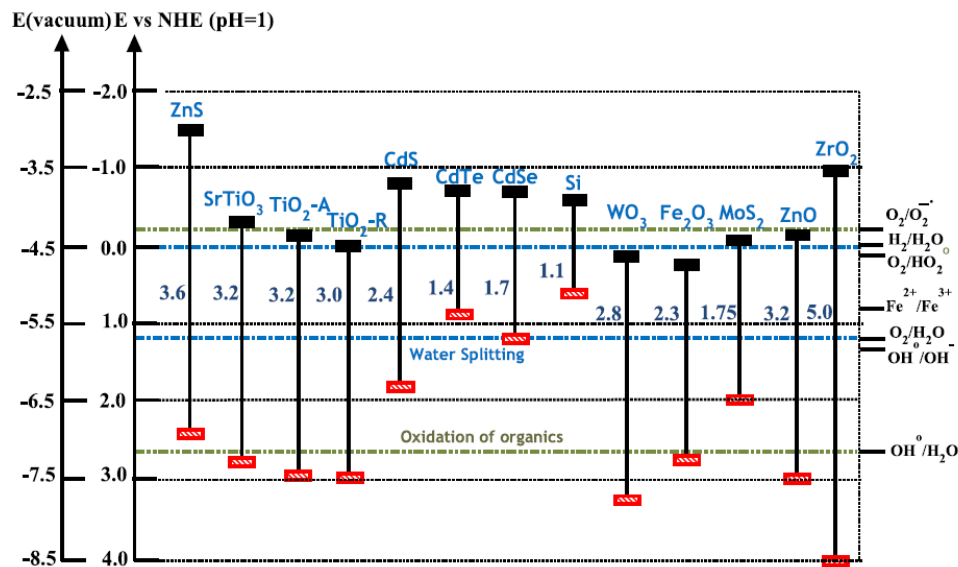
these quantities (equal to each other for metals, but not for materials with a band gap) are independent of the band gap.

Why is the distance of band gap from vacuum
(in praxis from normal hydrogen electrode, NHE) important?

Role of E_F distance from vacuum

Why is the distance of band gap from vacuum (in praxis from normal hydrogen electrode, NHE) important?

When catalyzing a process (water splitting, etc.) which utilizes photons, we want not only narrower band gap than the photon energy, but also energy levels where the process takes place inside the gap. See photoinduced properties in chapter 11.



Opaque insulators

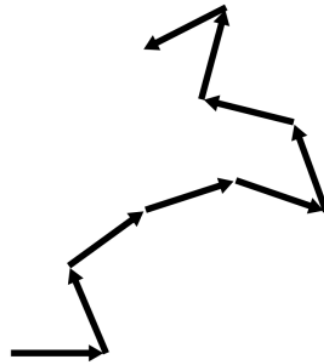
- Material (Al_2O_3 , SiO_2 , ZrO_2 , ...) is completely insulating
- $\Leftrightarrow$ has wide band gap (high excitation energy) which the electrons never jump over (usual criterion >3 eV)
 - $\Leftrightarrow$ energy of visible photons (1.5-3 eV) cannot be invested to excitations over the band gap
 - $\Leftrightarrow$ material is completely transparent for visible light

So why do exist materials (rubber, wood, snow, ...) which are insulating and opaque at the same time?

Opaque insulators

So why do exist materials (rubber, wood, snow, ...) which are insulating and opaque at the same time?

Because they are molecular solids - do not constitute a network of atoms, but a disordered mess of molecules. While the molecules have high excitation energy (band gap equivalent), photons reflects from them and change their direction until - most often - leave the material through the original surface.



This is valid in about the same way for all wavelengths, which is why snow, raw rubber, etc. are white.

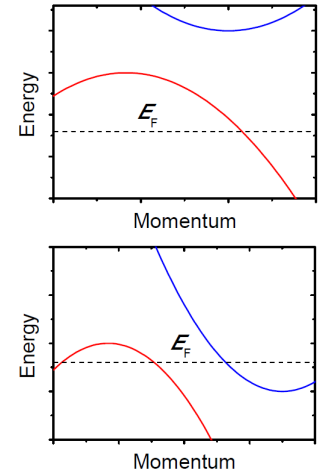
Free charge carrier density

We need delocalized electrons from partially filled bands

Odd number of el. per primitive cell, e.g. alkali metals **Li, Na, K, ...** $\Rightarrow$ fulfilled automatically

Even number of el. per cell, but overlapping bands, e.g. **Be, Mg, Ca, ...** where s- and p-orbitals (p- are empty for isolate atom) give rise to a single partially filled sp-band $\Rightarrow$ **fulfilled** by a "bypass", but for **twice as many electrons compared to alkali metals**

In transition metals, mostly s-electrons are the delocalized ones (chapter 2), their isolated atoms (let alone the hybridization with p- in condensed state) have 1 or 2. What constitutes a difference is the probability that they will jump into relatively localized d-orbitals $\Rightarrow$ the only sure case is when the d-orbital is full like in **Cu, Au, Ag, ...** (most conductive elements of all)

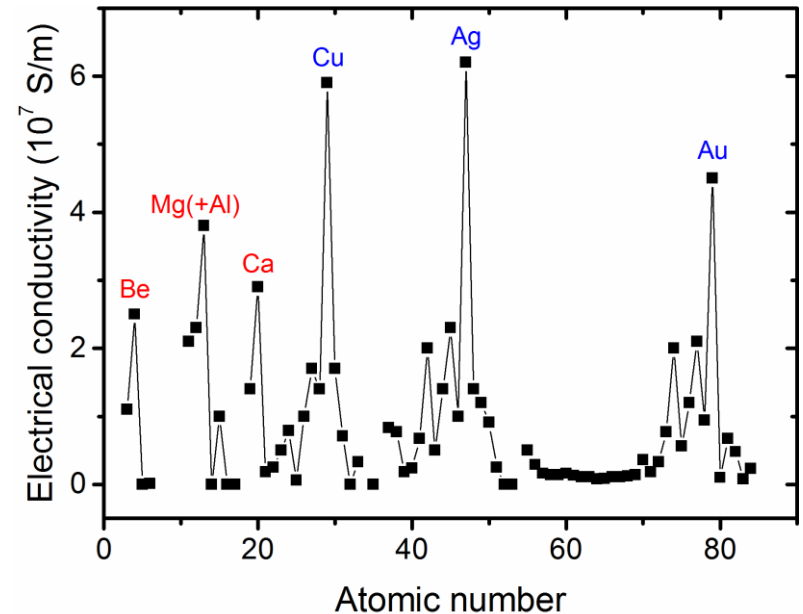


Free charge carrier density

The same in a graphical form

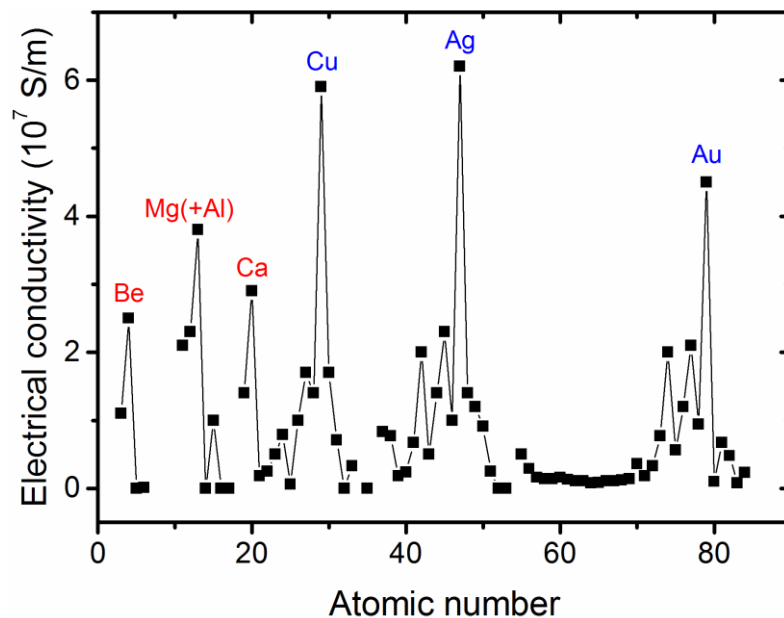
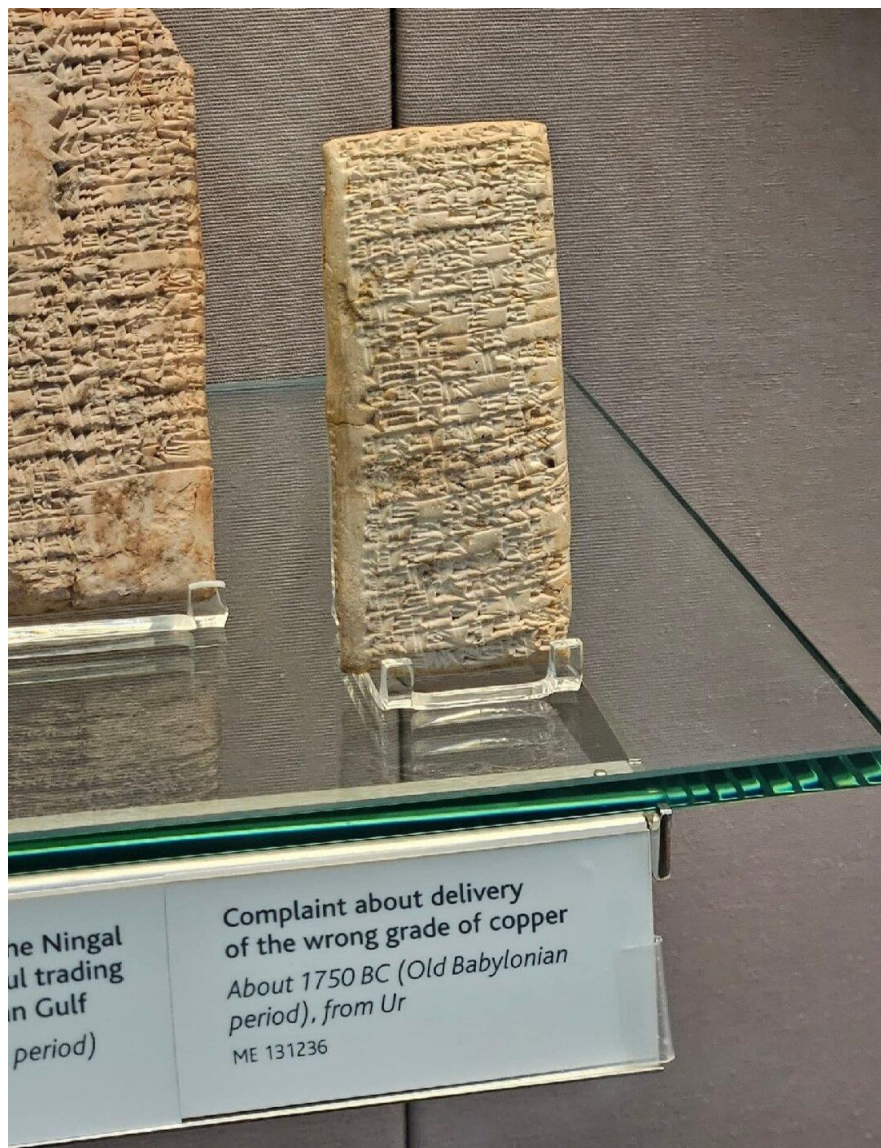
Local maxima for Be, Mg, Ca
 $\Leftrightarrow$ val. configuration $ns^2.np^0$, but
 bands arising from s- and p-
 orbitals have close energies
 and el. easily skip between
 them (sp band filled of 2/8)

Local maxima for Cu, Ag, Au
 (val. configuration $nd^{10}.[n+1]s^1$)
 $\Leftrightarrow$ d-band is full
 $\Leftrightarrow$ delocalized s-electrons can
 conduct current without any
 risk of ending up in localized
 d-orbital instead



1	1A																8A																18		
1	H																He																2		
Periods																		Groups																	
1.008																		4.003																	
3	Li																Be																10		
6.941																		9.012																	
11	Na																Mg																20		
22.990																		24.305																	
19	K																Ca																38		
39.098																		40.078																	
27	Co																Ni																46		
58.933																		58.693																	
35	Br																Kr																54		
79.904																		83.798																	
43	Rb																Sr																62		
85.468																		87.62																	
51	Cs																Ba																70		
132.905																		137.327																	
59	La																Ce																78		
138.905																		140.12																	
67	Pr																Nd																86		
140.908																		144.24																	
75	Pm																Sm																94		
144.913																		150.36																	
83	Eu																Gd																102		
151.964																		157.25																	
91	Tb																Dy																110		
158.925																		162.50																	
99	Ho																Er																118		
164.930																		167.26																	
107	Tm																Yb																126		
168.933																		173.054																	
115	Lu																Hf																134		
174.967																		178.49																	
123	Ta																W																142		
180.948																		183.84																	
131	Re																Os																150		
186.207																		190.23																	
139	Ir																Pt																158		
192.22																		195.08																	
147	Au																Hg																166		
196.967																		200.59																	
155	Tl																Pb																174		
204.38																		207.2																	
163	Bi																Po																182		
208.98																		209																	
171	At																Rn																190		
210																		222																	
179	Fr																Ra																198		
223																		226																	
187	Ac																Th																206		
227																		232.038																	
195	Pa																U																214		
231																		238.029																	
203	Np																Pu																222		
237																		244																	
211	Am																Cm																230		
243																		250																	
219	Bk																Cf																238		
247																		251																	
227	Es																Bh																246		
252																		264																	
235	Fm																Ob																254		
257																		268																	
243	Md																Lv																262		
258																		273																	
251	No																Ts																270		
259																		281																	
259	Lr																Og																278		
262																		284																	
267	Uu																Nh																286		
267																		289																	
275	Uub																Fl																294		
271																		298																	
283	Uut																Al																302		
288																		304																	
291	Uuq																Cn																310		
293																		311																	
300	Uup																Nh																318		
295																		315																	
308	Uus																Ts																326		
299																		315																	
316	Uuo																Og																334		
301																		311																	

However, carefully about Cu quality :-)



1 1A H Hydrogen 1.008	2 2A Be Beryllium 9.012	3 3A Li Lithium 6.941	4 4A Na Sodium 22.990	5 5A K Potassium 39.098	6 6A Rb Rubidium 84.468	7 7A Cs Cesium 132.905	8 8A Fr Francium 223.020	9 9A He Helium 4.003	10 10A Ne Neon 20.180	11 11A Ar Argon 39.948	12 12A Kr Krypton 84.798	13 13A Xe Xenon 131.294	14 14A Rn Radon 222.018	15 15A Uuo Ununseptium unknown	16 16A Uuo Ununseptium unknown	17 17A Uuo Ununseptium unknown	18 18A Uuo Ununseptium unknown
19 1A Na Sodium 22.990	20 2A Mg Magnesium 24.305	21 3A Al Aluminum 26.981	22 4A Si Silicon 28.086	23 5A P Phosphorus 30.974	24 6A S Sulfur 32.065	25 7A Cl Chlorine 35.453	26 8A Ar Argon 39.948	27 9A Kr Krypton 84.798	28 10A Xe Xenon 131.294	29 11A Rn Radon 222.018	30 12A Uuo Ununseptium unknown	31 13A Uuo Ununseptium unknown	32 14A Uuo Ununseptium unknown	33 15A Uuo Ununseptium unknown	34 16A Uuo Ununseptium unknown	35 17A Uuo Ununseptium unknown	36 18A Uuo Ununseptium unknown
37 1A K Potassium 39.098	38 2A Ca Calcium 40.078	39 3A Sc Scandium 44.956	40 4A Ti Titanium 47.867	41 5A V Vanadium 50.942	42 6A Cr Chromium 51.996	43 7A Mn Manganese 54.938	44 8A Fe Iron 55.845	45 9A Co Cobalt 58.933	46 10A Ni Nickel 58.693	47 11A Cu Copper 63.546	48 12A Zn Zinc 65.38	49 13A Ga Gallium 69.723	50 14A Ge Germanium 72.631	51 15A As Arsenic 74.922	52 16A Se Selenium 78.971	53 17A Br Bromine 84.798	54 18A Kr Krypton 84.798
55 1A Rb Rubidium 84.468	56 2A Sr Strontium 87.62	57 3A Y Yttrium 88.906	58 4A Zr Zirconium 91.224	59 5A Nb Niobium 92.906	60 6A Mo Molybdenum 95.95	61 7A Tc Technetium 98.907	62 8A Ru Ruthenium 101.07	63 9A Rh Rhodium 102.906	64 10A Pd Palladium 106.42	65 11A Ag Silver 107.868	66 12A Cd Cadmium 112.414	67 13A In Indium 114.818	68 14A Sn Tin 118.710	69 15A Pb Lead 118.710	70 16A Bi Bismuth 208.980	71 17A Po Polonium 209	72 18A At Astatine 210
87 1A Fr Francium 223.020	88 2A Ra Radium 226.025	89-103 3A Rf Rutherfordium [261]	104 4A Db Dubnium [262]	105 5A Sg Seaborgium [266]	106 6A Bh Bohrium [264]	107 7A Hs Hassium [269]	108 8A Mt Meitnerium [268]	109 9A Ds Darmstadtium [269]	110 10A Rg Roentgenium [272]	111 11A Cn Copernicium [277]	112 12A Nh Nihonium [278]	113 13A Fl Flerovium [277]	114 14A Uup Ununpentium [289]	115 15A Lv Livermorium [293]	116 16A Uus Ununseptium [294]	117 17A Uuh Ununheptium [294]	118 18A Uuo Ununseptium [294]

Poisons

We could spend more time on the periodic table

- e.g. by discussing which elements are most toxic and why -
- but this is not a topic for solid state physics anymore

1																	18																		
	1A																	VIIIA																	
1	H Hydrogen 1.008																	He Helium 4.003																	
3	Li Lithium 6.941																																		
		2	Be Beryllium 9.012																																
11	Na Sodium 22.990		12	Mg Magnesium 24.305													13	Al Aluminum 26.982	14	Si Silicon 28.086	15	P Phosphorus 30.974	16	S Sulfur 32.06	17	Cl Chlorine 35.453	18	Ar Argon 39.948							
19	K Potassium 39.098	20	Ca Calcium 40.078	21	Sc Scandium 44.956	22	Ti Titanium 47.867	23	V Vanadium 50.942	24	Cr Chromium 51.996	25	Mn Manganese 54.938	26	Fe Iron 55.845	27	Co Cobalt 58.933	28	Ni Nickel 58.693	29	Cu Copper 63.546	30	Zn Zinc 65.38	31	Ga Gallium 69.723	32	Ge Germanium 72.61	33	As Arsenic 74.922	34	Se Selenium 78.96	35	Br Bromine 79.904	36	Kr Krypton 83.798
37	Rb Rubidium 85.468	38	Sr Strontium 87.62	39	Y Yttrium 88.906	40	Zr Zirconium 91.224	41	Nb Niobium 92.906	42	Mo Molybdenum 95.94	43	Tc Technetium 98.907	44	Ru Ruthenium 101.07	45	Rh Rhodium 102.91	46	Pd Palladium 106.36	47	Ag Silver 107.868	48	Cd Cadmium 112.415	49	In Indium 114.818	50	Sn Tin 118.710	51	Sb Antimony 121.757	52	Te Tellurium 127.6	53	I Iodine 126.905	54	Xe Xenon 131.29
55	Cs Cesium 132.905	56	Ba Barium 137.327	57-71		72	Hf Hafnium 178.49	73	Ta Tantalum 180.948	74	W Tungsten 183.84	75	Re Rhenium 186.207	76	Os Osmium 190.23	77	Ir Iridium 192.22	78	Pt Platinum 195.085	79	Au Gold 196.967	80	Hg Mercury 200.59	81	Tl Thallium 204.384	82	Pb Lead 207.2	83	Bi Bismuth 208.980	84	Po Polonium 209	85	At Astatine 210	86	Rn Radon 222
87	Fr Francium 223	88	Ra Radium 226	89-103		104	Rf Rutherfordium 261	105	Db Dubnium 262	106	Sg Seaborgium 266	107	Bh Bohrium 264	108	Hs Hassium 277	109	Mt Meitnerium 268	110	Ds Darmstadtium 271	111	Rg Roentgenium 272	112	Cn Copernicium 285	113	Nh Nihonium 284	114	Fl Flerovium 289	115	Uup Ununpentium 288	116	Lv Livermorium 293	117	Uus Ununseptium 294	118	Uuo Ununoctium 294

classically toxic

radioactive (plus the line below)

harmless Bi

Role of how much are states localized

(inverse participation ratio)

Starting points:

- for each atom and electronic state, it is possible (by integration over 1st BZ = sum over all vectors $\mathbf{k}$) to provide weight of a state on an atom (sum of weights over all atoms is 1)
- in a real material (not infinite crystal), each electronic state is localized in a finite volume (on a finite set of atoms) ... and the question of interest is how large is this set

Sum of squares of weights of electronic states over all atoms (theor. over ∞ atoms, in praxis over N atoms):

- min. $1/N$, if the weights on all atoms are equal ($N \times [1/N]^2$)
- max. 1, if the state sits on single atom (other weights are 0)

The quantity is called **Inverse Participation Ratio (IPR)**

Role of how much are states localized (inverse participation ratio)

Higher inverse participation ratio



state is localized on less atoms



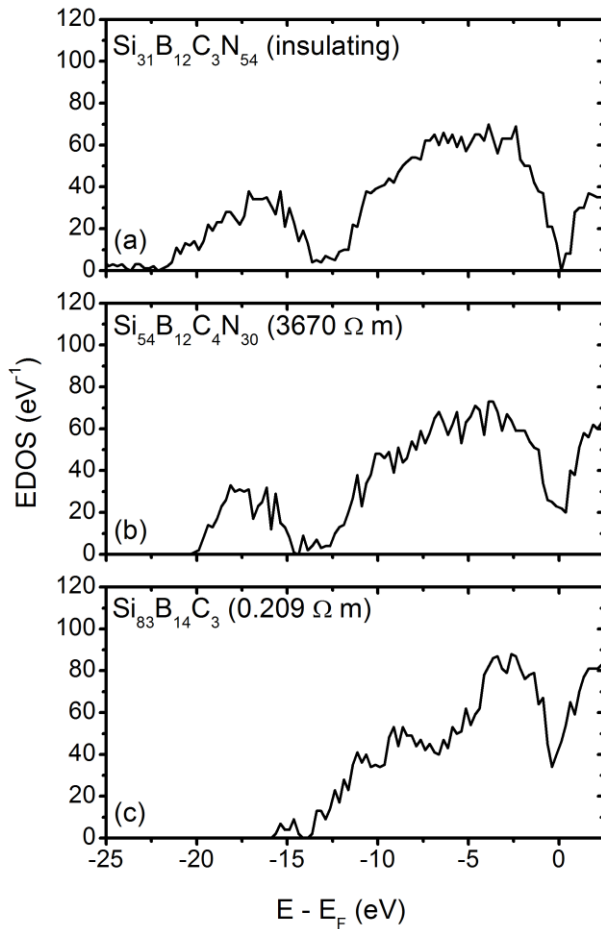
electron in this state has lower mobility



material has lower electrical conductivity (for given concentration of free charge carriers)

The importance of this is increased by frequently high IPR close to band gap edges (i.e. for states which are most responsible for the electrical conductivity, or would be it they were delocalized)

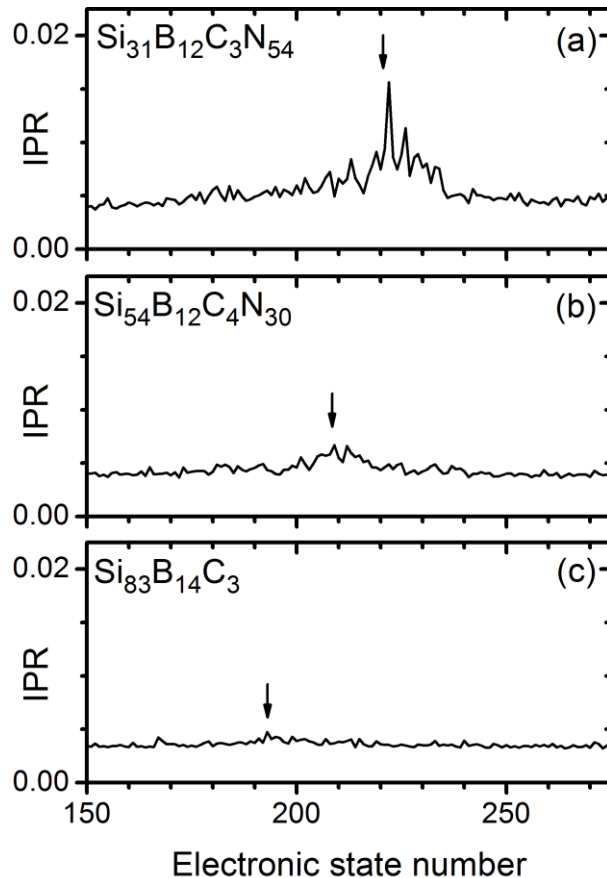
Role of how much are states localized (inverse participation ratio)



Calculated role of N in SiBCN

Decreasing N content leads to closing of band gap (around $E = E_F$), and in parallel the measured electrical resistivity decreases

Role of how much are states localized (inverse participation ratio)



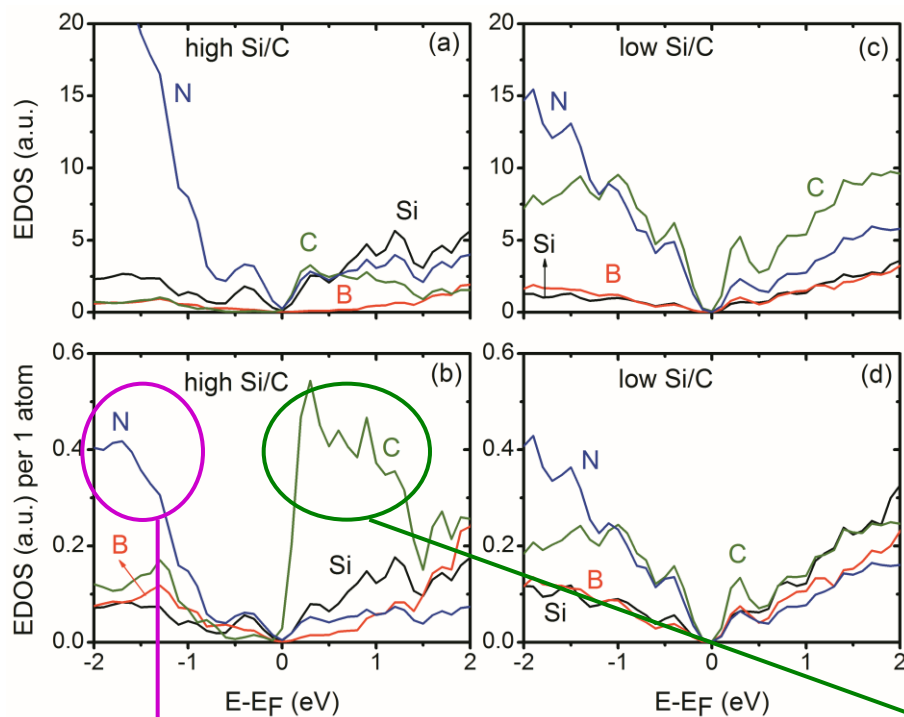
Calculated role of N in SiBCN

Decreasing N content leads to closing of band gap (arrow: Fermi level), and in parallel the measured electrical resistivity decreases

This is consistent with decreasing Inverse Participation Ratio (IPR) around the Fermi level - states are more delocalized, i.e. electronic mobility is higher

Role of where are states localized

example for amorphous $\text{Si}_{32}\text{B}_8\text{C}_6\text{N}_{54}$ and $\text{Si}_{11}\text{B}_{14}\text{C}_{39}\text{N}_{36}$



Occupied states are typically more localized on high-electronegativity elements (here N) and vice versa

Localization of states around Fermi level is most important

Sometimes it is clear (e.g. dopants in semiconductors)

Sometimes it is not that clear (amorphous materials). Figure shows that states around (above) E_F are localized on C much more than what would correspond to its content $\Rightarrow$ especially at a low C content ($\text{Si}_{32}\text{B}_8\text{C}_6\text{N}_{54}$), C has doping role

[J. Houska and S. Kos, J. Appl. Phys. 108, 083711 (2010)]

Role of where are states localized

hidden structure

Phys. Status Solidi A, 1-6 (2010) / DOI 10.1002/pssa.200982877



Hidden structure in amorphous solids

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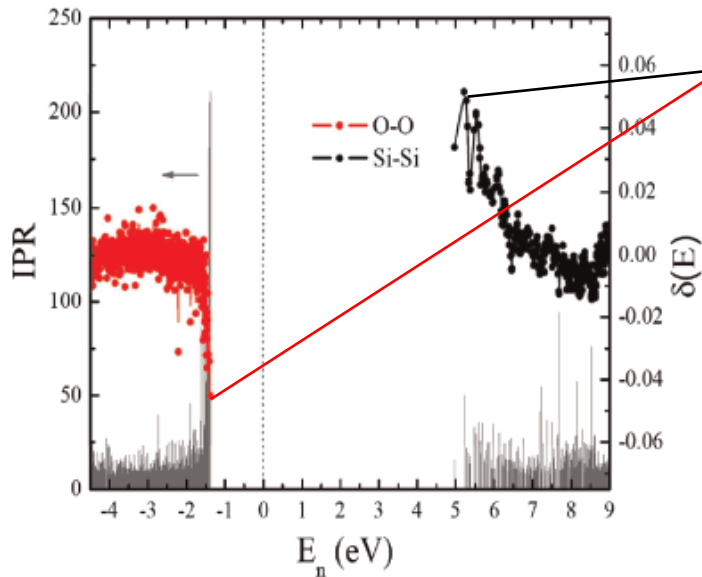
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PACS 31.15.ae, 61.43.Bn, 61.43.Dq, 71.23.Cq

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Recent theoretical studies of amorphous silicon (a-Si) [Pan et al., Phys. Rev. Lett. **100**, 206403 (2008)] have revealed subtle but significant structural correlations in network topology: the tendency for short (long) bonds to be spatially correlated with other short (long) bonds). These structures were linked to the

electronic band tails in the optical gap. In this paper, we further examine these issues for a-Si, and demonstrate that analogous correlations exist in amorphous SiO₂, and in the organic molecule, β -carotene. We conclude with a discussion of the origin of the effects and its possible generality.



Localization of states around Fermi level is most important

Even more hidden phenomena can be investigated in this context, e.g. localization

- below E_F on short bonds
- above E_F on long bonds

Different character of different orbitals

Consider cubic (rocksalt) TiC and its shear modulus

- 4. orbital is relatively directional (covalent) $\Rightarrow$ increases C_{44}
- 5. orbital is relatively non-directional (metallic) $\Rightarrow$ decreases C_{44}

The fourth orbital (orb. in fourth band) becomes fully occupied for 8.4 valence electron per primitive cell. TiC has 8 of them, TiN has 9 of them. Thus, solid solution $\text{TiC}_{0.6}\text{N}_{0.4}$ has maximum shear modulus ($\Rightarrow$ maximum hardness).

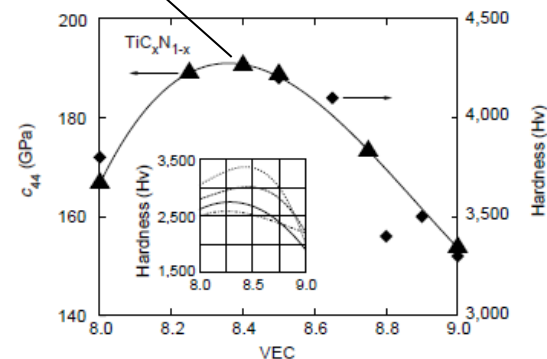
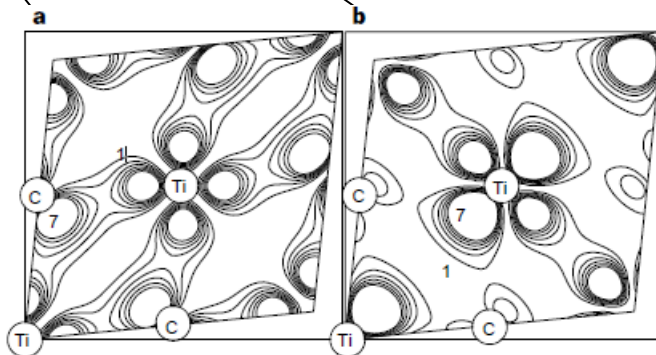
On the contrary, Cr has two extra val. el. compared to Ti $\Rightarrow$ the fourth orbital is full for both CrN and CrC $\Rightarrow$ no max. for $\text{CrC}_x\text{N}_{1-x}$.

Electronic mechanism of hardness enhancement in transition-metal carbonitrides

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7) Semiconductors

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

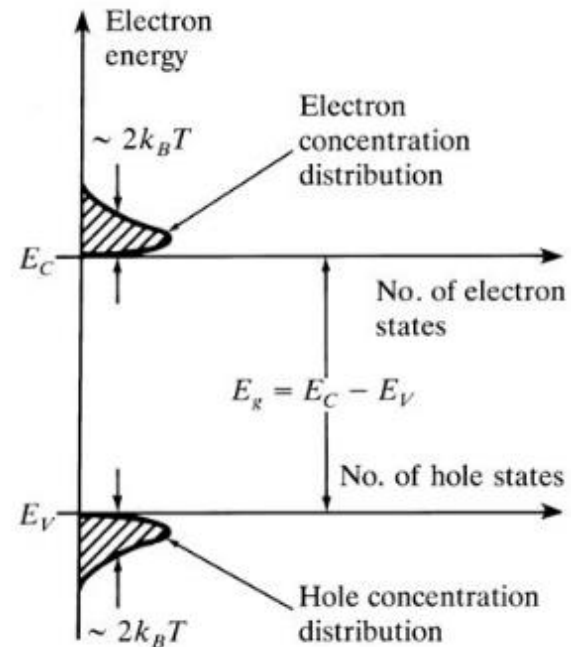
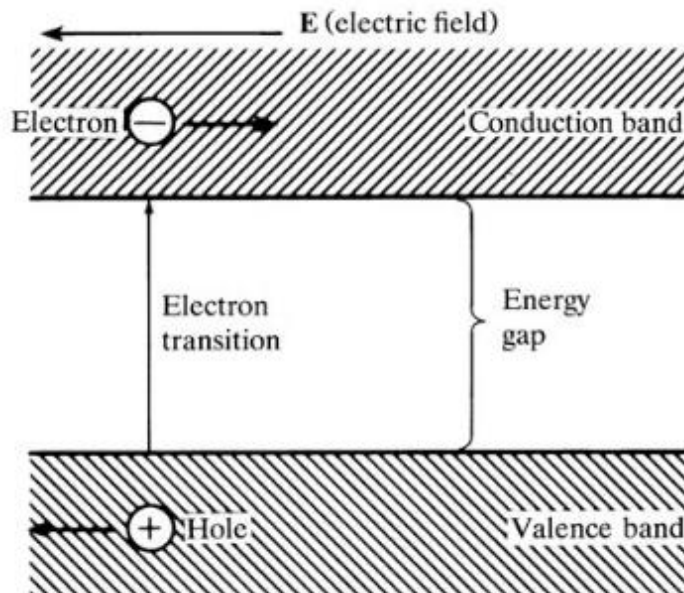
Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Semiconductors

Band gap is not zero, but sufficiently narrow to allow non-negligible excitations ($\Rightarrow$ concentrations of electrons in conduction & holes in valence band, following Fermi-Dirac)

The chapter includes related specific practical information, not included in the more general chapter 6



Semiconductors

Band gap is not zero, but sufficiently narrow to allow non-negligible excitations ($\Rightarrow$ concentrations of electrons in conduction & holes in valence band, following Fermi-Dirac)

Metals:

- el. resistivity is low (10^{-6} - $10^{-8} \Omega\text{m}$, note the Ioffe-Regel limit)
- el. resistivity (due to lattice vibrations) increases with T
- role of holes (el. with $m^* < 0$), see Hall effect, was surprising

×

Semiconductors:

- el. resistivity is higher than that of metals ($\approx 10^{-4}$ to $10^7 \Omega\text{m}$)
- el. resistivity (due to excitations) decreases with T
- roles of holes and electrons are equal
- possibility of doping

Doping

Atoms of another element (dopants or impurities depending on viewpoint) leading to new electronic states in band gap of a semiconductor can behave like

- 1) Shallow donors (of 1 electron more, e.g. P in Si):
new states just below ($<3k_B T = 78 \text{ meV}$) the upper band gap edge $\Rightarrow$ easy excitation to conduction band where free electrons appear, E_F moves up
- 2) Shallow acceptors (of 1 electron less, e.g. B in Si):
new states just above ($<3k_B T = 78 \text{ meV}$) the bottom band gap edge $\Rightarrow$ easy excitation from valence band where "free" holes appear, E_F moves down
- 3) Double donors / acceptors (of 2 electrons more / less)

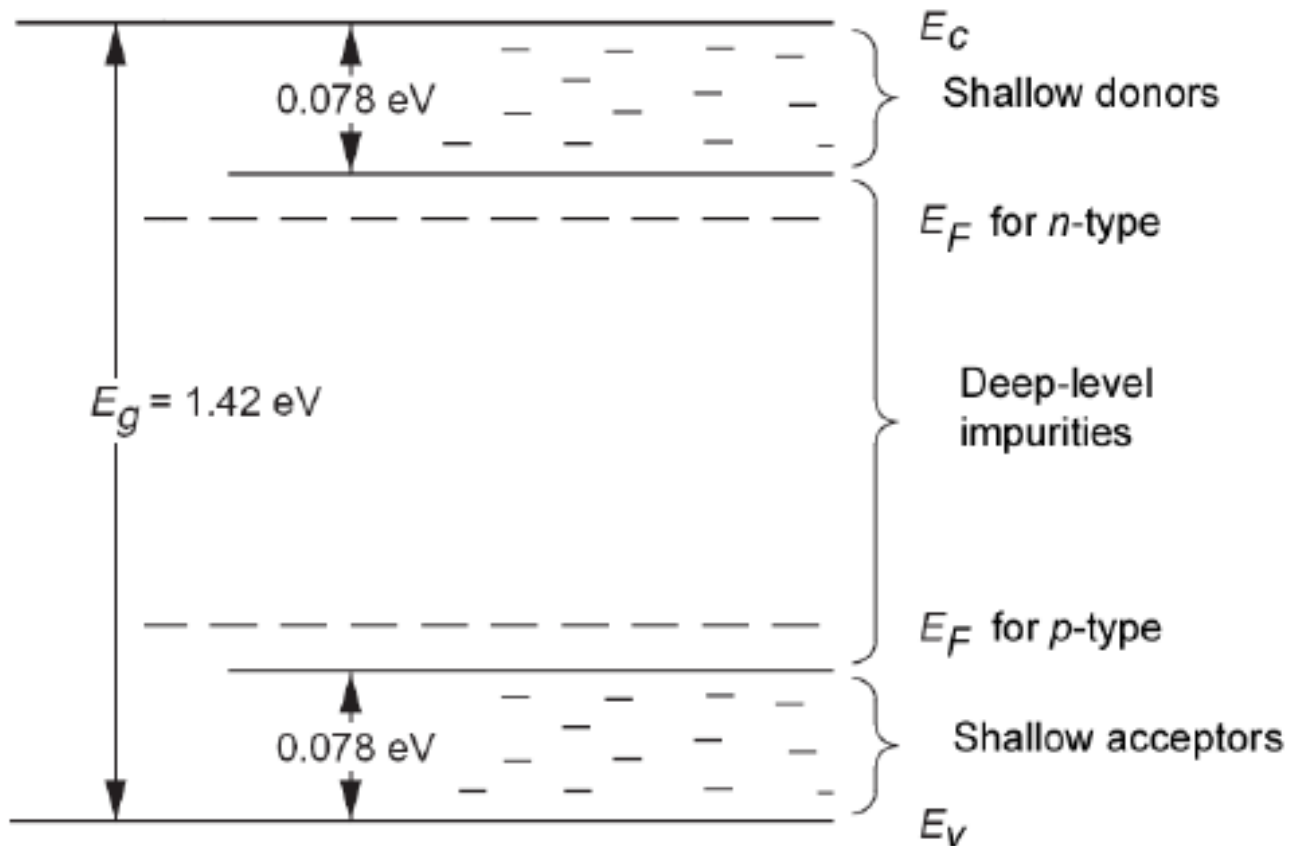
Doping

Atoms of another element (dopants or impurities depending on viewpoint) leading to new electronic states in band gap of a semiconductor can behave like

- 4) Deep-level impurities (e.g. metal atoms):
new states close to the middle of band gap.
Harmful from the conductivity point of view: do not bring free charge carriers anyway, and on the contrary act as recombination centers. Also called deep traps (electron / hole trap just above / below the middle of band gap).

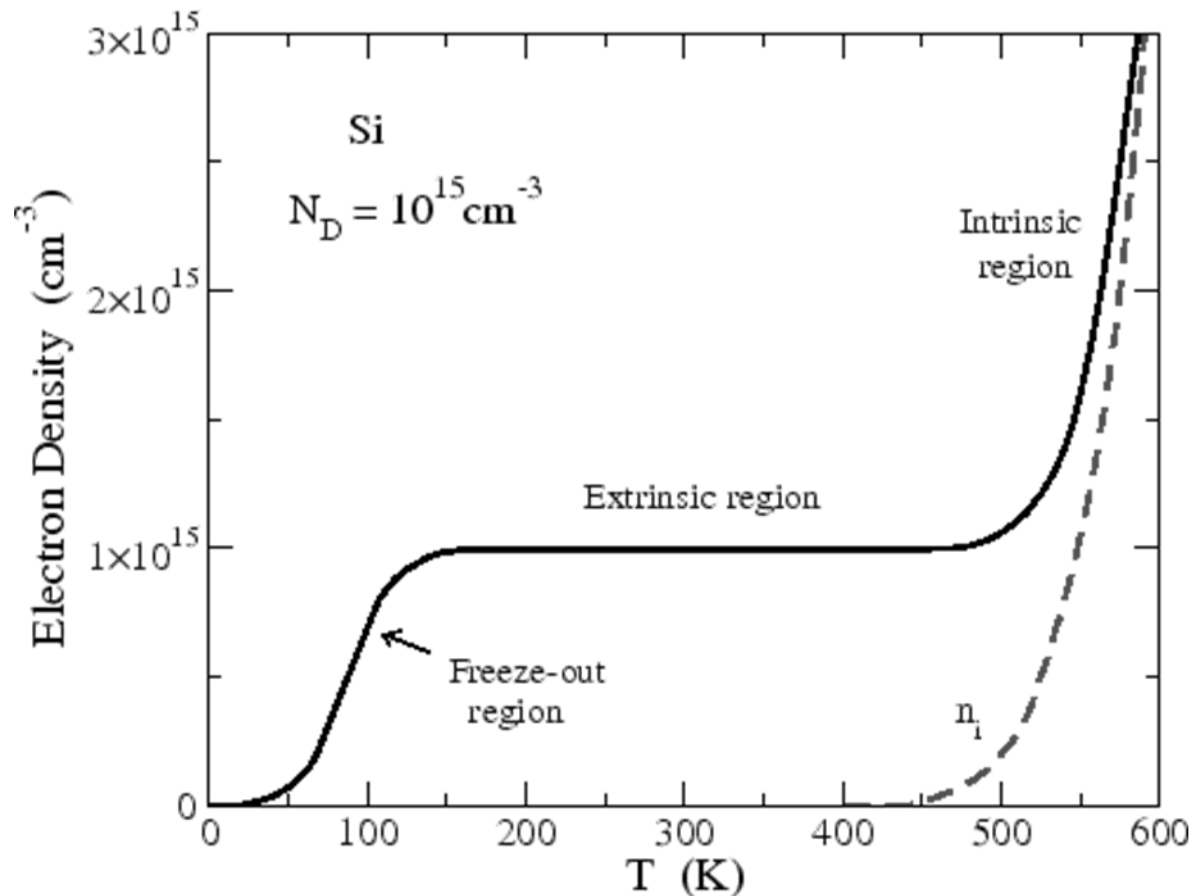
Doping

The same in a graphical form ($E_g = 1.42$ eV is valid for GaAs)



Doping

States localized on dopants are close to the band gap edge, so the temperature needed to ionize all dopants is much lower than that needed for excitation over whole band gap



Effective mass of charge carriers

Reminder

$$v = q\tau/m^*.E = \pm\mu.E$$

(frequent mistake $q\tau/2m^*.E$ discussed above)

and $j = nqv = nq^2\tau/m^*.E = \sigma.E = 1/\rho.E$

Where is the effective mass coming from
($\Leftrightarrow$ why does it differ from the el. mass)?

Why is effective mass of holes typically
higher than that of electrons (see the table)?

Group	Material	Electron	Hole
IV	Si (4K)	1.06	0.59
	Si (300K)	1.09	1.15
	Ge	0.55	0.37
III-V	GaAs	0.067	0.45
	InSb	0.013	0.6
II-VI	ZnO	0.29	1.21
	ZnSe	0.17	1.44

Effective mass of charge carriers

Where is the effective mass coming from?

- 2nd Newton law in macroworld: $a = dv/dt = F/m$
- 2nd Newton law or movement of electron in crystal
(substitute group velocity of corresponding wave for velocity):

$$a = dv_g/dt = d/dt [d\omega(k)/dk] = dk/dt [d^2\omega(k)/dk^2]$$

and in parallel

$$F = dp/dt = \hbar dk/dt \quad (\text{because } p = \hbar k)$$

↓

$$a = F/\hbar \cdot [d^2\omega(k)/dk^2] = F/\hbar^2 \cdot [d^2E(k)/dk^2] \quad (\text{because } E = \hbar\omega)$$

↓ (compare to $a = F/m$, and adapt for 3D)

$$1/m^* = 1/\hbar^2 \cdot \partial^2 E / \partial k_i \partial k_j$$

Effective mass of charge carriers

Where is the effective mass coming from? (another approach)

- free electron: relation between E and k is exactly parabolic:

$$E = mv^2/2 = p^2/2m = \hbar^2 \cdot k^2/2m$$

⇓

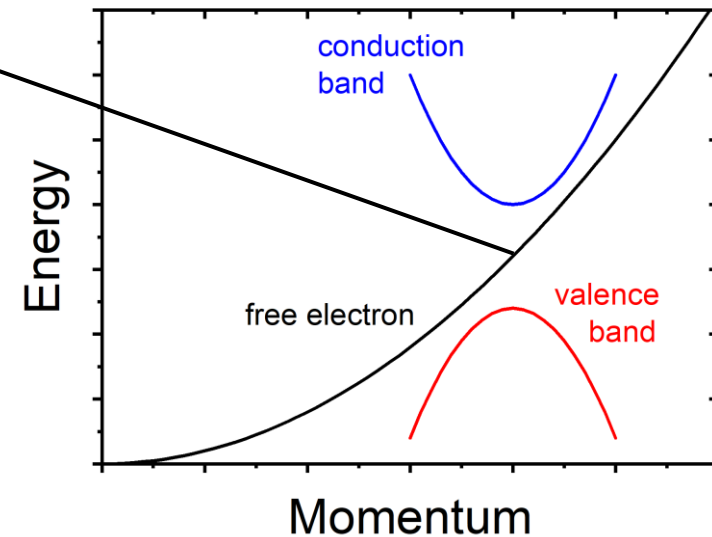
$$1/m = 1/\hbar^2 \cdot d^2E/dk^2$$

- electron in crystal: bottom of cond. (holes: top of valence) band is also approximated by parabola

$$E = E_0 + \hbar^2 \cdot k^2/2m^*$$

⇓ again

$$1/m^* = 1/\hbar^2 \cdot d^2E/dk^2 = (3D) \mathbf{1/\hbar^2 \cdot \partial^2 E / \partial k_i \partial k_j}$$



Effective mass of charge carriers

Reminder $v = q\tau/m^*.E = \pm\mu.E$

and $j = nqv = nq^2\tau/m^*.E = \sigma.E = 1/\rho.E$

Where is the effective mass coming from?

Why is effective mass of holes typically higher than that of electrons (see the table)?

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- **free electron** : law of motion (crucial for conduction; 2 slides above) as well as the relationship between energy of el. state and momentum (less crucial here; 1 slide above) contain $1/m$
- **electron in crystal** : these relationships contain $1/\hbar^2 \cdot \partial^2 E / \partial k_i \partial k_j$



effective mass is a mathematical construction,
allowing us to replace this term by a familiar letter:

$$1/m^* = 1/\hbar^2 \cdot \partial^2 E / \partial k_i \partial k_j$$

Effective mass of charge carriers

Reminder $v = q\tau/m^*.E = \pm\mu.E$

and $j = nqv = nq^2\tau/m^*.E = \sigma.E = 1/\rho.E$

Where is the effective mass coming from?

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$$1/m^* = 1/\hbar^2 \cdot \partial^2 E / \partial k_i \partial k_j$$

- mass of electron is given by curvature of conduction band
- mass of holes is given by curvature of valence band

Conduction band is usually more curved (especially for narrow band gaps) $\Rightarrow$ effective mass of electron is lower

Effective mass of charge carriers

$$1/m^* = 1/\hbar^2 \cdot \partial^2 E / \partial k_i \partial k_j$$

- mass of electron is given by curvature of conduction band
- mass of holes is given by curvature of valence band

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Conduction band is usually more curved (especially for narrow band gaps) $\Rightarrow$ effective mass of electron is lower

Or from another point of view:

- easy movement of an electron in a conduction band $\Rightarrow$ low m^*
- demanding collective movement of all electrons except the missing one ($\Leftrightarrow$ hole movement) in valence band $\Rightarrow$ high m^*

More precisely, there is a tensor $1/m_{i,j}^*$ (this does not mean that $m_{i,j}^*$ is also a tensor). $\mathbf{F}$ and $\mathbf{a}$ do not have to be parallel.

Sign of effective mass

$$1/m^* = 1/\hbar^2 \cdot \partial^2 E / \partial k_i \partial k_j$$

Electron at the bottom of (e.g. conduction) band $m^* > 0$

Electron in an inflection point $m^* \rightarrow \infty$
(interference of transverse and reflected wave)

Electron at the top of (e.g. valence) band $m^* < 0$
(reflected wave dominates)

Hole at the top of band which replaced it $m^* > 0$

Elsewhere: different directions (aforementioned tensor $1/m^*_{i,j}$)
can correspond to different signs, not only different values

Effective mass of charge carriers

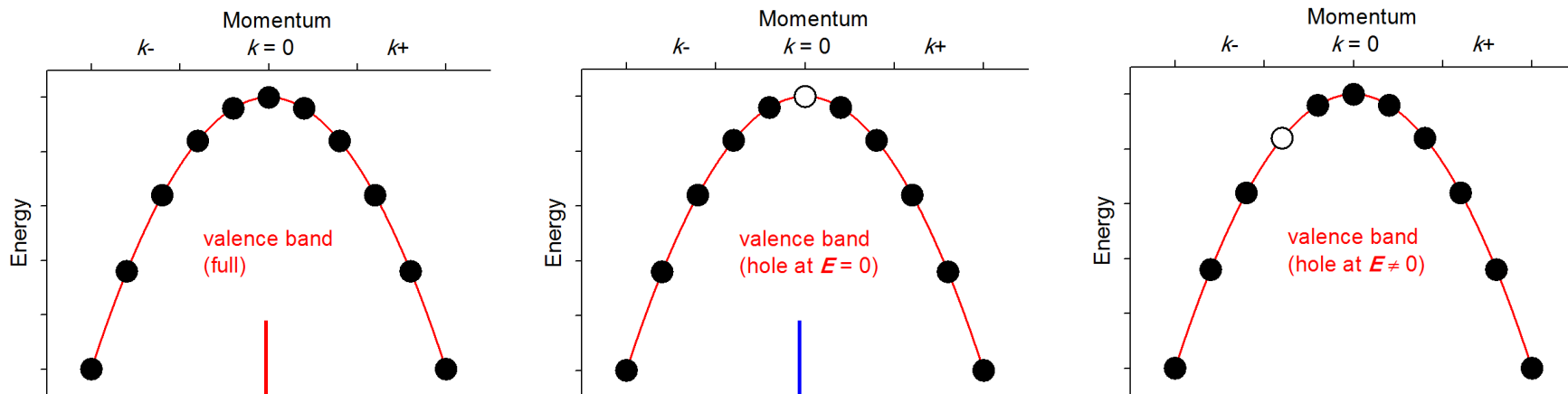
$$1/m^* = 1/\hbar^2 \cdot \partial^2 E / \partial k_i \partial k_j$$

The idea of holes (electrons with $m^* < 0$):

- works as long as we explain the effect of outer electromagnetic field (the inner field caused by particles of the matter is included in m^*)
- stops working when we explain experiments which include inertial forces (Stewart-Tolman effect: accelerated conductor) or gravitational forces



Dynamics of holes in valence band

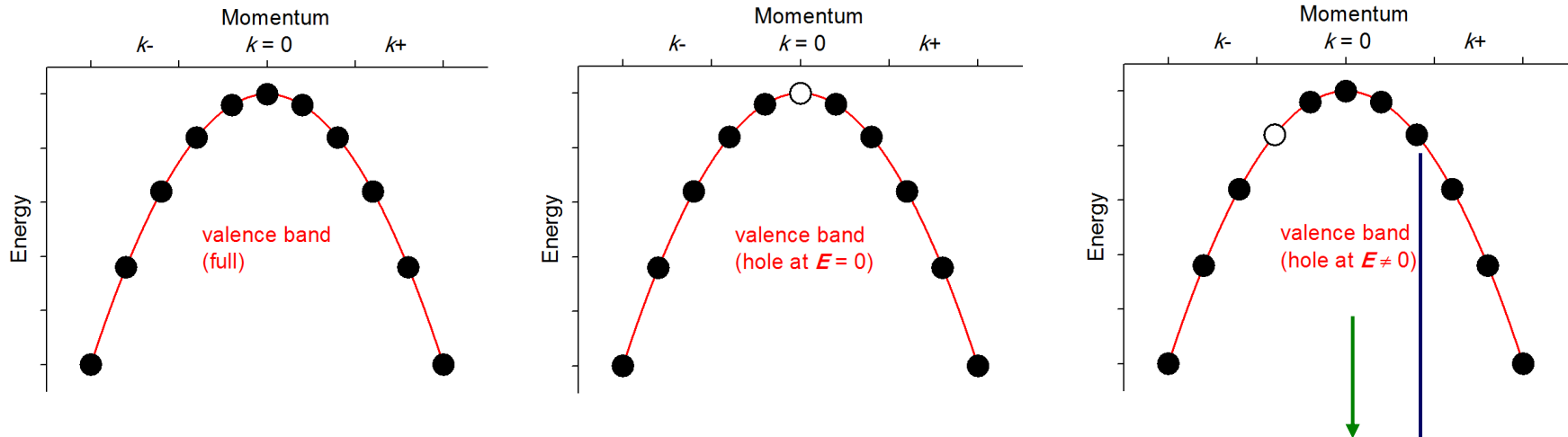


for simplicity symmetrical band with the top at $k = 0$

In a full band, the total $\Sigma k = 0$

At no electric field, the hole is at the top and still $\Sigma k = 0$

Dynamics of holes in valence band



Electrical field breaks symmetry $\Rightarrow \Sigma k \neq 0 \Rightarrow$ el. conduction.
The hole has the same velocity as missing electron (opposite signs of charge and mass cancel out in the eq. of motion).

The hole has opposite momentum than the missing electron (figure shows the momentum of the electron, not of the hole).

The current is in fact conducted by the unpaired electron (opposite signs of charge and velocity cancel out).

Concentration of electrons and holes

Metals (chapter 5):

single parabolic band

$$D(\varepsilon) = 1/2\pi^2 \cdot (2m^*/\hbar^2)^{3/2} \cdot \sqrt{\varepsilon}$$

Semiconductors:

parabolic valence band

$$D(E) = 1/2\pi^2 \cdot (2m^*/\hbar^2)^{3/2} \cdot \sqrt{(E_V - E)}$$

parabolic conduction band

$$D(E) = 1/2\pi^2 \cdot (2m^*/\hbar^2)^{3/2} \cdot \sqrt{(E - E_C)}$$

Concentration of electrons and holes

By integration of the product of

- (i) density of states in valence band (from $-\infty$ to E_V)
see chapter 5: $D(E) = 1/2\pi^2 \cdot (2m^*/\hbar^2)^{3/2} \cdot \sqrt{(E_V - E)}$, and
- (ii) occupation of states, where we for $k_B T \ll E - E_F$ approximate the Fermi-Dirac distribution by Boltzmann distr.: $e^{-(E - E_F)/k_B T}$

we can estimate density of holes

$$p = N_{eff}^V e^{\frac{(E_V - E_F)}{kT}} \quad \text{where} \quad N_{eff}^V = 2 \left[\frac{2\pi m_p^* kT}{h^2} \right]^{3/2}$$

Concentration of electrons and holes

By integration of the product of

- (i) density of states in valence band (from $-\infty$ to E_V) and
- (ii) occupation of states

we can estimate density of holes

$$p = N_{eff}^V e^{\frac{(E_V - E_F)}{kT}} \quad \text{where} \quad N_{eff}^V = 2 \left[\frac{2\pi m_p^* kT}{h^2} \right]^{3/2}$$

Similarly by integration of the product of

- (i) density of states in conduction band (from E_C to ∞) and
- (ii) occupation of states

we can estimate density of conduction electrons

$$n = N_{eff}^C e^{\frac{-(E_C - E_F)}{kT}} \quad \text{where} \quad N_{eff}^C = 2 \left[\frac{2\pi m_n^* kT}{h^2} \right]^{3/2}$$

Concentration of electrons and holes

$$p = N_{eff}^V e^{\frac{(E_V - E_F)}{kT}} \quad N_{eff}^V = 2 \left[\frac{2\pi m_p^* kT}{h^2} \right]^{3/2}$$
$$n = N_{eff}^C e^{\frac{-(E_C - E_F)}{kT}} \quad N_{eff}^C = 2 \left[\frac{2\pi m_n^* kT}{h^2} \right]^{3/2}$$

Product of both concentrations

$$np = N_{eff}^C e^{\frac{-(E_C - E_F)}{kT}} N_{eff}^V e^{\frac{(E_V - E_F)}{kT}} = N_{eff}^C N_{eff}^V e^{\frac{E_V - E_C}{kT}}$$

is independent of E_F . Thus, by doping (shifting of E_F) we change n , p and $n+p$, but not np .

This **mass action law** (usually given as $np = n_i^2$), and the resulting **concentration of minority charge carriers**, is important for construction / description of function of electronic components (e.g. description of function of solar cells below)

Koncentrace elektronů a děr

$$p = N_{eff}^V e^{\frac{(E_V - E_F)}{kT}} \quad N_{eff}^V = 2 \left[\frac{2\pi m_p^* kT}{h^2} \right]^{3/2}$$
$$n = N_{eff}^C e^{\frac{-(E_C - E_F)}{kT}} \quad N_{eff}^C = 2 \left[\frac{2\pi m_n^* kT}{h^2} \right]^{3/2}$$
$$np = N_{eff}^C e^{\frac{-(E_C - E_F)}{kT}} N_{eff}^V e^{\frac{(E_V - E_F)}{kT}} = N_{eff}^C N_{eff}^V e^{\frac{E_V - E_C}{kT}}$$

The fact that np is at a given T constant (but not the constant itself) results also from the assumption that the creation rate is independent of concentrations, while the recombination rate is proportional to the product of concentrations.

In stationary state

$$dn/dt = dp/dt = \text{creation} - \text{recombination} = A(T) - B(T).np = 0$$

$$\Rightarrow np = A(T)/B(T) = \text{const}(T)$$

Concentration of electrons and holes

$$p = N_{eff}^V e^{\frac{(E_V - E_F)}{kT}} \quad N_{eff}^V = 2 \left[\frac{2\pi m_p^* kT}{h^2} \right]^{3/2}$$

$$n = N_{eff}^C e^{\frac{-(E_C - E_F)}{kT}} \quad N_{eff}^C = 2 \left[\frac{2\pi m_n^* kT}{h^2} \right]^{3/2}$$

Furthermore, for undoped semiconductor

$$n = p = 2 \left[\frac{2\pi m_n^* kT}{h^2} \right]^{3/2} e^{\frac{-(E_C - E_F)}{kT}} = 2 \left[\frac{2\pi m_p^* kT}{h^2} \right]^{3/2} e^{\frac{(E_V - E_F)}{kT}}$$

$$\Rightarrow E_F = \frac{E_C + E_V}{2} + \frac{3}{4} kT \ln \left(\frac{m_p^*}{m_n^*} \right)$$

Clarification of the information from chapter 6 about Fermi level in the middle of band gap (almost valid for low temperatures)

PN junction

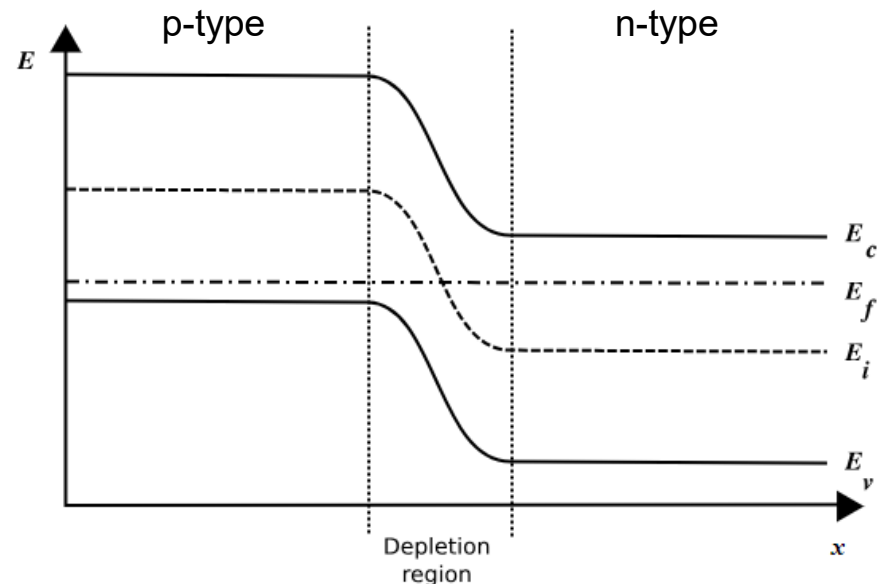
- p-doped semicond. has E_F close to the bottom of band gap
- n-doped semicond. has E_F close to the top of band gap
- in a stationary state there is only one E_F ,
i.e. the Fermi energies have to level at the junction



band gaps (whole electronic structures) of both semicond. shift with respect to each other, leading to a voltage difference ΔV

ΔV motivates

- electrons to drift from 'p' to 'n'
 - holes to drift from 'n' to 'p'
- i.e. motivates minority carriers to drift across the junction, for majority charge carriers the junction constitutes a barrier



PN junction

Another argument leading to the same conclusion:

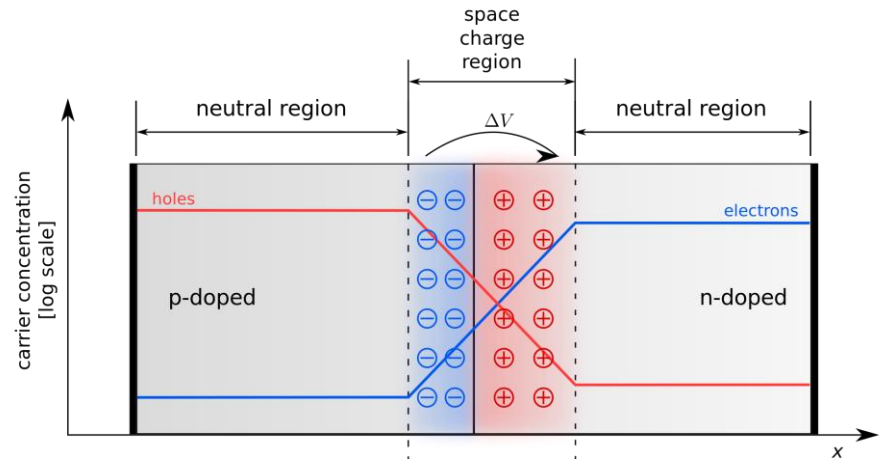
at a junction of p- and n-doped semiconductor, diffusion of majority charge carriers leads to their recombination



only immobile ions (of the same sign which have majority charge carriers in the other semiconductor) remain there



majority charge carriers from the other semiconductor are repulsed by these ions, i.e. the junction is impassable for them

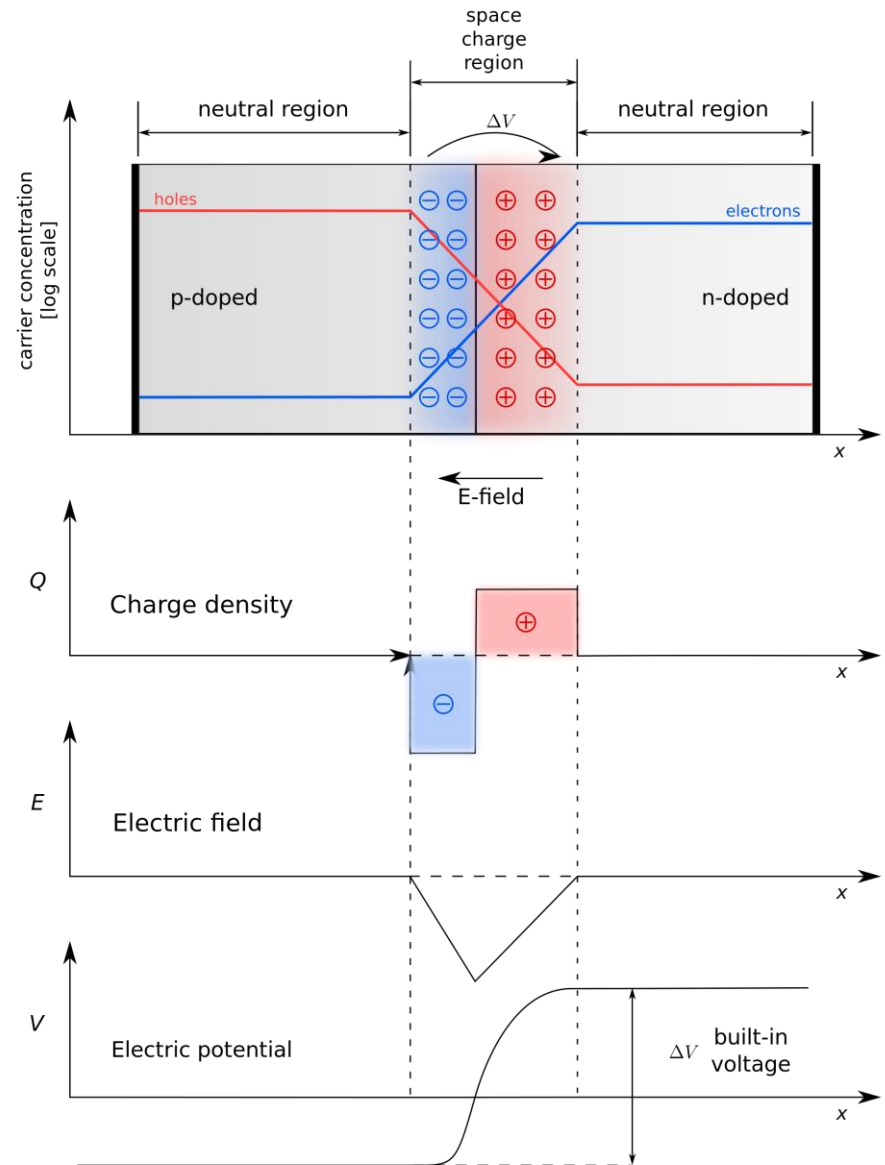


PN junction

Another argument leading to the same conclusion:

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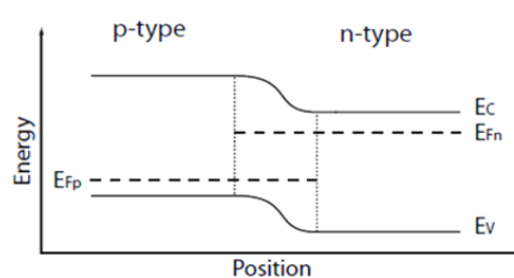
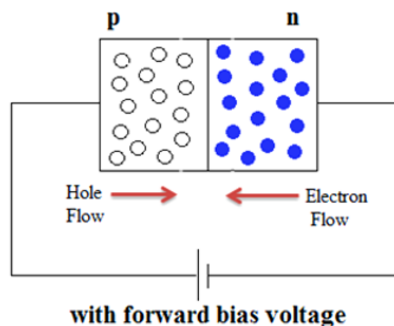
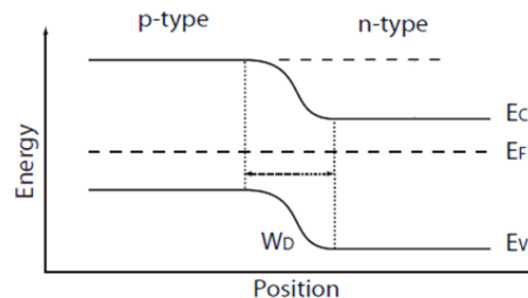
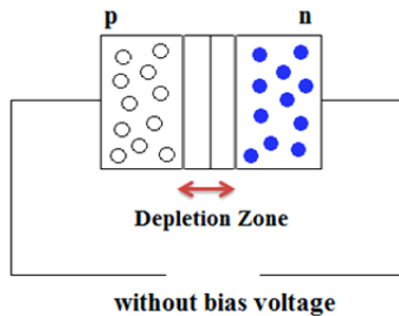
the same in graphical form (do not confuse energy E and electric field intensity E)



PN diode

In an electrical circuit the total barrier for majority charge carriers is sum of the original barrier ΔV and the voltage

'+' on 'p' (forward bias): orientation which decreases the resulting barrier, voltage $-\Delta V$ (tenths of volt) are sufficient for disappearing the barrier and dramatic drop of the resistance

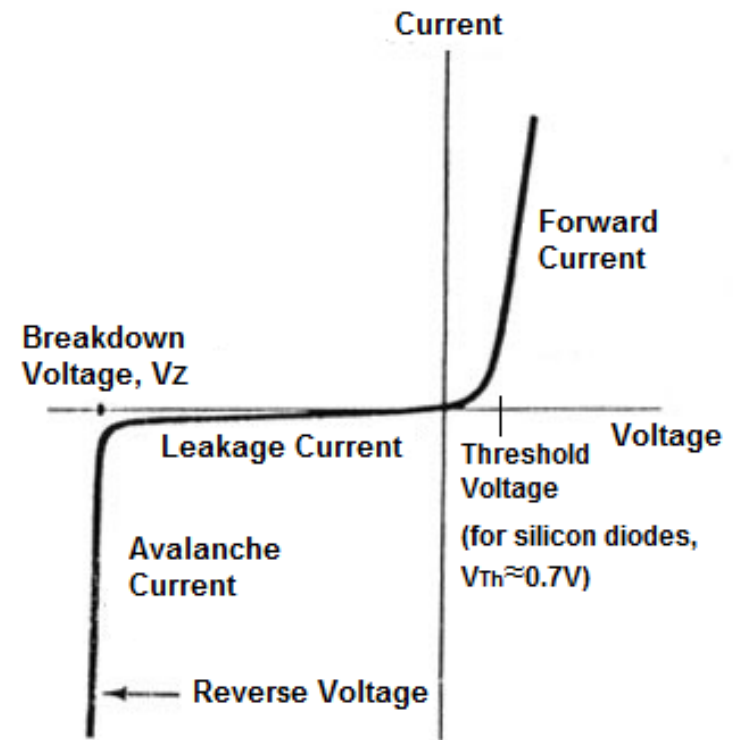


PN diode

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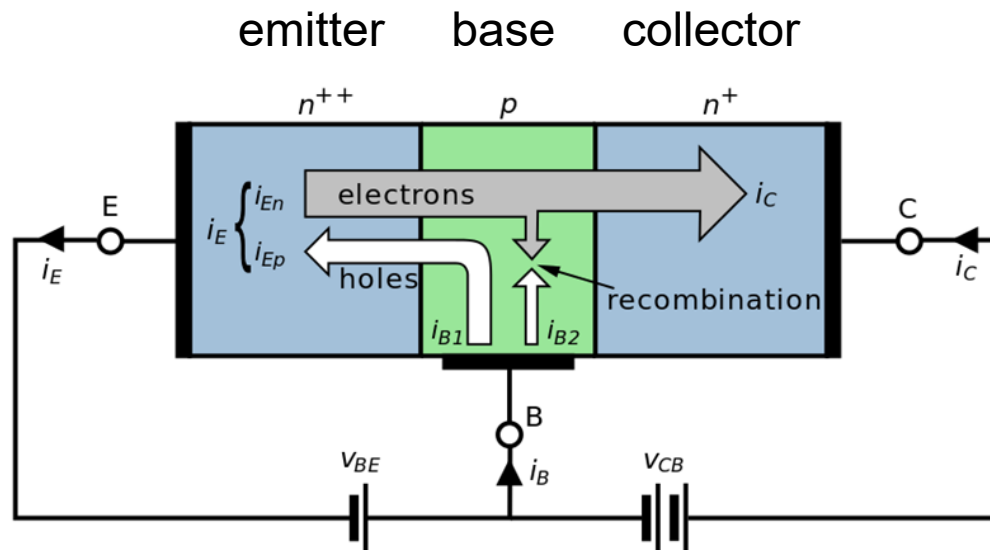
'-' on 'p' (reverse bias): orientation which yet increases the resulting barrier, up to a breakthrough voltage (tens volts) there is only a small current due to minority charge carriers



NPN transistor

PN junction between emitter and base is in forward direction. Thus, low voltage V_{BE} makes it passable, and many majority charge carriers (emitter is heavily doped) make it into base.

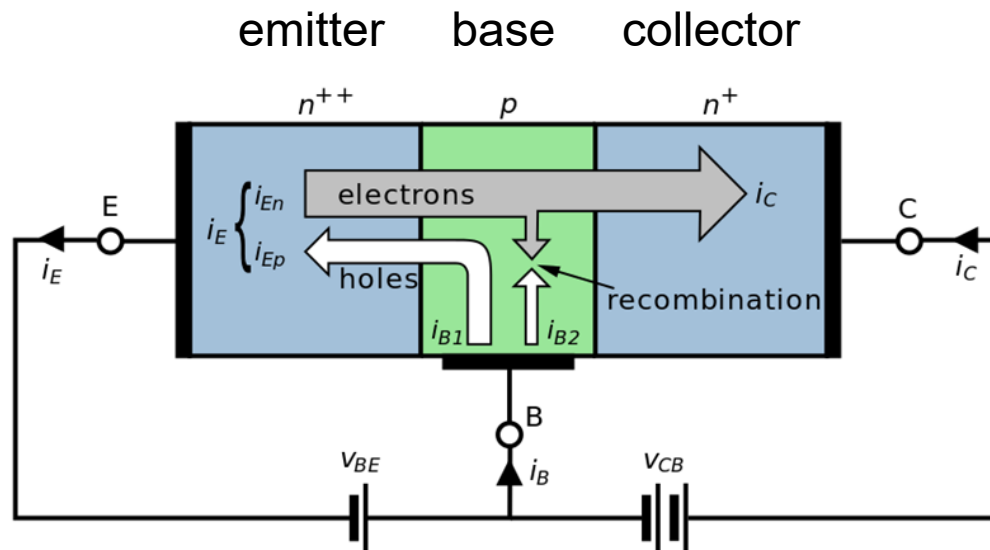
These guys are minority carriers in the base. But only few of them recombine, because (i) the base is less doped, and (ii) the base is thin, i.e. they manage to diffuse through it.



NPN transistor

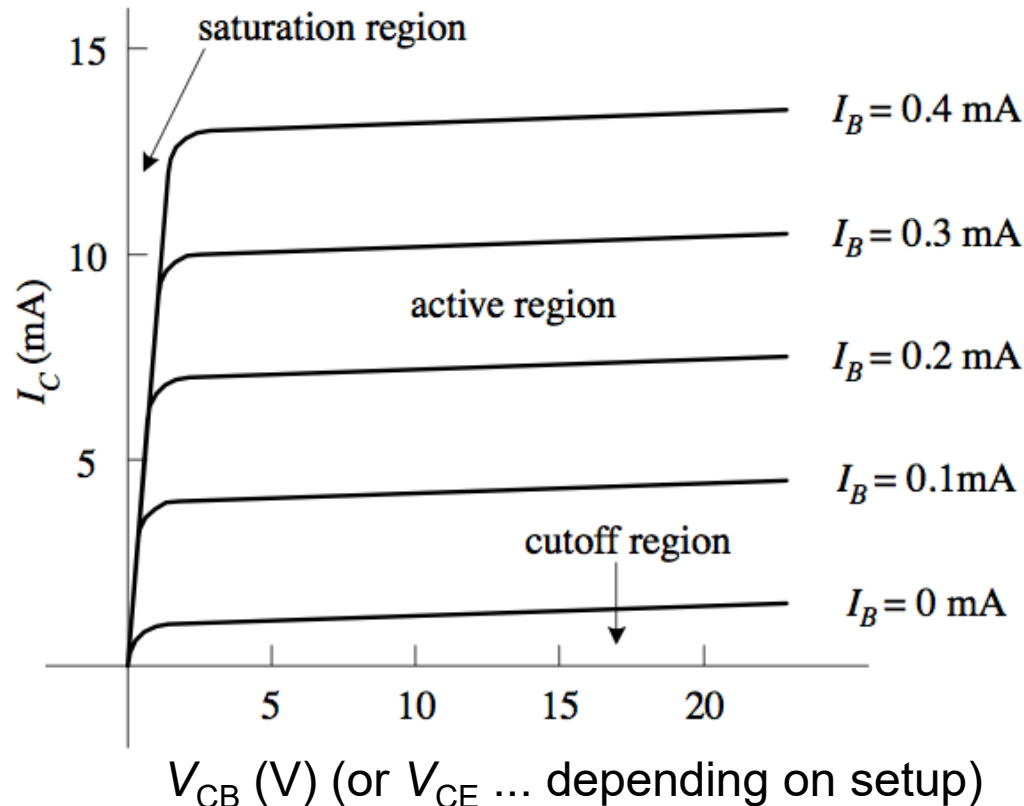
PN between base and collector is in reverse direction, i.e. it is passable for those charge carriers which are minority in the basis, but in high numbers got there from the emitter and managed to diffuse through it before they recombined

Thus, low current i_B allows much higher current i_C (amplification $\approx 100\times$). NP 1958 (Bardeen, Brattain, Shockley).



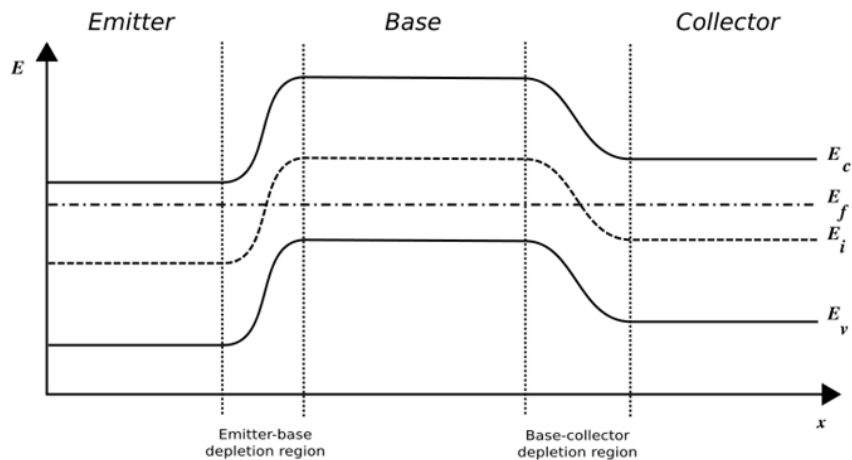
NPN transistor

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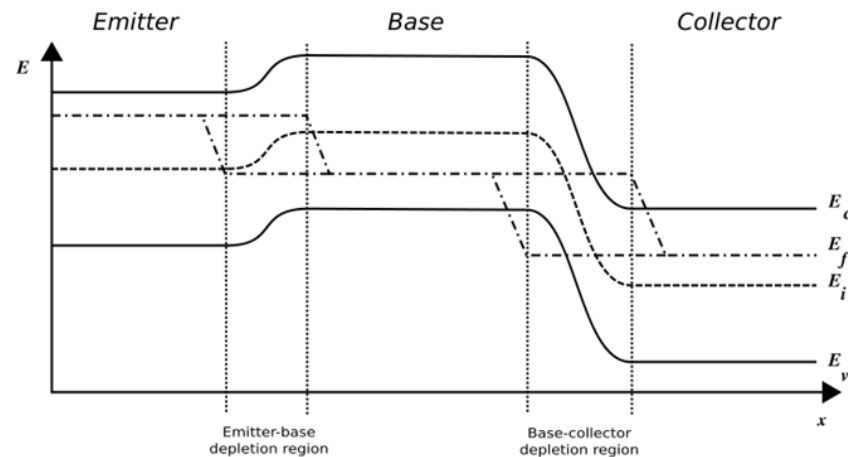


NPN transistor

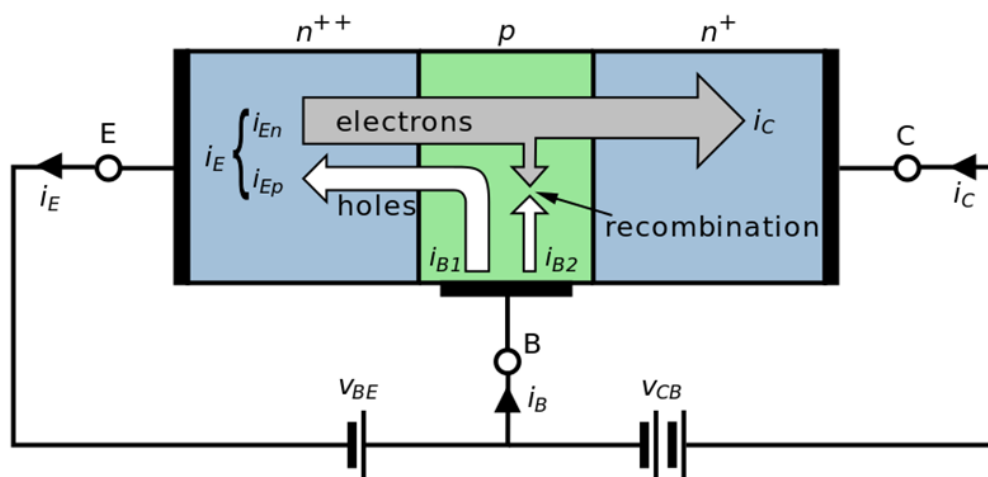
without voltage



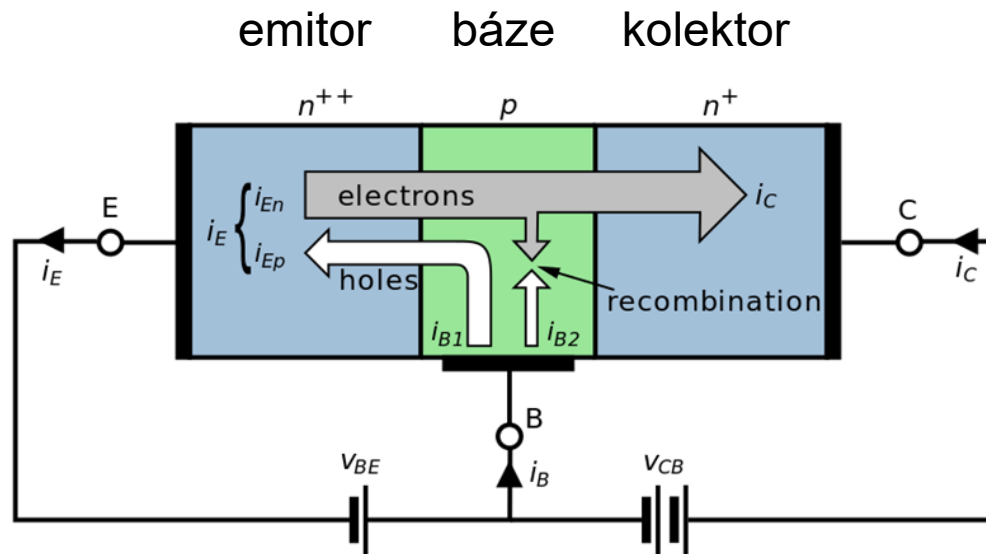
with voltage



emitter base collector



NPN transistor



This allowed the company **Tokyo Tsushin Kogyo Kabushiki Kisha**

... to produce the first transistor radios, and to improved the worldwide pronounceability of its name to **Sony**

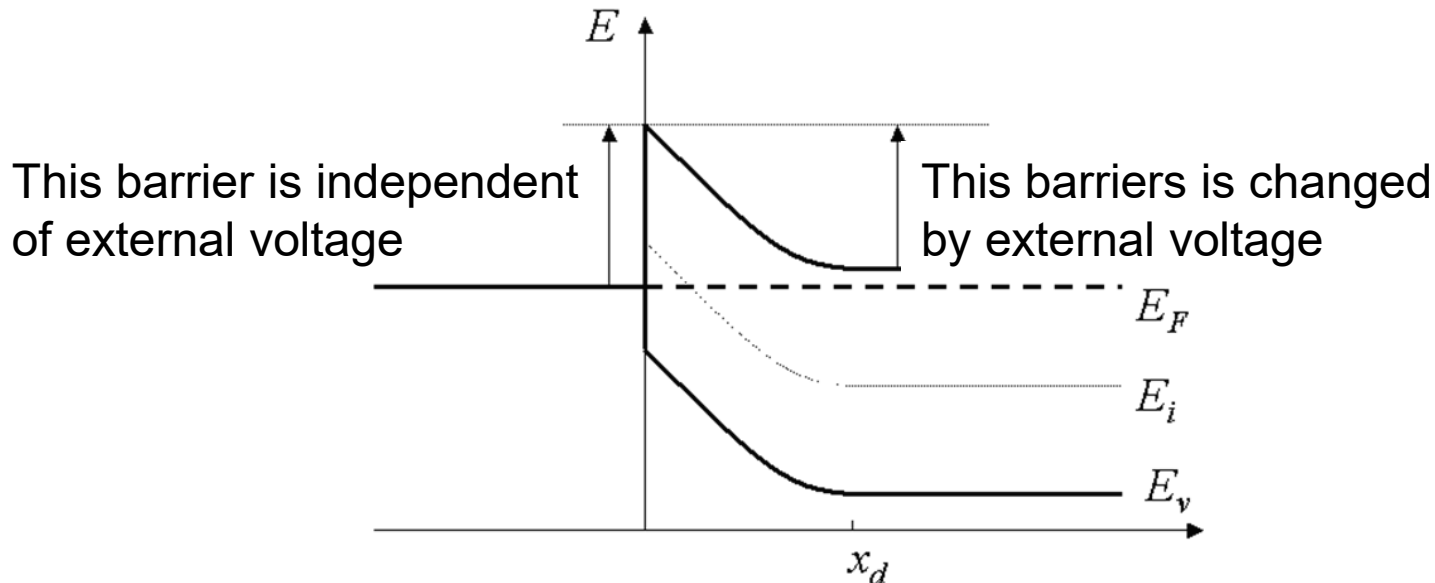


Schottky junction

Not P+N but metal+N (or metal+P)

What is the same as for PN: only one value of E_F , zone without free charge carriers close to the junction, band structure curves and forms a barrier, the barrier can be suppressed by voltage in the forward direction (for metal+N: '-' on N)

The difference is that there is no role of free charge carriers



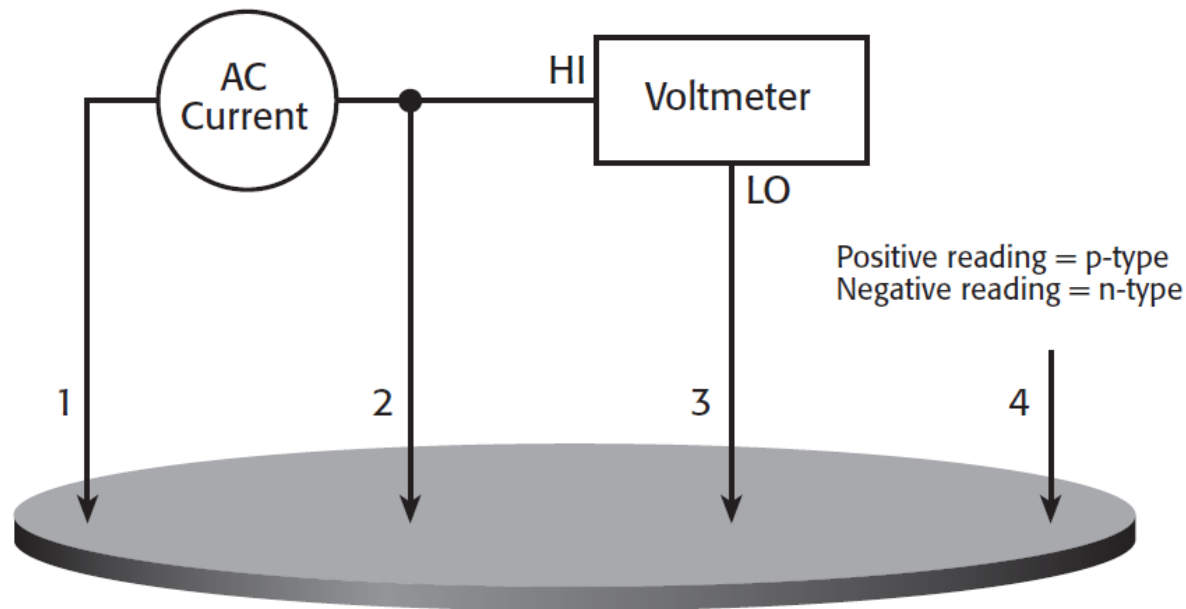
How to measure the type of cond.

Resistivity can be measured by four-point technique. How to find the type of conductivity ($p \times n$) using the same hardware?

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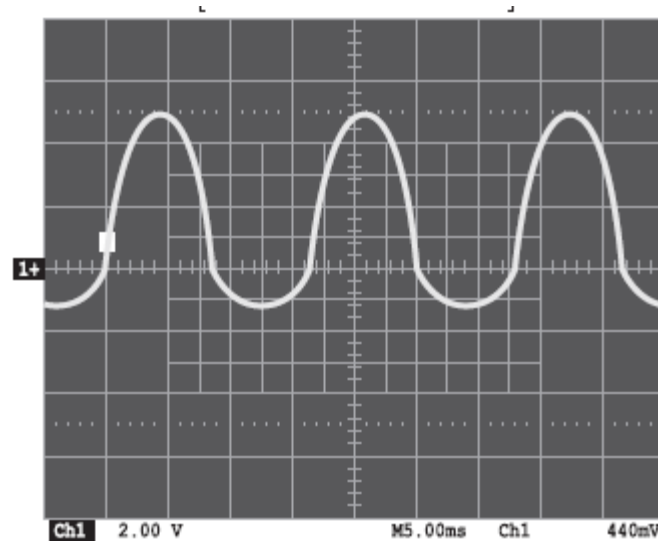
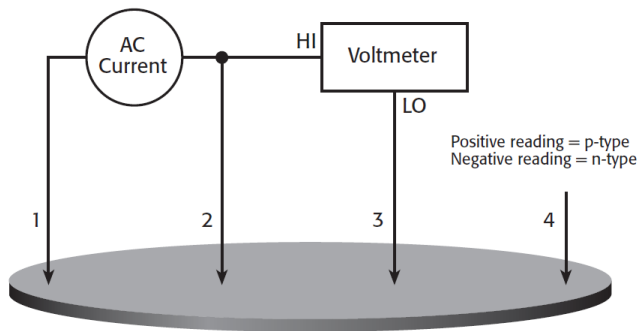
1st option (for low concentrations of charge carriers)
utilize Schottky junction between semiconductor and metal tip



How to measure the type of cond.

Resistivity can be measured by four-point technique. How to find the type of conductivity ($p \times n$) using the same hardware?

1st option (for low concentrations of charge carriers)
utilize Schottky junction between semiconductor and metal tip



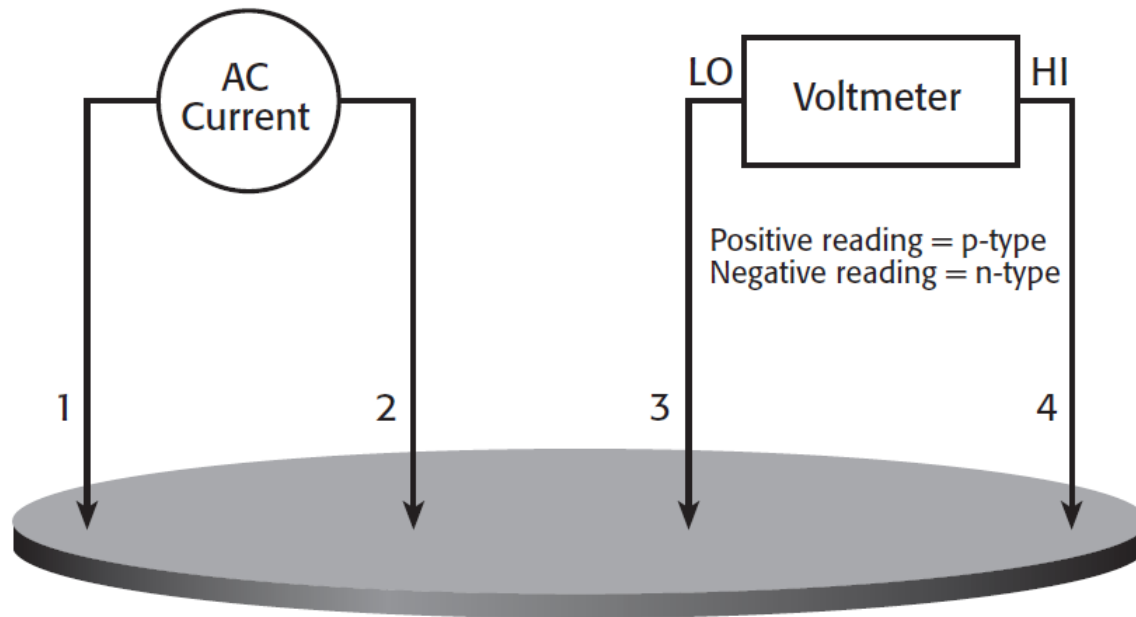
output of oscilloscope (prone to be averaged by a dc voltmeter) for p-type
[Keithley application note]

How to measure the type of cond.

Resistivity can be measured by four-point technique. How to find the type of conductivity ($p \times n$) using the same hardware?

2nd option (for high concentrations of charge carriers)

Utilize thermoelectric effect (majority charge carrier concentrate in colder area, details in chapter 12)



Transparent conductive oxides

	conductive	insulating
transparent	last case not discussed yet: TCOs	clear (high E_g)
opaque	clear (low / zero E_g)	see above (some molecular solids)

Transparent conductive oxides

Transparency due to a sufficiently wide band gap (that's why oxides). E.g. ZnO has E_g around 3.5 eV, In_2O_3 around 3.7 eV $\Rightarrow$ includes visible spectrum 1.5-3 eV, and is not unnecessarily wide (which would complicate effective doping).

Electrical conductivity due to non-zero concentration of free charge carriers, which can be caused by

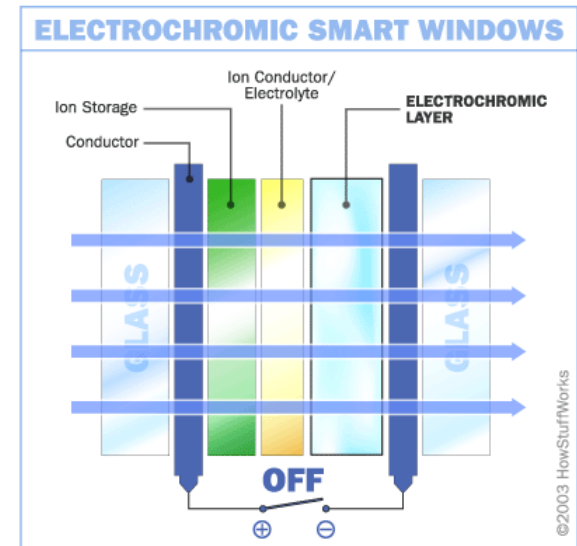
- doping by another element (ZnO:Al , $\text{In}_2\text{O}_3\text{:Sn}$, etc.) - like that of Si (but Si is opaque due to its narrow band gap of 1.1 eV)
- slightly understoichiometric composition (sometimes supported by hydrogen content) - the "dopant" are oxygen vacancies (or interstitial metal atoms)

Typical resistivity (at sufficient transparency) 10^{-3} - $10^{-4} \Omega\text{cm}$ (of 2 orders worse than conductors like Cu, but often sufficient)

Transparent conductive oxides

Utilization (examples)

- touch panels
- LEDs
- solar cells - producing energy (charge) is not enough, we must also conduct it away, and without shadowing the cell itself
- electrochromic windows (described above; figure here)
- etc. ... basically where we need a transparent electrode



Transparent conductive oxides

Brief reminder from chapter 6: contribution of free charge carriers to the total permittivity is

$$\epsilon_{\text{Drude}} = -\hbar^2 \sigma_{\text{dc}} / \epsilon_0 \cdot [(\tau E^2 - i\hbar E) / (\tau^2 E^4 + \hbar^2 E^2)]$$

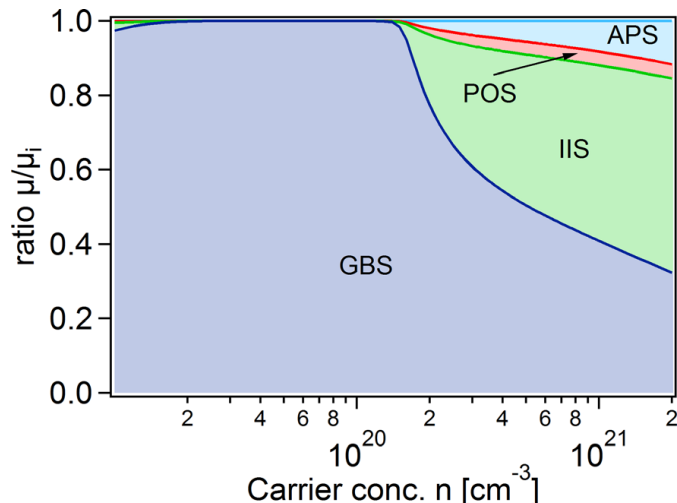
In NIR (& above) the dominant term in denominator is $\tau^2 E^4 \Rightarrow$ at fixed electrical conductivity (fixed $n\tau$), **better transparency is achieved for less but more mobile charge carriers**

Mobility of free charge carriers is limited especially by

- scattering on defects, so called **ionized impurity scattering** (but these defects are at the same time responsible for the presence of charge carriers - see the remark about doping)
- difficult crossing / tunneling through grain boundaries (also kind of defect from the el. structure point of view), so called **grain boundary scattering, grain barrier limited transport**

Transparent conductive oxides

- scattering on defects, so called **ionized impurity scattering** (but these defects are at the same time responsible for the presence of charge carriers - see the remark about doping), therefore this is a **dominant process at high n**)
- difficult crossing / tunneling through grain boundaries (also kind of defect from the el. structure point of view), so called **grain boundary scattering - dominant process at low n**



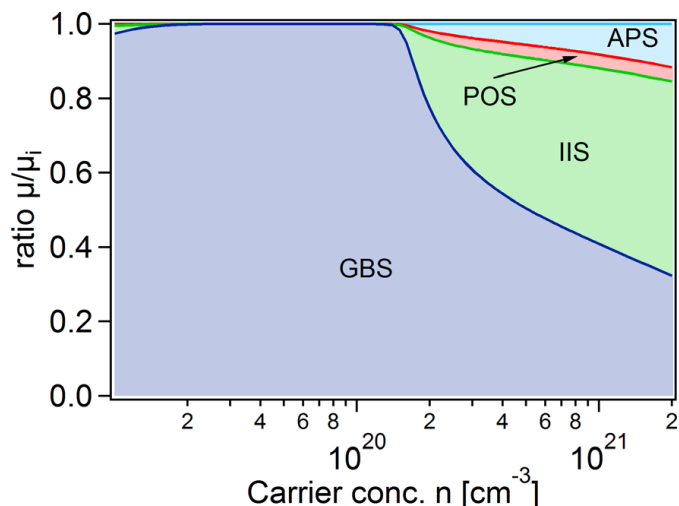
APS: acoustical mode phonon scattering
POS: optical mode phonon scattering
IIS: ionized impurity scattering
GBS: grain boundary scattering

Transparent conductive oxides

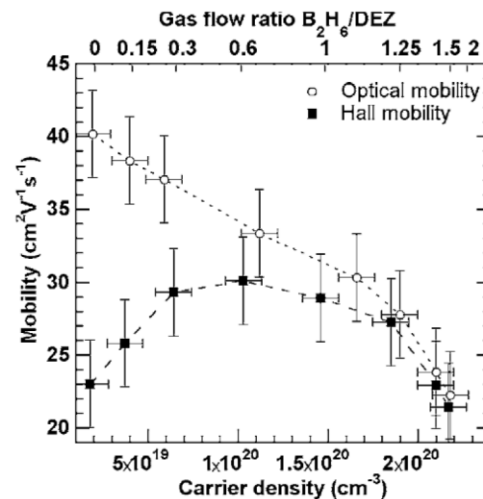
2 slides above $\varepsilon_{\text{Drude}} = -\hbar^2 \sigma_{\text{dc}} / \varepsilon_0 \cdot [(\tau E^2 - i\hbar E) / (\tau^2 E^4 + \hbar^2 E^2)]$

at fixed electrical conductivity (fixed $n\tau$), **better transparency is achieved for less but more mobile charge carriers**

GBS is less important during light absorption than during current conduction (electrons only oscillate inside of grains, do not cross their boundaries) $\Rightarrow$ "optical" mobility is higher than "electrical"



[A. Bikowski, J. Appl. Phys. 116, 143704 (2014)]



[Steinhauser et al., Appl. Phys. Lett. 90, 142107 (2007)]

8) Quantum calculations

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

brief version, see KFY/MPPL for details

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

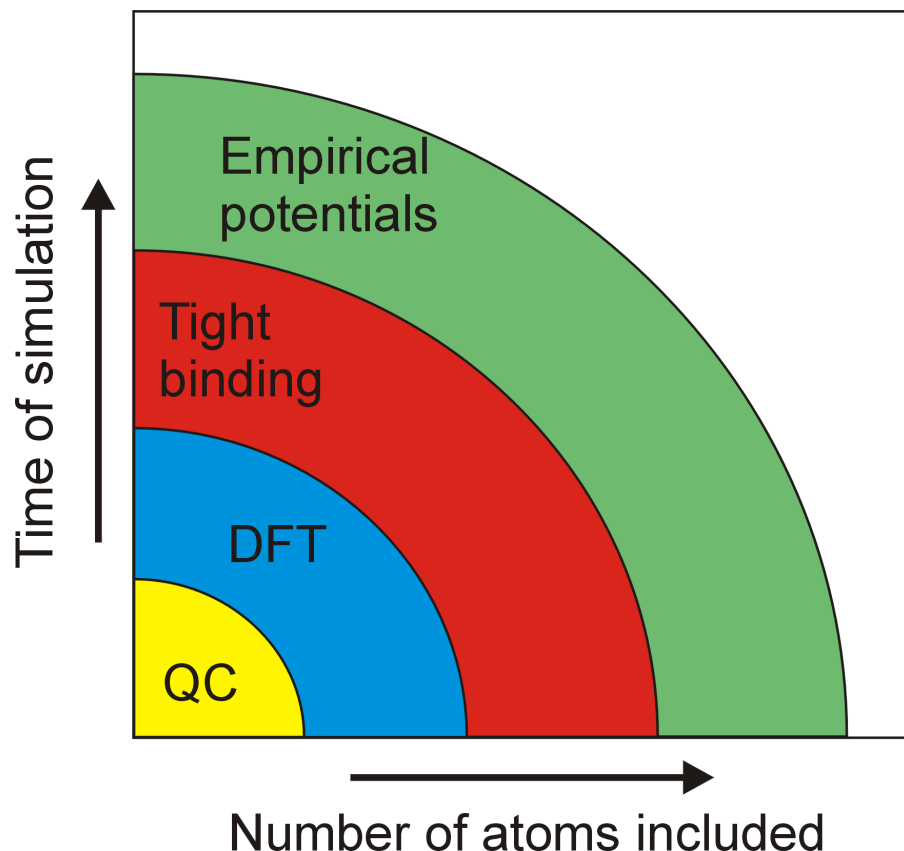
Motivation

an comparison with classical calculations (emp. pot.)

- (1) Calculation of quantities discussed in chapters 6-7
(direct and indirect band gap, density and mobility of charge carriers, localization of states, role of individual elements, ...)
doing that using EPs impossible by definition (atoms = balls)
- (2) Calculations of energy differences for different structures
(e.g. stability of solid solutions in chapter 13) and different deformations (e.g. mechanical properties in chapter 9)
doing that using EPs possible in principle, but too inaccurate
- (3) Energy calculations give us energy gradient $\Rightarrow$ force $\Rightarrow$ ability to capture the time evolution - molecular dynamics
(e.g. prediction of amorphous structures in chapter 16)
can be done using EPs (examples at the end of chapter 4), less accurate but faster - choice depends on specific simul.

Description of interatomic interactions

(reminder from chapter 4)



From fastest =
least accurate

- **Empirical potentials**
(chapter 4)
- **Tight binding**
(one of methods which are not very popular since introduction of DFT)
- **Density Functional Theory**
(chapter 8)
- **Quantum Chemistry**
(Hartree-Fock, post HF methods more precise & slower than DFT)

relevant especially for the third (last) point at previous slide

What do we need

(= what is described below

= what has to be implemented in the software)

- (1) Method of wavefunction calculation
(equations where the electronic wavefunction $\psi(\mathbf{r})$
and the potential due to cores $V(\mathbf{r})$ "in only as a letter")
- (2) Way how to mathematically express $\psi(\mathbf{r})$ (formula containing
"some" coefficients: looking for $\psi(\mathbf{r})$ = looking for their values)
- (3) Way how to mathematically express $V(\mathbf{r})$ (formula containing
"some" coefficients: determine $V(\mathbf{r})$ = determine their values)
- (4) Practical way how to visualize the wavefunctions $\psi(\mathbf{r})$

So how can we find many-body wavefunction / electronic structure

There are more methods how to find the ground state. Below we show one of them (the most frequent one in praxis), other methods are discussed in KFY/MPPL. Starting points:

- We are considering electrons (i.e. **fermions**)
- There will be (only) **non-relativistic time-independent** Schrödinger equation
- Light electrons orbit around immovable heavy cores (i.e. the atom cores are present in the calculation as a source of Coulombian force, but we do not have to care about their wavefunction): **Born-Oppenheimer approximation**
- Similarly to atomic orbitals used to describe atoms, here we will consider **molecular orbitals** (the same term is used for molecules and solids) - el. states shared by more atoms

So how can we find many-body wavefunction / electronic structure

When looking for a ground state, the equations can (and, for the selected method, do) contain

- 1) **Kinetic energy** of electrons
- 2) **Coulombian energy** of electron-cores interactions
- 3) **Coulombian energy** of electron-electron interaction:
we do not consider interaction between electrons having exact coordinates ("balls"), but between clouds of electronic charge (density of clouds corresponds to the probability of occurrence of an electron: mean field approximation)
- 4) **Exchange and correlation energy**: guarantees considering electronic spin and electronic self-interaction in a correct way (more precise definition in KFY/MPPL)

So how can we find many-body wavefunction / electronic structure

Obtain N -body wavefunction from N single-body wavefunctions using the (antisymmetric!) **Slater determinant**

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \dots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \dots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \dots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

First crosscheck: switch $\mathbf{x}_i$ and $\mathbf{x}_j \Rightarrow$ change of sign

e.g. for 2×2 : change from $1/\sqrt{2} [\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) - \psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)]$
to $1/\sqrt{2} [\psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1) - \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)]$

Second crosscheck: $\psi_i = \psi_j \Rightarrow$ two columns are identical $\Rightarrow 0$

Density functional theory

Other (more intuitive, but slower) methods are **wavefunction-based**: minimizing energy which depends on wavefunction Ψ_e

$$E^{opt} = \min_{\Psi} E[\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)]$$

3N-dimensional problem

Density functional theory (DFT) is density-based: minimizing energy which depends on electronic density ρ_e (also denoted n_e), or densities $\rho_e^{\uparrow}$ and $\rho_e^{\downarrow}$ for unpaired spins

$$E^{opt} = \min_{\rho_e} E[\rho_e(\mathbf{r})] \text{ or } E[\rho_e^{\uparrow}(\mathbf{r}), \rho_e^{\downarrow}(\mathbf{r})]$$

3-dimensional problem

Density functional theory

Reason why is the transition from a wavefunction-based to the density-based method allowed: 2 **Hohenberg-Kohn theorems**

- 1) electronic density uniquely defines all other characteristics of a system (including energy)
- 2) variational principle holds, i.e. electronic density leading to the lowest energy ($\Leftrightarrow$ its zero derivative) is the ground state electron density

Nobel prize (Walter Kohn) 1998

Good thing is shorter calculation time (and its slower increase with number of electrons $\Rightarrow$ description of larger systems)

Bad thing is that we do not know how the functional $E[\rho]$ exactly looks like (the aforementioned theorem only says that it exists)

Before the equations: atomic units

(also a.u. ... not to be confused with arbitrary units)

Motivation: clearer equations, clearer i/o of programs

- resting mass of electron $m_0 = 1$
- reduced Planck constant $\hbar = 1$
- elementary charge $e = 1$
- Coulomb constant $1/4\pi\epsilon_0 = 1$

And the resulting derived units

- length: Bohr, Bohr radius $0.529177 \text{ \AA}$
- time: 0.02419 fs
- energy: Hartree, Ha 27.211 eV
often used is also Rydberg, Ry $13.606 \text{ eV} = \text{Ha}/2$

DFT - Kohn-Sham equations

System of N equations, connected by density of a single electron cloud $\rho_e(\mathbf{r})$: **Kohn-Sham equations** ("Schrödinger-like")

$$\hat{H}^{\text{KS}}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

With detailed Hamiltonian

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \int \rho_e(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}' + \mu_{\text{xc}}(\rho_e(\mathbf{r})) \right] \psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$-\frac{1}{2}\nabla^2$$

Kinetic energy (in SI $-\hbar^2/2m_0 \nabla^2$)

$$V(\mathbf{r})$$

Coulombian energy (interaction with atom cores)

$$\int \rho_e(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}'$$

Coulombian energy (interaction with other el.)

$$\mu_{\text{xc}}[\rho_e(\mathbf{r})]$$

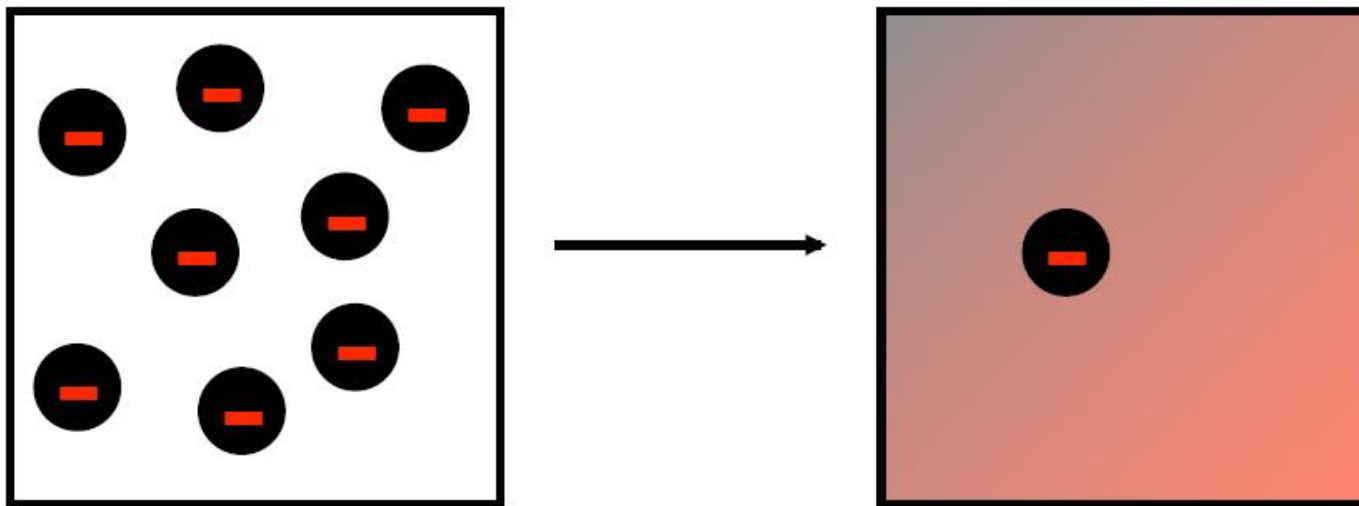
Exchange and correlation (xc) functional
(also xc potential: derivative of xc energy by ρ_e)

DFT - Kohn-Sham equations

$$\hat{H}^{\text{KS}}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \int \rho_e(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}' + \mu_{\text{xc}}(\rho_e(\mathbf{r})) \right] \psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

- Strictly speaking the equations describe a fictitious system of non-interacting electrons (interact with the electron cloud arising from them, but not explicitly one with another)



DFT - Kohn-Sham equations

$$\hat{H}^{\text{KS}}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \int \rho_e(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}' + \mu_{\text{xc}}(\rho_e(\mathbf{r})) \right] \psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

- Strictly speaking the equations describe a fictitious system of non-interacting electrons (interact with the electron cloud arising from them, but not explicitly one with another) having the same electron density $\rho_e(\mathbf{r})$ like the real system
- Hohenberg-Kohn theorems allow us to believe the total energy of a system, while neither single-electron wavefunctions ψ_i (**Kohn-Sham orbitals**) nor energies of individual orbitals ε_i "officially" do not have a physical meaning (there is no rigorous mathematical proof that they have any)
- However, in praxis the orbitals ψ_i as well as trends resulting from ε_i **"are reasonable"**

DFT - Exchange-correlation functional

In the KS Hamiltonian $-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \int \rho_e(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}' + \mu_{xc}(\rho_e(\mathbf{r}))$ we know the first 3 terms exactly, μ_{xc} requires approximation. Briefly here, see KFY/MPPL for details.

- 1) μ_{xc} depends only on electron density in the corresponding point: local density approximation, **LDA**
- 2) μ_{xc} on electron density in the corresponding point and on its derivative (gradient): generalized gradient approx., **GGA**
- 3) μ_{xc} on electron density in the corresponding point, on its first derivative and second derivative: **meta-GGA**
- 4) Parallel to points 1-3: in the case of unpaired spins, it is necessary to separately consider density of spins up and spins down: instead of local density approximation, LDA, we have local spin density, **LSD**

Representation of the wavefunction

(motivation)

So we have a system of single-electron KS equations

$$\left[-\frac{1}{2} \nabla^2 + V(\mathbf{r}) + \int \rho_e(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + \mu_{xc}(\rho_e(\mathbf{r})) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

Writing the equations is much simpler than solving them

So far, the wavefunctions ψ were in the equations without closer specification. In order to solve this system of equations, we have to represent ψ analytically, in some basis f_j :

$$\psi(\mathbf{r}) = \sum_j c_j f_j(\mathbf{r})$$

Then, looking for ψ means looking for values of coefficients c_j

There are many options which functions f_j (which basis set) to choose, in a periodic system (simulation cell with periodic boundaries) plane waves are a frequent choice - see below

Representation of the wavefunction

(specifics for a periodic system)

The **Bloch theorem** (chapter 6) justifies the possibility (not obligation) of representation in the form of linear combination of planewaves ("decomposition into sinusoids")

$$\psi_{n,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,k}(\mathbf{G}) e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}$$

Wavefunction calculation = calculation of values $c_{n,k}$

There is an infinite number of relevant planewaves. We have to choose a finite subset of them, i.e. choose

- (1) density of vectors $\mathbf{k}$ (k-points) in the 1st Brillouin zone
(this defines "upper bound of wavelengths of sinusoids")
- (2) the longest considered vectors $\mathbf{G}$
(this defines "lower bound of wavelengths of sinusoids")

See below for further details concerning the finite subset choice

k-points - which of them to choose

Chosen k-points are given in terms of $2\pi/a_{1-3}$, from $-1/2$ to $1/2$

1st option: manual picking of important k-points

- the most important one is Γ -point 0,0,0
- others can result from the crystal system, etc.

2nd option (more frequent): Monkhorst-Pack grid (mesh)

- e.g. grid "2 2 2" (8×)

0	0	0
1/2	0	0
0	1/2	0
0	0	1/2
1/2	1/2	0
1/2	0	1/2
0	1/2	1/2
1/2	1/2	1/2

- e.g. grid "3 3 3" (14×)

0	0	0	1/3	-1/3	0
1/3	0	0	1/3	0	-1/3
0	1/3	0	0	1/3	-1/3
0	0	1/3	1/3	1/3	-1/3
1/3	1/3	0	1/3	-1/3	1/3
1/3	0	1/3	-1/3	1/3	1/3
0	1/3	1/3			
1/3	1/3	1/3			

k and **$-k$** are always equivalent (only one of them is above)

other subsets of k-points can be equivalent due to symmetries of individual crystal systems

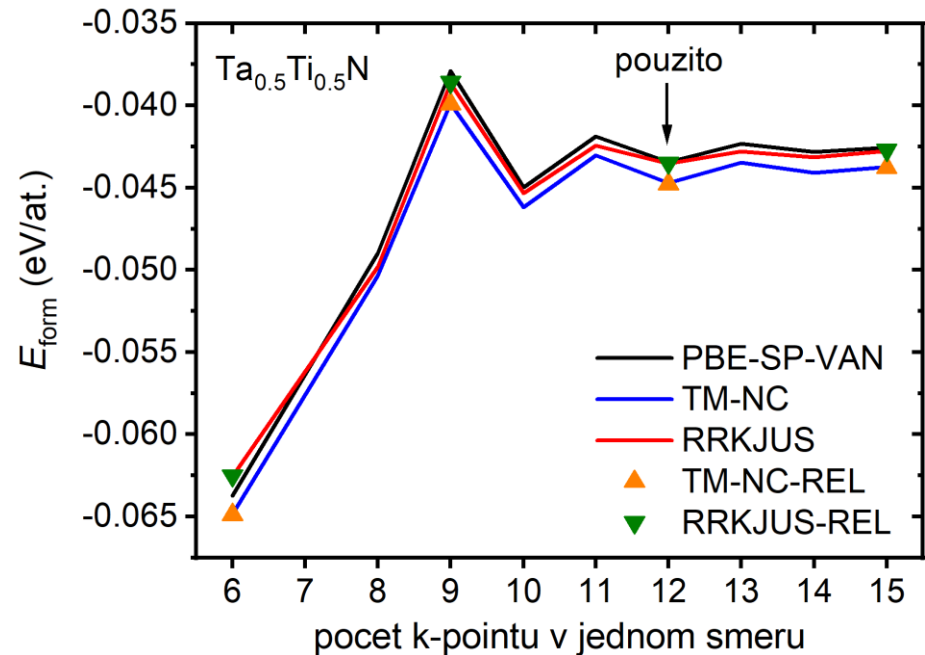
Individual k-points can have different weights

k-points - example of convergence

Formation energy of the solid solution $\text{Ta}_{0.5}\text{Ti}_{0.5}\text{N}$
($E_{\text{Ta}_{0.5}\text{Ti}_{0.5}\text{N}} - 0.5 \times E_{\text{TiN}} - 0.5 \times E_{\text{TaN}}$)

To the right-hand side:

- exactness increases
- but computing time increases as well



[from master thesis of V. Petrman]

G vectors (energy cutoff)

Opposite situation than for vectors **k**: here we do know the minimum length of vectors **G** (given by primitive reciprocal lattice vectors) and we are setting their maximum length used.

Again, a **compromise between exactness and speed** (that for k-points matters for crystalline materials, this for all materials).

In Hamiltonian there is a term corresponding to kinetic energy:
 $-\hbar^2/2m_0 \nabla^2$ in SI units ($-\frac{1}{2}\nabla^2$ in atomic units)

So we introduce kinetic energy of plane wave $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$:

$\hbar^2/2m_0 (\mathbf{k}+\mathbf{G})^2$ in SI units ($\frac{1}{2}(\mathbf{k}+\mathbf{G})^2$ in atomic units)

Quantity given in praxis is not maximum length of vectors **G**, but directly the maximum value of this energy: **energy cutoff** (typically hundreds eV, i.e. tens Ha or Ry)

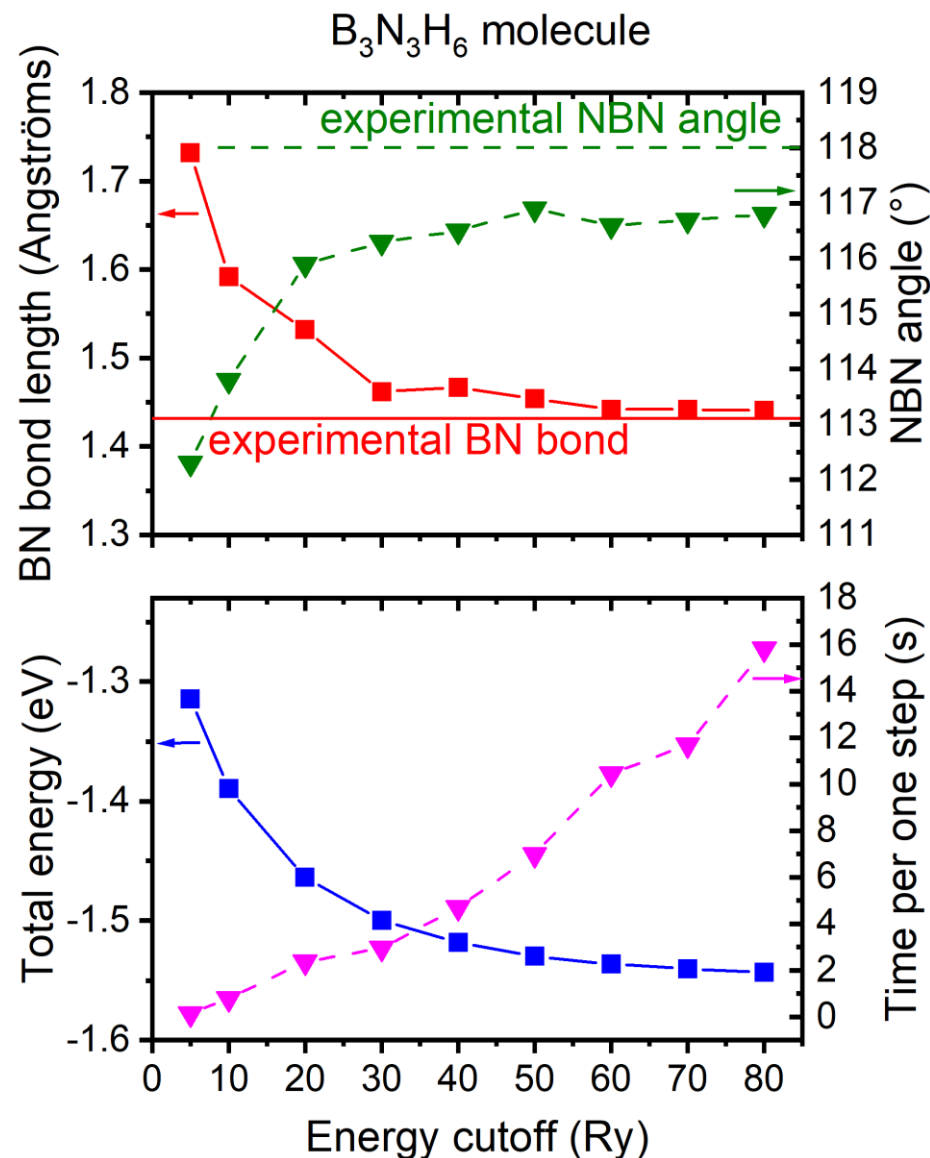
Energy cutoff - ex. of convergence

Simple molecule $\text{B}_3\text{N}_3\text{H}_6$
"where we know the
correct result"

To the right there is
increasing exactness of

- bond lengths
- bonding angles
- total energy

Increasing computing time



Example of necessary exactness

Calculation

Computed energy of $\alpha\text{-Al}_2\text{O}_3$	1133.3904 eV/at.
Computed energy of $\gamma\text{-Al}_2\text{O}_3$	1133.3466 eV/at.
Difference in the sixth valid digit	0.044 eV/at.

Experiment

$$21.7 \text{ kJ/mol} = 0.045 \text{ eV/at.}$$

[S. Zuzjakova et al., *Ceram. Int.* 41, 6020 (2015)]

⇒ "it works", but we need 7-8 valid digits in the result
(the difference of energies fortunately converges faster
than the energies themselves - many errors cancel out)

What is represented by $V(r)$

Recall $\hat{H}^{\text{KS}} = -\frac{1}{2} \nabla^2 + V(r) + \int \rho_e(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}' + \mu_{\text{xc}}(\rho_e(r))$

If we describe quantum-mechanically (Kohn-Sham equations) all electrons, $V(r)$ represent the **role of cores**.

However, computational costs increase with the number of quantum-mechanically described electrons (almost $t \sim N^3$).

Thus, it is more practical to

- assume that inner (non-valence) electrons are frozen in the same states as in isolated atoms
- describe q.-mech. (Kohn-Sham eq.) only valence electrons

$V(r)$ then represent the **role of "ions"** (cores + inner shells)

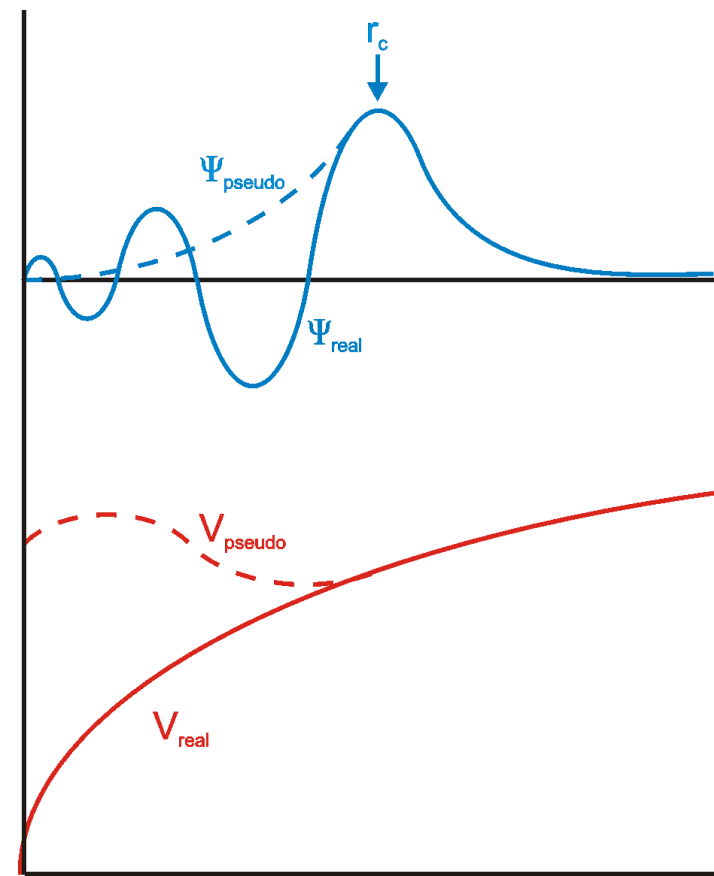
Transition metals: for high exactness, it is necessary to describe quantum-mechanically also one shell below valence electrons (semicore el., e.g. not only 3d².4s² but also 3s².3p⁶ for Ti).

Replace $V(r)$ by pseudopotentials

As pointed out above: if we speed up calculations by describing quantum-mechanically (Kohn-Sham eq.) only valence electrons, $V(r)$ represents interaction with core + inner (non-valence) electrons. **The more complicated shape it has.**

In order to simplify and speed up, we use **pseudopotentials**. Compared to the real potentials, they ignore high-frequency changes of $\psi(r)$ close to atom core (closer than r_c - see the figure)

Again: more details in KFY/MPPL



Software - ab-initio calculations

Commercial

- **VASP** (www.vasp.at)
- Gaussian (www.gaussian.com)
- GAMESS (www.cfs.dl.ac.uk)
- Crystal (www.chimifm.unito.it/teorica/crystal)

Free

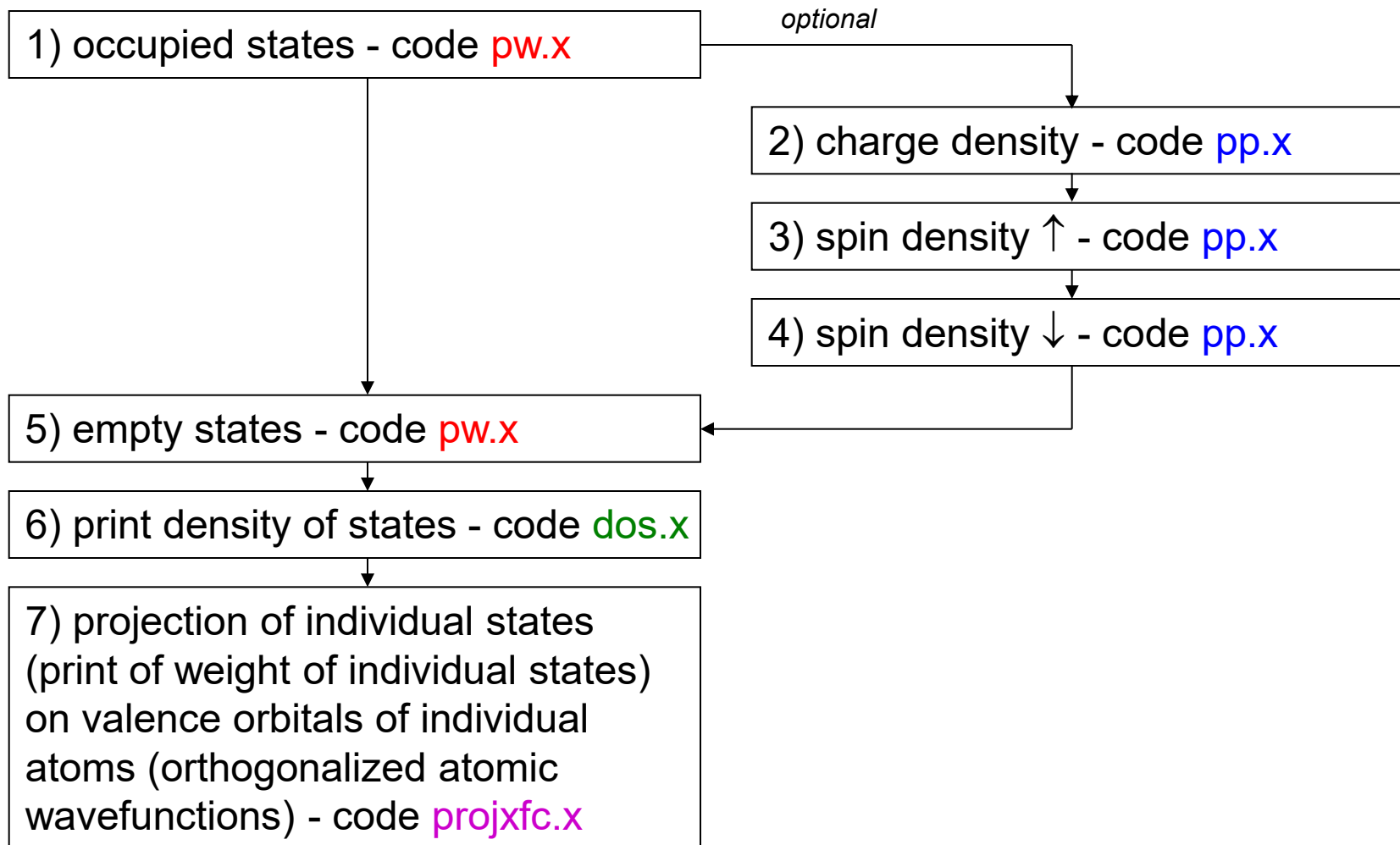
- **ESPRESSO** (www.quantum-espresso.org / www.pwscf.org)
- CPMD (www.cpmd.org)
- ABINIT (www.abinit.org)

Something is implemented practically everywhere
(DFT, ground state calculations)

Something is implemented only somewhere
(Hartree-Fock and other methods, description of ψ by plane waves and k-points, molecular dynamics, visualization)

Electronic structure calculations

input files of the package Quantum Espresso



9) Mechanical properties

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Elastic tensor, strain tensor

Hooke's law

- scalar (high school) form
- tensor (realistic) form
- or for individual components

$$F = k_{\text{stiffness}} \cdot x, \text{ etc.}$$

$$[\sigma] = [\mathbf{C}] \cdot [\varepsilon]$$

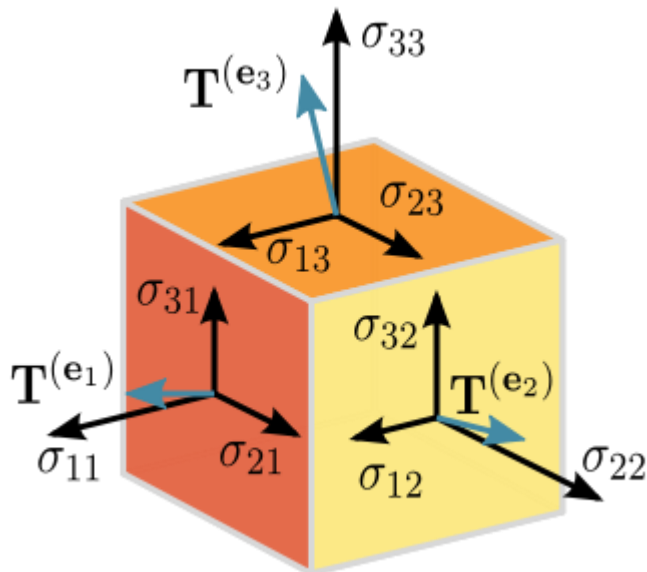
$$\sigma_{ij} = \sum_k \sum_l C_{ijkl} \cdot \varepsilon_{kl} \quad (i,j,k,l = 1-3)$$

Stress tensor

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix}$$

$$\text{or } \sigma_{11} = \sigma_{xx}, \text{ etc.}$$

$$\sigma_{12} = \tau_{xy}, \text{ etc.}$$



Elastic tensor, strain tensor

Hooke's law

- scalar (high school) form

$$F = k_{\text{stiffness}} \cdot x, \text{ etc.}$$

- tensor (realistic) form

$$[\sigma] = [\mathbf{C}] \cdot [\varepsilon]$$

or for individual components

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$$\text{or } \sigma_{11} = \sigma_{xx}, \text{ etc.}$$

$$\sigma_{12} = \tau_{xy}, \text{ etc.}$$

Stiffness tensor

$$C_{ijkl} = \partial^2(E/V_0) / \partial \varepsilon_{ij} \partial \varepsilon_{kl}$$

$$\text{or } S_{ijkl} = C_{ijkl}^{-1}$$

Strain tensor

$$\epsilon = \begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{bmatrix}$$

$$\varepsilon_{ij} = \frac{1}{2} (du_i/dx_j + du_j/dx_i)$$

$\mathbf{u}$ is displacement vector

Elastic tensor, strain tensor

Stiffness tensor $C_{ijkl} = \partial^2(E/V_0)/\partial \varepsilon_{ij} \partial \varepsilon_{kl}$

Regarding the difference between (n-dimensional) matrix and tensor: it is not the same. Tensor is an object which has (due to the rules for its transformation between different coordinate systems) geometrical meaning (note 1D vector). However, for a fixed coordinate system tensor can be represented by a matrix more or less safely.

By the way: it should not be surprising that we are talking about tensors - this is the field which the tensor calculus (lat. *tensio* = tension) was originally developed for (Voigt, 1898)



Elastic tensor, strain tensor

Thanks to symmetries ($ij = ji$, $kl = lk$, $ijkl = klij$) the notation can utilize Voigt notation $11 \rightarrow 1$, $22 \rightarrow 2$, $33 \rightarrow 3$, $23 \rightarrow 4$, $13 \rightarrow 5$, $12 \rightarrow 6$

$\Rightarrow$ Hooke's law $\sigma_{ij} = \sum_k \sum_l C_{ijkl} \cdot \varepsilon_{kl}$
 converts to $\sigma_i = C_{ij} \cdot \varepsilon_j$ (ε_j is also labelled e_j)

$$[\sigma] = \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{bmatrix} \equiv \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \quad [\epsilon] = \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ 2\epsilon_{23} \\ 2\epsilon_{13} \\ 2\epsilon_{12} \end{bmatrix} \equiv \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix}$$

$$[C] = \begin{bmatrix} c_{1111} & c_{1122} & c_{1133} & c_{1123} & c_{1131} & c_{1112} \\ c_{2211} & c_{2222} & c_{2233} & c_{2223} & c_{2231} & c_{2212} \\ c_{3311} & c_{3322} & c_{3333} & c_{3323} & c_{3331} & c_{3312} \\ c_{2311} & c_{2322} & c_{2333} & c_{2323} & c_{2331} & c_{2312} \\ c_{3111} & c_{3122} & c_{3133} & c_{3123} & c_{3131} & c_{3112} \\ c_{1211} & c_{1222} & c_{1233} & c_{1223} & c_{1231} & c_{1212} \end{bmatrix} \equiv \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix}$$

Elastic tensor, strain tensor

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converts to $\sigma_i = C_{ij} \cdot \varepsilon_j$ (ε_j is also labelled e_j)

definition $C_{ijkl} = \partial^2(E/V_0)/\partial \varepsilon_{ij} \partial \varepsilon_{kl}$
converts to $C_{ij} = \partial^2(E/V_0)/\partial \varepsilon_i \partial \varepsilon_j$

$\Rightarrow$ deformation energy $\Delta E/V_0 = \sum_i \sum_j \frac{1}{2} C_{ij} \varepsilon_i \varepsilon_j$
(used below)

Elastic tensor, strain tensor

Be careful about physical meaning: factor '2' at ε_{23} , ε_{13} and ε_{12}

Mathematical point of view:

in sums $\sum_k \sum_l C_{ijkl} \cdot \varepsilon_{kl}$ there was separately ε_{kl} and separately ε_{lk} , now we have only 1 term

$$[\epsilon] = \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ 2\epsilon_{23} \\ 2\epsilon_{13} \\ 2\epsilon_{12} \end{bmatrix} \equiv \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix}$$

Physical point of view:

- $du_1/dx_2 + du_2/dx_1$ represents change of angle between previously normal vectors (shear angle)

$$\gamma_{12} = \arctg (du_1/dx_2) + \arctg (du_2/dx_1) ,$$

- for small angles ($\tg \alpha = \alpha$ [rad.]) it holds

$$\gamma_{12} = du_1/dx_2 + du_2/dx_1 ,$$

$$\varepsilon_{12} \text{ defined as } = \frac{1}{2}(du_1/dx_2 + du_2/dx_1)$$

therefore corresponds to half of shear angle $\gamma_{12} = \varepsilon_6$

Elastic tensor, strain tensor

Be careful about physical meaning: factor '2' at ϵ_{23} , ϵ_{13} and ϵ_{12}

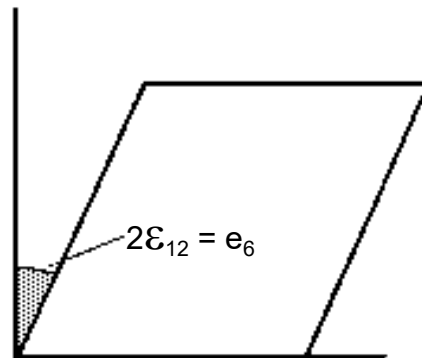
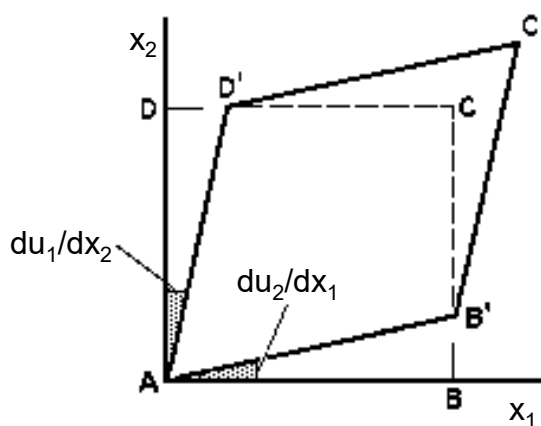
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Physical point of view:

- $du_1/dx_2 + du_2/dx_1$ represents change of angle between previously normal vectors (shear angle)



No. of independent components of C_{ij}

General case **21**

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix}$$

Orthotropic system max. **9**

(3 perpendicular planes of symmetry: cubic, hexagonal, orthorhombic, some tetragonal)

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$$

Various crystal lattices **3-21** (next slide)

Isotropic system **2**

(amorphous on atomic scale;
polycrystalline on macroscale)

$$\frac{E}{(1+\nu)(1-2\nu)} \begin{bmatrix} 1-\nu & \nu & \nu & 0 & 0 & 0 \\ \nu & 1-\nu & \nu & 0 & 0 & 0 \\ \nu & \nu & 1-\nu & 0 & 0 & 0 \\ 0 & 0 & 0 & (1-2\nu)/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & (1-2\nu)/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & (1-2\nu)/2 \end{bmatrix}$$

$$= \frac{1}{E} \begin{bmatrix} 1 & -\nu & -\nu & 0 & 0 & 0 \\ -\nu & 1 & -\nu & 0 & 0 & 0 \\ -\nu & -\nu & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(1+\nu) & 0 & 0 \\ 0 & 0 & 0 & 0 & 2(1+\nu) & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(1+\nu) \end{bmatrix}^{-1}$$

No. of independent components of C_{ij}

Depends on crystal symmetry (crystal system)

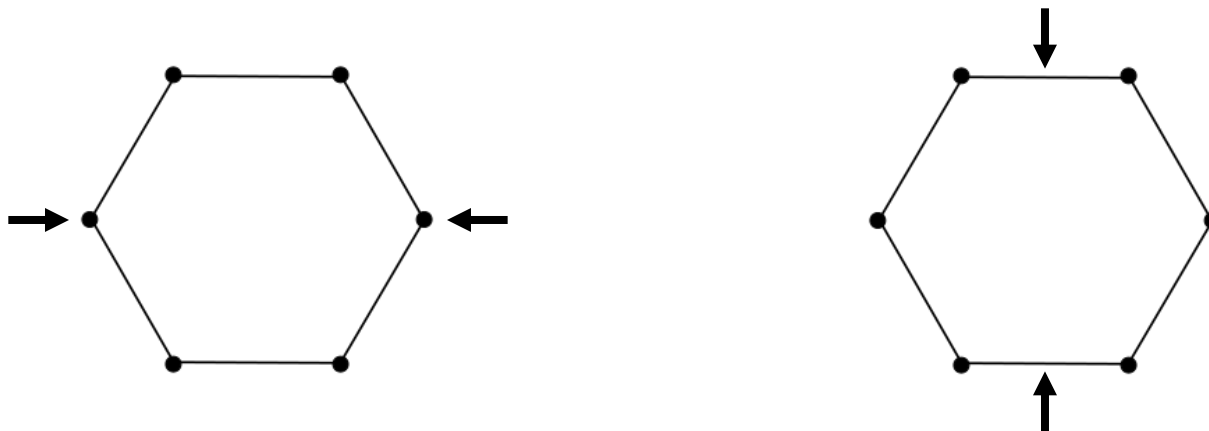
Triclinic		21	
Monoclinic		13	
Orthorhombic		9	$(C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55}, C_{66})$
Tetragonal 4/m	$(hkl \neq khl)$	7	$(C_{11}, C_{12}, C_{13}, C_{16}, C_{33}, C_{44}, C_{66})$
Tetragonal 4/mmm	$(hkl = khl)$	6	$(C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, C_{66})$
Trigonal $\bar{3}$	$(hkl \neq khl)$	7	$(C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{33}, C_{44})$
Trigonal $\bar{3}m$	$(hkl = khl)$	6	$(C_{11}, C_{12}, C_{13}, C_{14}, C_{33}, C_{44})$
Hexagonal		5	$(C_{11}, C_{12}, C_{13}, C_{33}, C_{44})$
Cubic		3	(C_{11}, C_{12}, C_{44})

Tetragonal, trigonal: depends on Laue class (hexagonal and cubic system also split to two Laue classes, but no effect on C_{ij})

No. of independent components of C_{ij}

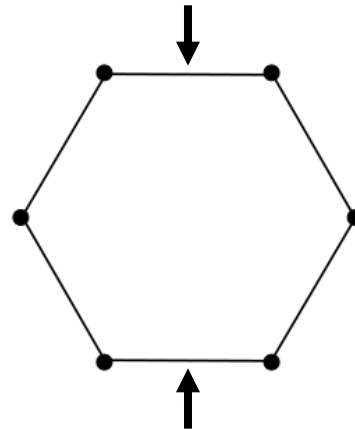
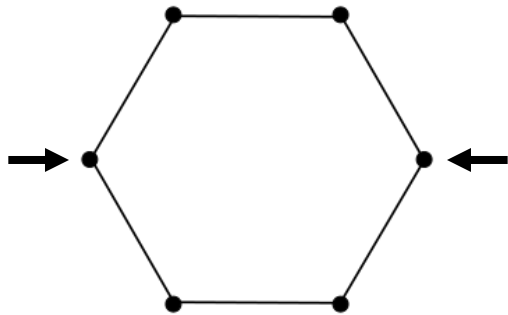
Trigonal $\bar{3}$	$(hkl \neq khl)$	7	$(C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{33}, C_{44})$
Trigonal $\bar{3}m$	$(hkl = khl)$	6	$(C_{11}, C_{12}, C_{13}, C_{14}, C_{33}, C_{44})$
Hexagonal		5	$(C_{11}, C_{12}, C_{13}, C_{33}, C_{44})$

Some crystal systems have threefold or even sixfold rotational axis, normal to the plane $(x,y) = (1,2)$ (let alone cubic and tetragonal which have it elsewhere). Does it really hold $C_{11} = C_{22}$, despite the apparently non-equivalent stresses?



No. of independent components of C_{ij}

Trigonal $\bar{3}$	$(hkl \neq khl)$	7	$(C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{33}, C_{44})$
Trigonal $\bar{3}m$	$(hkl = khl)$	6	$(C_{11}, C_{12}, C_{13}, C_{14}, C_{33}, C_{44})$
Hexagonal		5	$(C_{11}, C_{12}, C_{13}, C_{33}, C_{44})$



Mathematician: invariance of a 2nd-order tensor against rotation of $<180^\circ \Rightarrow$ inv. against rotation of any angle around this axis

Physicist: invariance of C_{ij} against rotation of 120° (hexagonal, trigonal) leads to invariance against rotation of 90° ($C_{11} = C_{22}$), despite the geometrical difference between directions '1' and '2'

No. of independent components of C_{ij}

Depends on crystal symmetry (crystal system)

Triclinic 21

Monoclinic 13

Orthorhombic 9

Tetragonal 4/m $(hkl \neq khl)$ 7

Tetragonal 4/mmm $(hkl = khl)$ 6

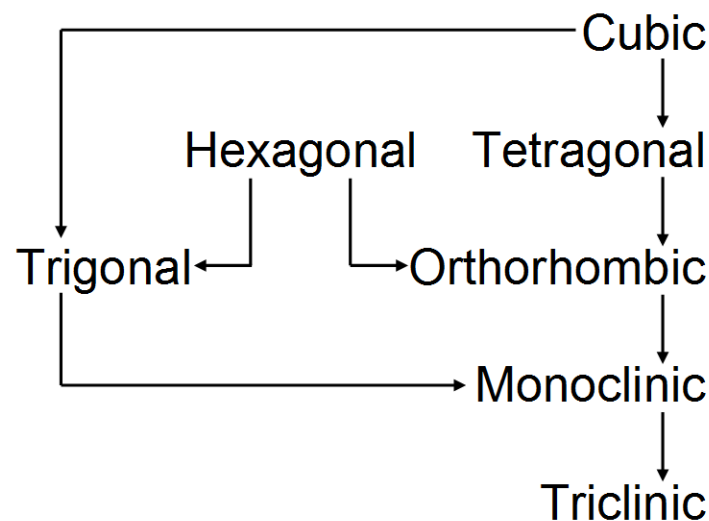
Trigonal $\bar{3}$ $(hkl \neq khl)$ 7

Trigonal $\bar{3}m$ $(hkl = khl)$ 6

Hexagonal 5

Cubic 3

See also the hierarchy of crystal systems in the first chapter

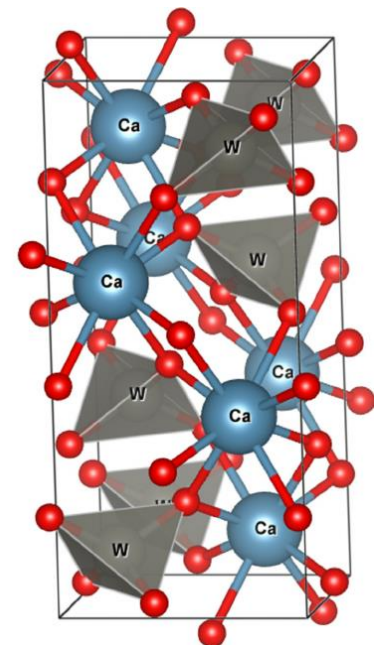


No. of independent components of C_{ij}

Tetragonal 4/m $(hkl \neq khl)$ 7 ($C_{11}, C_{12}, C_{13}, C_{16}, C_{33}, C_{44}, C_{66}$)

Tetragonal 4/mmm $(hkl = khl)$ 6 ($C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, C_{66}$)

Example of relatively unsymmetrical structure which is tetragonal, but does not have three perpendicular planes of symmetry $\Leftrightarrow$ 7, not 6, independent comp. of C_{ij} : **Scheelite** CaWO_4 (point group 4/m, space group $I4_1/a$ $\Rightarrow$ only one slip plane)



No. of independent components of C_{ij}

Cubic

$$\begin{pmatrix} C_{11} & C_{12} & C_{12} & & & \\ \cdot & C_{11} & C_{12} & & & \\ \cdot & \cdot & C_{11} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{44} \end{pmatrix}$$

Trigonal 6

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & & \\ \cdot & C_{11} & C_{13} & -C_{14} & & \\ \cdot & \cdot & C_{33} & & & \\ \cdot & \cdot & & C_{44} & & \\ & & & & C_{44} & C_{14} \\ & & & & \cdot & C_{66} \end{pmatrix}$$

Hexagonal,
Tetragonal 6

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & & & \\ \cdot & C_{11} & C_{13} & & & \\ \cdot & \cdot & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{66} \end{pmatrix}$$

Trigonal 7

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & \\ \cdot & C_{11} & C_{13} & -C_{14} & -C_{15} & \\ \cdot & \cdot & C_{33} & & & \\ \cdot & \cdot & & C_{44} & & -C_{15} \\ \cdot & \cdot & & & C_{44} & C_{14} \\ \cdot & \cdot & & & \cdot & C_{66} \end{pmatrix}$$

Tetragonal 7

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & & C_{16} & \\ \cdot & C_{11} & C_{13} & & -C_{16} & \\ \cdot & \cdot & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ \cdot & \cdot & & & & C_{66} \end{pmatrix}$$

Orthorhombic

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & & & \\ \cdot & C_{22} & C_{23} & & & \\ \cdot & \cdot & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{55} & \\ & & & & & C_{66} \end{pmatrix}$$

Hexagonal and Trigonal: $C_{66} = (C_{11} - C_{12})/2$

Elastic moduli

Isotropic material: 4 most important moduli

- | | |
|--|-------------------------|
| 1) Bulk modulus | B |
| 2) Shear modulus | G |
| 3) Young's modulus (σ/ε) | $E = 9BG/(3B+G)$ |
| 4) Poisson's ratio ($-\varepsilon_{\text{transverse}}/\varepsilon_{\text{axial}}$) | $\nu = (3B-2G)/(6B+2G)$ |

Which well known solid has zero Poisson's ratio
(fixed dimension perpendicular to the stress)?

Elastic moduli

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Which well known solid has zero Poisson's ratio
(fixed dimension perpendicular to the stress)?

Cork:
this is why it is relatively
easy to unplug bottles



Elastic moduli

Isotropic material: 4 most important moduli

- 1) Bulk modulus B
- 2) Shear modulus G
- 3) Young's modulus (σ/ε) $E = 9BG/(3B+G)$
- 4) Poisson's ratio ($-\varepsilon_{\text{transverse}}/\varepsilon_{\text{axial}}$) $\nu = (3B-2G)/(6B+2G)$

Only two moduli are independent, the other can be calculated:

$$E = 9BG/(3B+G) = 2G(1+\nu) = 3B(1-2\nu)$$

Monocrystals have directionally dependent E and other moduli
tungsten, by chance,
does not: here almost
exactly holds

$$C_{44} = (C_{11}-C_{12})/2$$

<i>Metal</i>	<i>Modulus of Elasticity (GPa)</i>		
	<i>[100]</i>	<i>[110]</i>	<i>[111]</i>
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

[R.W. Hertzberg, Deformation and Fracture Mechanics of Engineering Materials]

Elastic moduli

Isotropic material: 4 most important moduli

- | | |
|--|-------------------------|
| 1) Bulk modulus | B |
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| 3) Young's modulus (σ/ε) | $E = 9BG/(3B+G)$ |
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Only two moduli are independent, the other can be calculated:

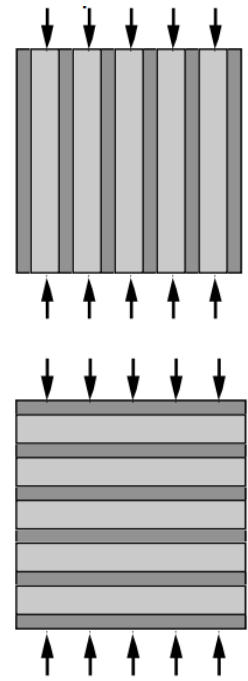
$$E = 9BG/(3B+G) = 2G(1+\nu) = 3B(1-2\nu)$$

Anisotropic material, fixed strain everywhere: **Voigt**
(averaging C_{ij} over all orientations),

polycr. mat.: B_{Voigt} & G_{Voigt} = upper bounds of B & G

Anisotropic material, fixed stress everywhere: **Reuss**
(averaging $S_{ij} = C_{ij}^{-1}$ over all orientations),

polycr. mat.: B_{Reuss} & G_{Reuss} = lower bounds of B & G



Relation of [C] and elastic moduli

starting format

Voigt (averaging C_{ij}):

$$A = (C_{11} + C_{22} + C_{33})/3, B = (C_{23} + C_{13} + C_{12})/3, C = (C_{44} + C_{55} + C_{66})/3$$



$$B_{\text{Voigt}} = (A + 2B)/3$$

e.g. for cubic $(C_{11} + 2C_{12})/3$

$$G_{\text{Voigt}} = (A - B + 3C)/5$$

e.g. for cubic $(C_{11} - C_{12} + 3C_{44})/5$

Reuss (averaging $S_{ij} = C_{ij}^{-1}$):

$$A' = (S_{11} + S_{22} + S_{33})/3, B' = (S_{23} + S_{13} + S_{12})/3, C' = (S_{44} + S_{55} + S_{66})/3$$



$$B_{\text{Reuss}} = 1/(3[A' + 2B'])$$

e.g. for cubic $(C_{11} + 2C_{12})/3$

$$G_{\text{Reuss}} = 5/(4[A' - B'] + 3C')$$

e.g. for cubic $5/(4/[C_{11} - C_{12}] + 3/C_{44})$

Relation of $[C]$ and elastic moduli

simplification due to symmetries of some crystal systems

$$A = (C_{11} + C_{22} + C_{33})/3, B = (C_{23} + C_{13} + C_{12})/3, C = (C_{44} + C_{55} + C_{66})/3$$

$$A' = (S_{11} + S_{22} + S_{33})/3, B' = (S_{23} + S_{13} + S_{12})/3, C' = (S_{44} + S_{55} + S_{66})/3$$

Formulas include 9 (not all 21) comp. C_{ij} a S_{ij} . Even less of them are independent (cubic 3, trigonal & hexagonal 5, tetragonal 6)

Tetragonal with 6 × 7 components C_{ij} : difference in the comp. C_{16} which is not explicitly included in formulas on previous slide
⇒ the same formulas for Voigt limits as functions of C_{ij}
⇒ the same formulas for Reuss limits as functions of S_{ij}

Trigonal with 6 × 7 components C_{ij} (and hexagonal): difference in C_{15} (and C_{14}) which is not on previous slide ⇒ same formulas

Orthorhombic, monoclinic and triclinic: all 9 components C_{ij} from previous slide are independent ⇒ same formulas

Relation of $[C]$ and elastic moduli

simplification due to symmetries of some crystal systems

Tetragonal with 6×7 components C_{ij}

Trigonal with 6×7 components C_{ij} (and hexagonal)

Orthorhombic, monoclinic and triclinic

⇒ the same formulas for Voigt limits as functions of C_{ij}

⇒ **the same formulas for Reuss limits as functions of S_{ij}**

Although some components of C_{ij} , e.g. C_{14} for trigonal, are not in Voigt formulas, they are hidden in the calculation of $S_{ij} = C_{ij}^{-1}$

⇒ **different formulas for Reuss limits as functions of C_{ij}** ,
differences between aforementioned crystals start to play role
(see two following slides for some of them)

Relation of [C] and elastic moduli

user format (for selected crystal systems)

$B_{\text{Voigt}} =$

$$(C_{11} + 2C_{12})/3$$

[cubic]

$$(2C_{11} + 2C_{12} + C_{33} + 4C_{13})/9$$

[hexagonal, trigonal, tetragonal]

$B_{\text{Reuss}} =$

$$(C_{11} + 2C_{12})/3$$

[cubic]

$$c^2/M$$

[hexagonal, trigonal, tetragonal]

where $c^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2$ a $M = C_{11} + C_{12} + 2C_{33} - 4C_{13}$
(in some sources c instead of c^2)

Relation of [C] and elastic moduli

user format (for selected crystal systems)

$G_{\text{Voigt}} =$

$$(C_{11} - C_{12} + 3C_{44})/5$$

[cubic]

$$(M + 12C_{44} + 12C_{66})/30$$

[hexagonal, trigonal] where $C_{66} = (C_{11} - C_{12})/2$

$$(7C_{11} - 5C_{12} - 4C_{13} + 2C_{33} + 12C_{44})/30$$

[hexagonal, trigonal] after subst. for M and C_{66}

$$(M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66})/30$$

[tetragonal]

$G_{\text{Reuss}} =$

$$5/(4/[C_{11} - C_{12}] + 3/C_{44})$$

[cubic]

$$5c^2 C_{44} C_{66} / (6B_{\text{Voigt}} C_{44} C_{66} + 2c^2 [C_{44} + C_{66}])$$

[hexagonal]

$$5c^2 (C_{44} C_{66} - C_{14}^2) / (6B_{\text{Voigt}} [C_{44} C_{66} - C_{14}^2] + 2c^2 [C_{44} + C_{66}])$$

[trigonal 6]

$$5c^2 (C_{44} C_{66} - C_{14}^2 - C_{15}^2) / (6B_{\text{Voigt}} [C_{44} C_{66} - C_{14}^2 - C_{15}^2] + 2c^2 [C_{44} + C_{66}])$$

[trigonal 7]

$$5/(6B_{\text{Voigt}}/c^2 + 2/[C_{11} - C_{12}] + 2/C_{44} + 1/C_{66})$$

[tetragonal 6]

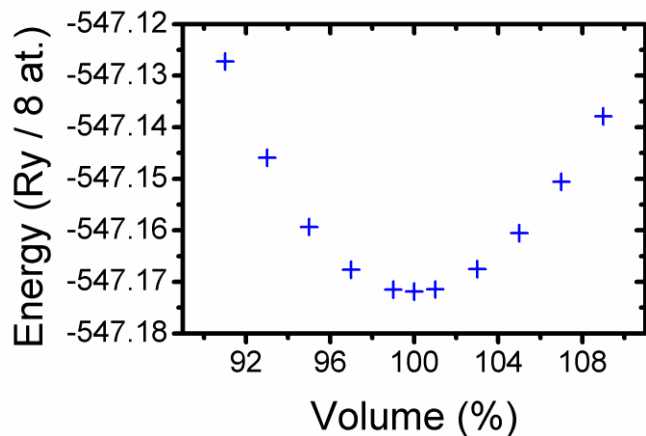
$$5/(6B_{\text{Voigt}}/c^2 + 2/[C_{11} - C_{12}] + 2/C_{44} + \{[C_{11} - C_{12}]^2 + 4C_{16}^2\} / \{[C_{11} - C_{12}]^2 C_{66} - 2\{C_{11} - C_{12}\} C_{16}^2\})$$

[tet. 7]

Relation of B and mater. deformation

Assume change of materials volume (compression) at fixed ratios of lengths of lattice vectors and angles between them

Let's calculate ground state energy (i.e. wavefunction optimization) for several volumes V (example for TiN) ...

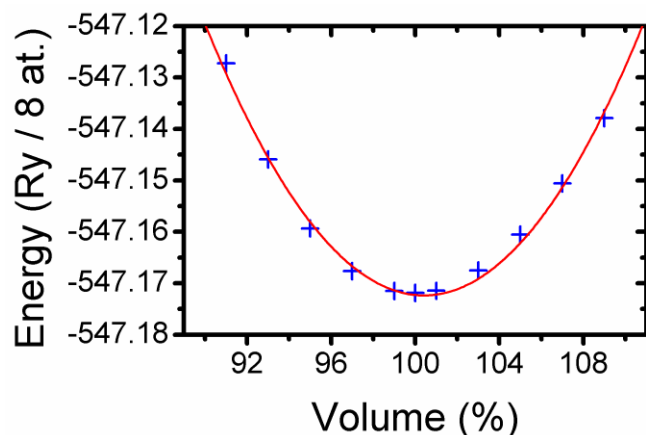


... and fit proper curve $E(V)$

Relation of B and mater. deformation

Definition $B = [d^2(E/V_0)/d(V/V_0)^2]_{V_0} = V_0[d^2E/dV^2]_{V_0}$

$\Rightarrow$ Parabolic fir seems natural $E = E_0 + \frac{1}{2} B (V-V_0)^2 / V_0$



$$B = 277 \text{ GPa}$$

$$V_0 = 100.42 \% \text{ of first assumption}$$

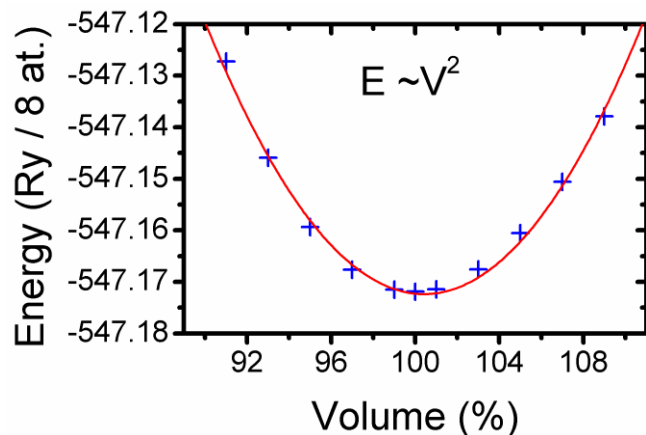
$$a_0 = 4.255 \text{ \AA}$$

Parabolic fir is not exact, because B is pressure dependent:

$$B = B_0 + B'P, \text{ where}$$

- B_0 is the value of B for preferred volume V_0 (zero pressure)
- B' is derivative of B by pressure P (typically around 4 [-])

Relation of B and mater. deformation



$$B = 277 \text{ GPa}$$

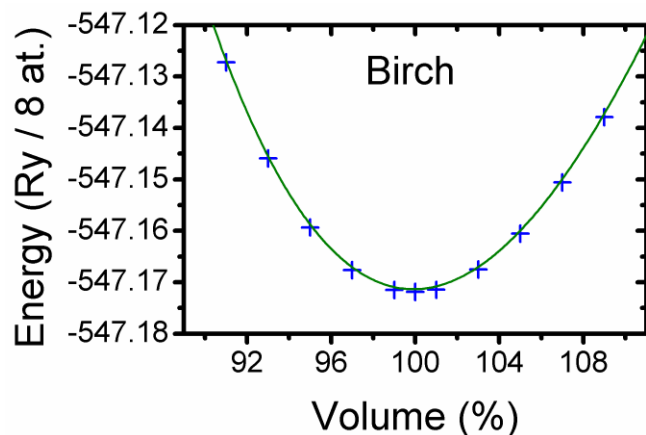
$$V_0 = 100.42 \% \text{ of first assumption}$$

$$a_0 = 4.255 \text{ \AA}$$

$$B' = 0 \text{ (assumption)}$$

Better fit can be obtained e.g. by **Birch equation of state**

$$E = E_0 + 9/8 B_0 V_0 ([V_0/V]^{2/3} - 1)^2 + 9/16 B_0 (B' - 4) V_0 ([V_0/V]^{2/3} - 1)^3$$



$$B_0 = 272 \text{ GPa}$$

$$V_0 = 99.92 \% \text{ of first assumption}$$

$$a_0 = 4.248 \text{ \AA}$$

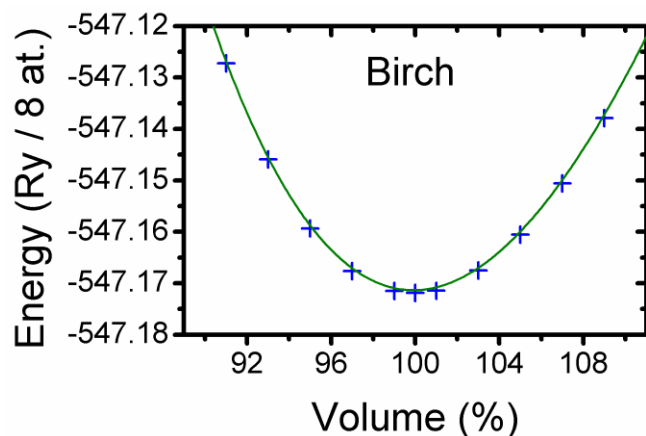
$$B' = 4.2$$

Despite "similar" curves, differences in B_0 & a_0 are measurable

Relation of B and mater. deformation

Better fit can be obtained e.g. by **Birch equation of state**

$$E = E_0 + 9/8 B_0 V_0 ([V_0/V]^{2/3} - 1)^2 + 9/16 B_0 (B' - 4) V_0 ([V_0/V]^{2/3} - 1)^3$$



$$B_0 = 272 \text{ GPa}$$

$$V_0 = 99.92 \% \text{ of first assumption}$$

$$a_0 = 4.248 \text{ \AA}$$

$$B' = 4.2$$

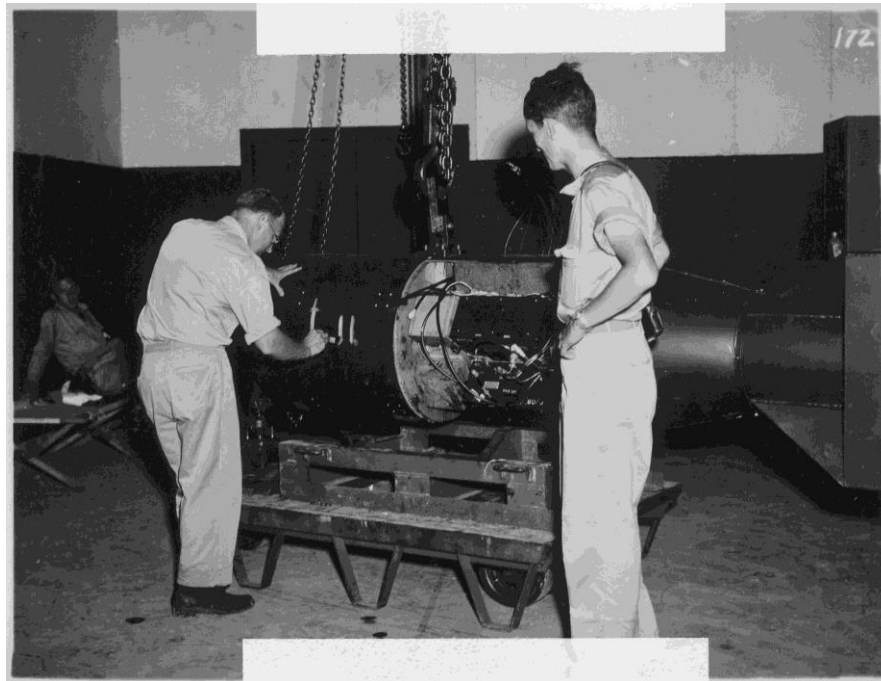
Values of B'

- often $B' \approx 4$
- sometimes $B' < 0$ (pressure induced softening in some range), associated with negative thermal expansion coefficient (chapter 3)

Relation of B and mater. deformation

Better fit can be obtained e.g. by **Birch equation of state**

$$E = E_0 + 9/8 B_0 V_0 ([V_0/V]^{2/3} - 1)^2 + 9/16 B_0 (B' - 4) V_0 ([V_0/V]^{2/3} - 1)^3$$



Los Alamos 1945: Jens Birch took a leave at Harvard, and
- as a Lieutenant Commander of US Navy - works on the bomb
Little Boy of Hiroshima (on the right Norman Ramsey, NC 1989).

Relation of B and mater. deformation

There are more equations of state

a) the traditional Murnaghan's equation of state

$$E_{\text{Murn}}(V) = -E_0 + \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1}$$

b) the Birch's equation

$$E_{\text{Birch}}(V) = -E_0 + \frac{9}{8} B_0 V_0 [(V_0/V)^{2/3} - 1]^2 + \frac{9}{16} B_0 V_0 (B'_0 - 4) [(V_0/V)^{2/3} - 1]^3$$

c) and the Vinet's equation

$$E_{\text{Vinet}}(V) = -E_0 + \frac{-4B_0 V_0}{(B'_0 - 1)^2} \left[1 - \frac{3}{2} (B'_0 - 1) \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] \right] \exp \left[\frac{3}{2} (B'_0 - 1) \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] \right].$$



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Phase stabilities of self-organized nc-TiN/a-Si₃N₄ nanocomposites and of Ti_{1-x}Si_xN_y solid solutions studied by *ab initio* calculation and thermodynamic modeling

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	Present calculation			
	Directly	Mumaghan	Birch–Murnaghan	Vinet
fcc-TiN				
V_0 (Å ³)	77.1456	76.940	77.068	77.1619
E_0 (eV)	-78.0994	-78.0688	-78.0949	-78.1052
B_0 (GPa)		275.7852	291.4567	297.6469
B'_0		4.734	4.543	4.433
β-Si ₃ N ₄				
V_0 (Å ³)	148.786	148.799	148.745	148.72709
E_0 (eV)	-115.1575	-115.1543	-115.1564	–
B_0 (GPa)		237.207	240.1785	241.471
B'_0		3.902	3.992	4.02129

Relation of C_{ij} and mater. deformation

Again, express energy as a function of deformation (more generally, not isotropic deformation $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \delta$ used above)

$$\Delta E/V_0 = \sum_i \sum_j \frac{1}{2} C_{ij} \varepsilon_i \varepsilon_j \quad (\text{see above}),$$

and apply as many deformation tensors, as many independent components of C_{ij} are we looking for

$$[\epsilon] = \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ 2\epsilon_{23} \\ 2\epsilon_{13} \\ 2\epsilon_{12} \end{bmatrix} \equiv \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix}$$

Diagonal terms (C_{11} , C_{22} , etc.) can be calculated by single def.
Non-diagonal terms (C_{12} , C_{13} , etc.) from system of equations.

It is welcomed when a deformation $[\epsilon]$ preserves

- fixed volume
- crystal symmetry

How to calculate [C] - cubic system

3 independent components C_{11} , C_{12} , $C_{44} \Rightarrow$ 3 def. tensors
(one of them can be that one which is anyway used for
- usually preceding - calculation of B and a_0)

$$\Delta E/V_0 = \sum_i \sum_j \frac{1}{2} C_{ij} \varepsilon_i \varepsilon_j =$$

$$\frac{1}{2} C_{11} (\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2) + C_{12} (\varepsilon_1 \varepsilon_2 + \varepsilon_2 \varepsilon_3 + \varepsilon_3 \varepsilon_1) + \frac{1}{2} C_{44} (\varepsilon_4^2 + \varepsilon_5^2 + \varepsilon_6^2)$$

	[ε]	$\Delta E/V_0$	note
1	$\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \delta$	$\frac{3}{2}(C_{11} + 2C_{12})\delta^2$ cross-check from the definition of B : $\frac{1}{2}(\Delta V/V_0)^2 B = \frac{1}{2}(3\delta)^2 B = \frac{9}{2}\delta^2 B$	see calc. of B : for cubic system $B = (C_{11} + 2C_{12})/3$
2	$\varepsilon_1 = \delta, \varepsilon_2 = -\delta,$ $\varepsilon_3 = \delta^2/(1 - \delta^2)$	$(C_{11} - C_{12})\delta^2 + O[\delta^3]$	volume conserving
3	$\varepsilon_3 = \delta^2/(4 - \delta^2)$ $\varepsilon_6 (2\varepsilon_{12}) = \delta$	$\frac{1}{2}C_{44}\delta^2 + O[\delta^3]$	volume conserving

There is an important possibility to decrease the error to $O[\delta^4]$
by averaging energies calculated for δ and $-\delta$

How to calculate [C] - tetragonal sys.

6 independent comp. $C_{11}=C_{22}$, C_{12} , $C_{13}=C_{23}$, C_{33} , $C_{44}=C_{55}$, C_{66}
 $\Rightarrow$ 6 deformation tensors (again: or 5 + 1 used for B_0 , a_0)

	$[\varepsilon]$	$\Delta E/V_0$	note
1	$\varepsilon_1 = \varepsilon_2 = \delta$	$(C_{11}+C_{12})\delta^2 + O[\delta^3]$	
2	$\varepsilon_1 = \varepsilon_2 = \delta$, $\varepsilon_3 = -\delta(2+\delta)/(1+\delta)^2$	$(C_{11}+C_{12}+2C_{33}-4C_{13})\delta^2 + O[\delta^3]$	
3	$\varepsilon_3 = \delta$	$\frac{1}{2}C_{33}\delta^2 + O[\delta^3]$	
4	$\varepsilon_1 = [(1+\delta)/(1-\delta)]^{0.5} - 1$, $\varepsilon_2 = [(1-\delta)/(1+\delta)]^{0.5} - 1$	$(C_{11}-C_{12})\delta^2 + O[\delta^4]$	
5	$\varepsilon_3 = \delta^2/4$ $\varepsilon_4 (2\varepsilon_{23}) = \varepsilon_5 (2\varepsilon_{13}) = \delta$	$C_{44}\delta^2 + O[\delta^4]$	example of aforementioned efforts to preserve symmetry (non-zero ε_4 and ε_5 , although only ε_4 or ε_5 would be enough)
6	$\varepsilon_1 = \varepsilon_2 = (1+\delta^2/4)^{0.5} - 1$, $\varepsilon_6 (2\varepsilon_{12}) = \delta$	$\frac{1}{2}C_{66}\delta^2 + O[\delta^4]$	

There is an important possibility to decrease the error to $O[\delta^4]$ by averaging energies calculated for δ and $-\delta$

How to calculate [C] - hexagonal sys.

5 independent comp. $C_{11}=C_{22}$, C_{12} , $C_{13}=C_{23}$, C_{33} , $C_{44}=C_{55}$
 $\Rightarrow$ 5 deformation tensors (again: or 4 + 1 used for B_0 , a_0)

Deformations can be the same as used or tetragonal system
(i.e. let's omit another table); 5 deformations is enough because
here $C_{66} = \frac{1}{2}[C_{11}-C_{12}]$

How to calculate [C] - hexagonal sys.

Important "peculiarity": consider deformation tensor $\varepsilon_4 = \delta$

- for perpendicular vectors, δ is the change of angle (in rad.)

$$\begin{vmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{vmatrix} \times \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & \delta/2 \\ 0 & \delta/2 & 1 \end{vmatrix} = \begin{vmatrix} a & 0 & 0 \\ 0 & b & b\delta/2 \\ 0 & c\delta/2 & c \end{vmatrix}$$

the order of multiplication is valid for row lattice vectors
for column lattice vectors
(also frequent convention) the order has to be opposite

i.e. $\cos \alpha = \delta$ (scalar product of 2nd and 3rd vector) $\Rightarrow \alpha = 90^\circ - \delta$

- in the case of hexagonal system we get

$$\begin{vmatrix} a & 0 & 0 \\ -a/2 & \sqrt{3}a/2 & 0 \\ 0 & 0 & c \end{vmatrix} \times \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & \delta/2 \\ 0 & \delta/2 & 1 \end{vmatrix} = \begin{vmatrix} a & 0 & 0 \\ -a/2 & \sqrt{3}a/2 & \sqrt{3}a\delta/4 \\ 0 & c\delta/2 & c \end{vmatrix}$$

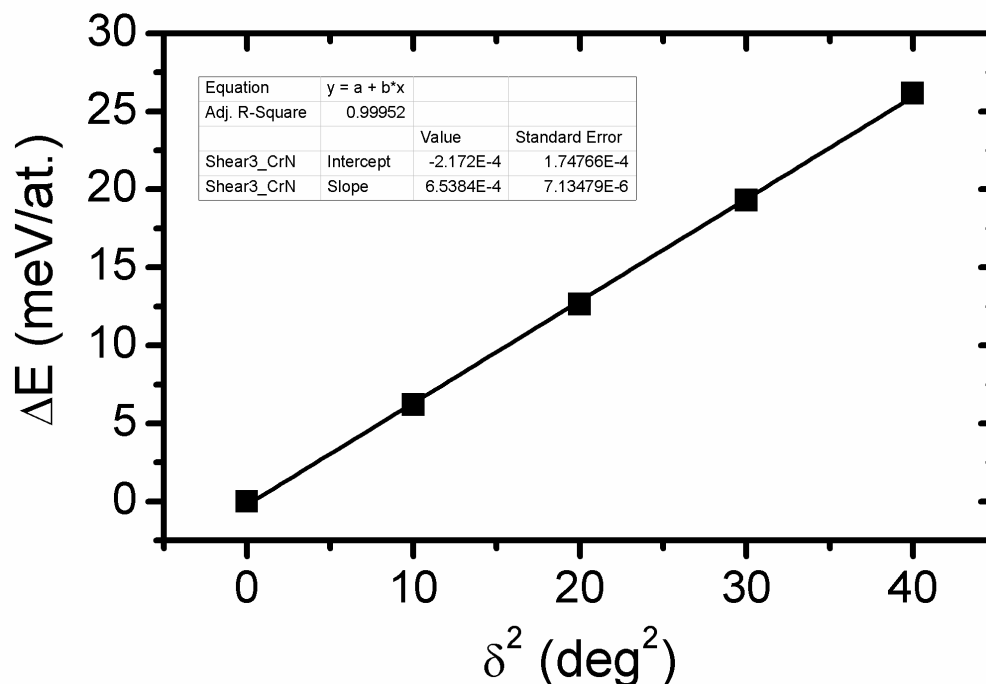
i.e. $\cos \alpha = \sqrt{3}\delta/2 \Rightarrow \alpha = 90^\circ - \sqrt{3}\delta/2$

If the construction of deformed hexagonal cell included incorrect angle change of δ and not of $\sqrt{3}\delta/2$, we would get

$$\Delta E/V = \frac{1}{2}C_{44_{\text{right}}} (2\delta/\sqrt{3})^2 = \frac{1}{2}C_{44_{\text{wrong}}} \delta^2, \text{ i.e. } C_{44_{\text{right}}} = \frac{3}{4} C_{44_{\text{wrong}}}$$

How to calculate [C] - example

Cubic CrN, the above deformation $\varepsilon_3 = \delta^2/(4-\delta^2)$, $\varepsilon_6 (2\varepsilon_{12}) = \delta$ with the aim to find $C_{44} (= C_{55} = C_{66})$: $\Delta E/V_0 = \frac{1}{2}C_{44}\delta^2$



Similarly like for B and a_0 : the fit has to be VERY good for exact C_{ij} (correlation ≥ 0.9995 for the present range and number of points therein; e.g. 0.99 is catastrophically low)

Born stability criteria

Relationships which have to hold in order to allow material's existence (in stable or metastable state). In general

$$\sum_i \sum_j \frac{1}{2} C_{ij} \varepsilon_i \varepsilon_j > 0 \text{ for any deformation } [\varepsilon]$$

Cubic system:

$$C_{11} + 2C_{12} > 0$$

$$C_{11} - C_{12} > 0$$

$$C_{44} > 0$$

Hexagonal and tetragonal system

$$(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0$$

$$C_{11} - C_{12} > 0$$

$$C_{44} > 0$$

$$C_{66} > 0 \text{ (for hexagonal guaranteed by } C_{66} = \frac{1}{2}[C_{11} - C_{12}])$$

Uniqueness of calculated results (contrary to "differently well" performed experiments)

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(ENGLISH LETTERS)
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Theoretical study of the elastic properties of titanium nitride

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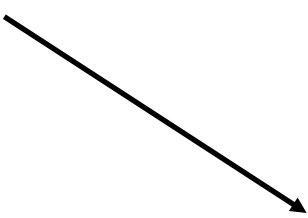
The equilibrium lattice parameter, relative volume V/V_0 , elastic constants C_{ij} , and bulk modulus of titanium nitride are successfully obtained using the *ab initio* plane-wave pseudopotential (PW-PP) method within the framework of density functional theory. The quasi-harmonic Debye model, using a set of total energy *vs* molar volume obtained with the PW-PP method, is applied to the study of the elastic properties and vibrational effects. We analyze the relationship between the bulk modulus and temperature up to 2000 K and obtain the relationship between bulk modulus B and pressure at different temperatures. It is found that the bulk modulus B increases monotonously with increasing pressure and decreases with increasing temperature. Moreover, the Debye temperature is determined from the non-equilibrium Gibbs functions.

KEY WORDS Elastic constants; Debye temperature; *Ab initio* calculations; Titanium nitride

1 Introduction

Like most refractory transition metal nitrides, TiN has a NaCl-type structure (space group FM-3M). The Ti atom occupies the 1a (0, 0, 0) site, and the N atom occupies the 1b (0, 0.5, 0) site. It has been widely used as coating owing to its special properties such as high melting point, high hardness, high corrosion resistance, high specific strength and metallic conductivity^[1-3]. However, TiN coatings are usually subject to high internal stresses between the coating and the substrate. High internal stress will reduce bonding strength between the substrate and the coating layer. Only when the elastic constants are known, the internal stress can be determined by X-ray diffraction. Sometimes, the same residual stress in the literature may associate with quite different strains. For example, for the well-known thin film TiN, its Young's modulus is widely accepted as 640 GPa^[4] in Europe, however, in Japan, the value is 250 GPa^[5,6].

The single-crystal elastic constants of solids are essential for the interpreting seismic wave velocities and their lateral variations. A study of the elastic properties for materials



For example,
for the well-known thin film TiN, its Young's modulus is widely accepted as 640 GPa^[4] in Europe, however, in Japan, the value is 250 GPa^[5,6].

Agreement of theory and experiment

■ Calculation for TiN

[from elastic tensor -

J. Houska et al., J. Phys.: Condens. Matter 21, 285302 (2009)]

$B = 274 \text{ GPa}$ (bulk modulus)

$G = 191 \text{ GPa}$ (shear modulus)

$E = 464 \text{ GPa}$ (Young's modulus)

■ Experiment for TiN

[surf. Brillouin scattering, vibrating reed - S. Veprek et al., J. Phys. Chem. Solids 71, 1175 (2010)]

$B = 295 \pm 25 \text{ GPa}$

$G = 190 \pm 15 \text{ GPa}$

$E = 445 \pm 15 \text{ GPa}$

- It is necessary to measure the moduli correctly (e.g. by more demanding - but more reliable - techniques than indentation)
- It is necessary to measure "correct material" (without impurities, defects, content of amorphous phase, etc.)

Hardness

one of few exclamation marks in the presentation

Contrary to elastic moduli, this is not a physical quantity !
So it is not exactly part of solid state physics (but it should be part of a lecture about mechanical properties) ... so only briefly



Dependence on the way of processing the loading-unloading curves. Stormy debates.



Hardness

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Dependence on the way of processing the loading-unloading curves. Stormy debates, for illustration:

dr. Fischer-Cripps: *"using our new technique of processing the Veprek's loading-unloading curves, we get hardness of his nc-TiN/Si₃N₄ of 55 GPa, not his claim of 100 GPa"*

prof. Veprek: *"I explained to you years ago that hardness of diamond measured using your technique is 55 GPa as well, so we prepared materials as hard as diamond anyway ... and furthermore, your technique leads to less correct value of Young's modulus of superhard materials"*

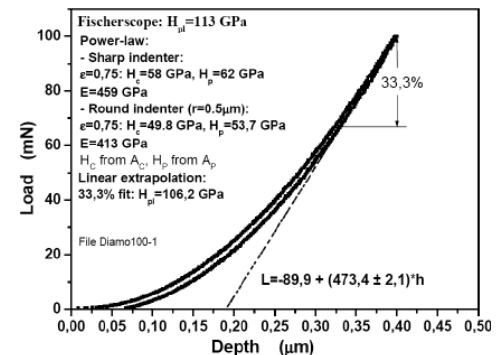
Critical review of claims for ultra-hardness in nanocomposite coatings

A.C. Fischer-Cripps^a, S.J. Bull^b & N. Schwarzer^c
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Available online: 07 Feb 2012



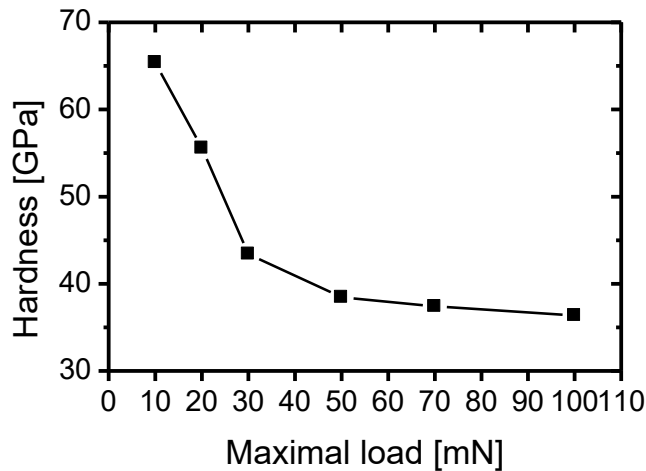
Hardness

one of few exclamation marks in the presentation

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Dependence on maximum load used for the indentation.



Example for SiBCN (7.2 μm thick)
[figure from thesis of J.H.]

Fortunately, indentation yields also the Young's modulus, which is - contrary to hardness - physical quantity and as such can be independently checked by other techniques and calculations.

Hardness

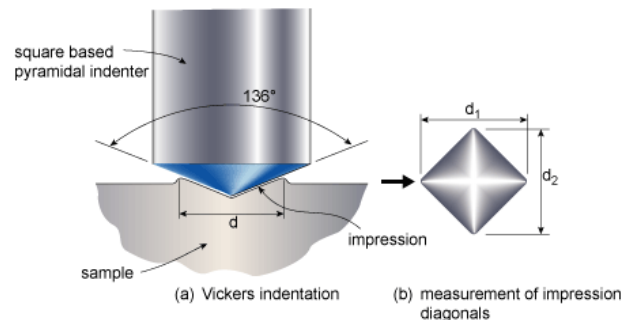
Which elastic modulus best correlates with hardness?

For a long time, bulk modulus **B** was a candidate ($\Rightarrow$ and candidate for hard-as-diamond material [$B = 443$ GPa] was/is β - C_3N_4 [predicted - Liu and Cohen - $B = 427$ GPa])

Counterexample: metals with high-density of valence electrons (right part of the table) have high B (dense cloud of electrons is difficult to compress), but low hardness. E.g. Os has $B = 395$ - 462 GPa (like diamond), but $H = 4$ GPa (diamond 100 GPa).

Better correlation with hardness exhibits shear modulus **G** .

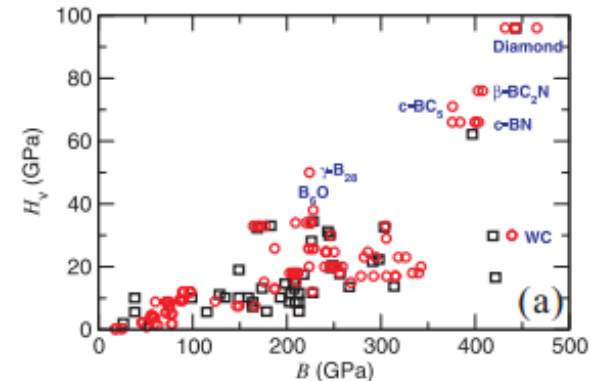
No surprise - shear is what we perform when indenting a tip into material.



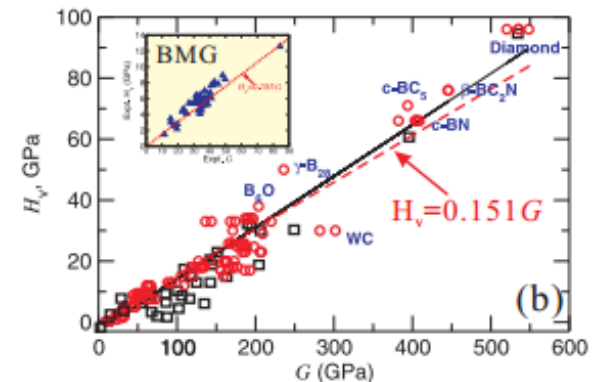
Hardness

Which elastic modulus best correlates with hardness?

For a long time, bulk modulus ***B*** was a candidate



Better correlation with hardness exhibits shear modulus ***G***



More ambitious empirical formulas exist as well, e.g. in the cited paper

$$H = 2(G^3/B^2)^{0.585} - 3$$



Modeling hardness of polycrystalline materials and bulk metallic glasses

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Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Wenhua Road No. 72, Shenyang 110005, Liaoning, PR China

Hardness

The topic is even more complicated when it does not include only small deformations of ideal crystals. Again, for illustration:

1953 A.H. Cottrell:

Work hardening was the first problem to be attempted by dislocation theory and may be the last to be solved

2003 U.F. Kocks & H. Mecking:

Work hardening is as hopeless as ever

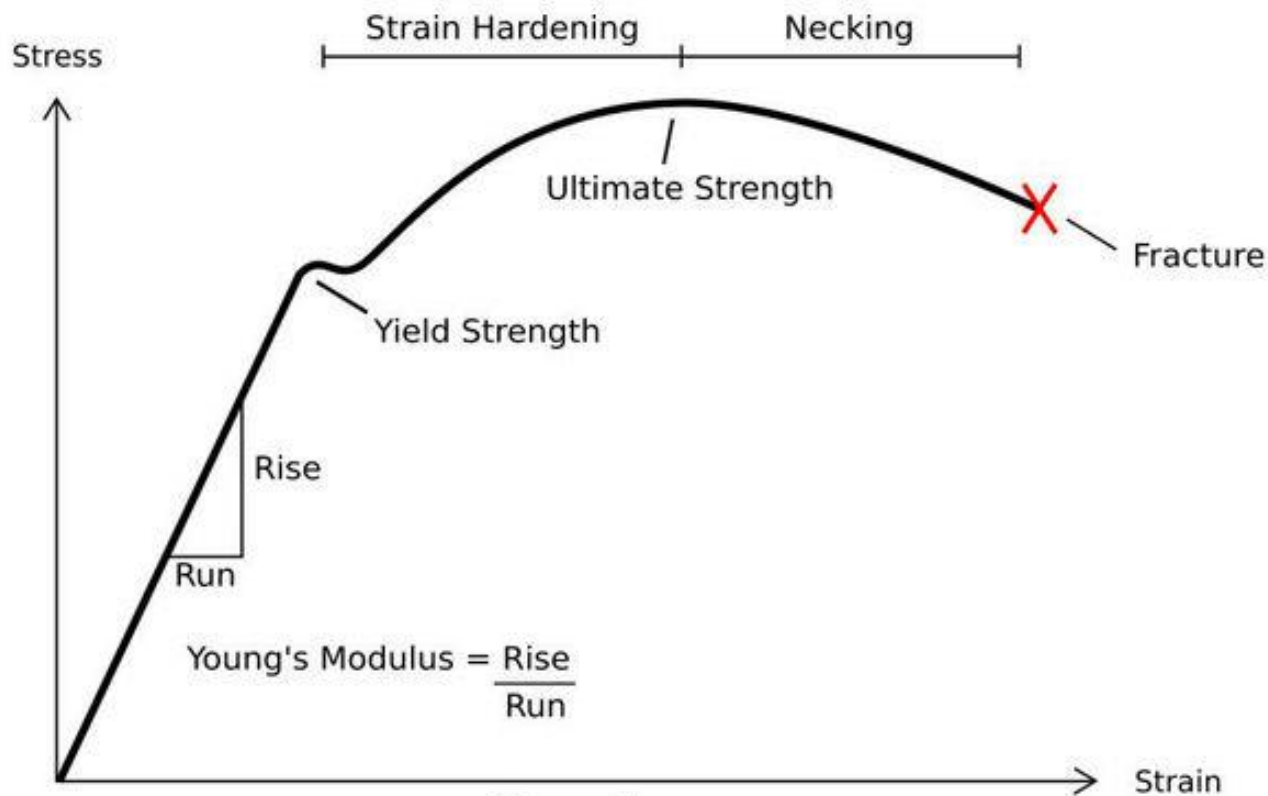
2009 L. Kubin:

There is presently no generally accepted theory explaining how and why organized dislocation microstructures emerge during plastic flow

[presentation of K. Davoudi 2015]

Other mechanical properties

What is the difference between **ductility** and **toughness**?



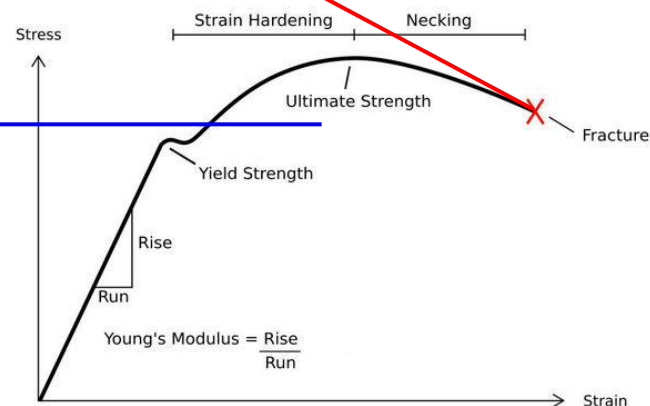
Other mechanical properties

What is the difference between **ductility** and **toughness**?

Ductility says how high deformation (geometrically - regardless the deformation energy) can be absorbed by the material (x-coordinate of the end of curve)

Toughness says how high deformation energy can be absorbed by the material (area below the curve)

Thus, the quantities are not proportional - for high toughness we need not only high ductility, but also high strength



Other mechanical properties

How long fiber of various materials (for now alphabetically) tears due to its own weight in the Earth's gravity field?

Material

Ag

Al

Au

Cu

Fe

kevlar fiber

nylon fiber

steel
(strongest found)

spider fiber
(example)

Pb

glass

Ti

carbon fiber
(really produced)

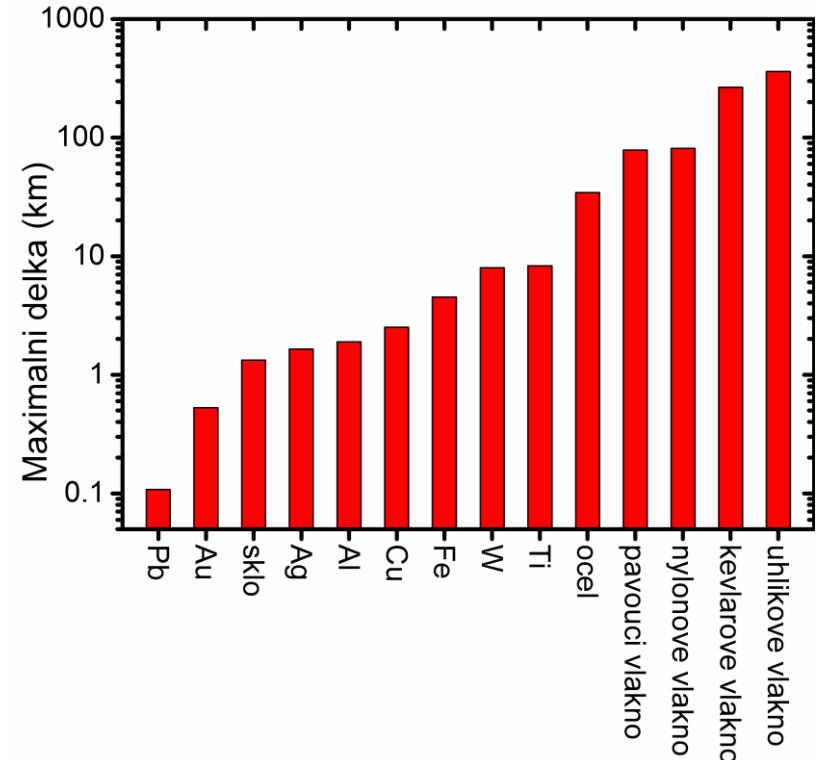
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Other mechanical properties

How long fiber of various materials (for now alphabetically) tears due to its own weight in the Earth's gravity field?

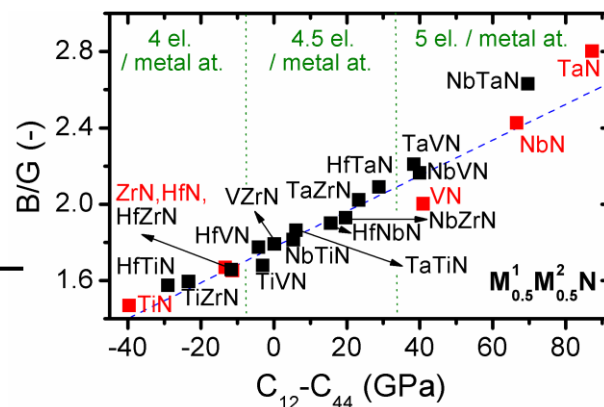
$$d_{\max} = \sigma_{\max} / (\rho \cdot g)$$

Material	Ultimate tensile strength (MPa)	Density (gcm ⁻³)	Maximal length (km)
Pb	12	11.35	0.11
Au	100	19.32	0.53
sklo	33	2.53	1.3
Ag	170	10.5	1.7
Al	50	2.7	1.9
Cu	220	8.92	2.5
Fe	350	7.87	4.5
W	1510	19.25	8.0
Ti	370	4.54	8.3
steel (strongest found)	2693	8	34
spider fiber (example)	1000	1.3	78
nylon fiber	900	1.13	81
kevlar fiber	3757	1.44	266
carbon fiber (really produced)	6370	1.8	361



Other mechanical properties

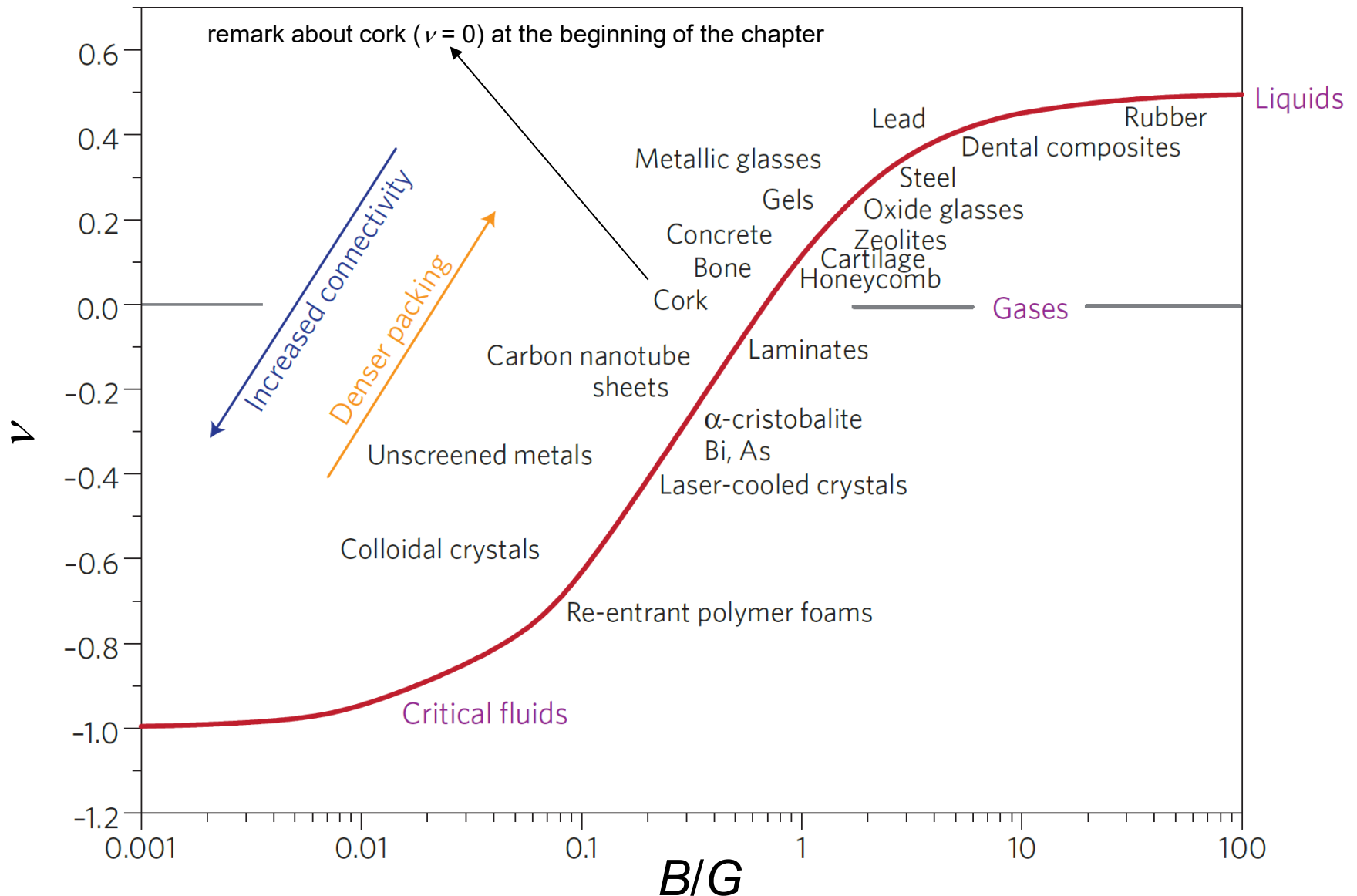
- Ratio B/G : ~ductility
- Cauchy pressure, for cubic system $C_{12}-C_{44}$:
also ~ductility (sometimes directly
limit $C_{12}-C_{44} > 0 \Leftrightarrow$ ductile)
 - thus, these quantities are also mutually proportional
 - for similar materials both of them increase with valence el. density



[Petrman et al., J. Mater. Sci. 48, 7642 (2013)]

- Ratio H/E : officially ~elastic strain to failure
(e.g. Leyland a Mathews 2000)
- Ratio H^3/E^2 : officially ~resistance to plastic deformation
(e.g. Tsui 1995; overlaps with definition of H)

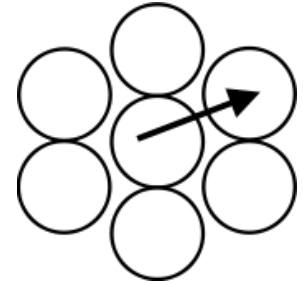
Achievable mechanical properties



Relationship of ductility and structure

Deformation (of ductile materials) most easily takes place along slip planes - planes with high atomic density, ideally close packed

Slip plane + slip direction in the slip plane
= slip system

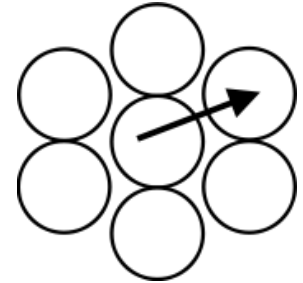


Von Mises criterion for ductile material:
at least **5 different slip systems**. Why this number?

Relationship of ductility and structure

Deformation (of ductile materials) most easily takes place along slip planes - planes with high atomic density, ideally close packed

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= slip system



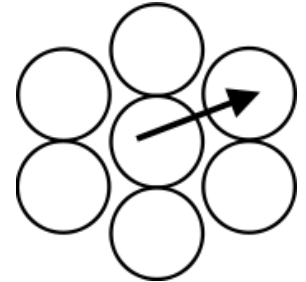
Von Mises criterion for ductile material:
at least **5 different slip systems**. Why this number?

Deformation tensor has 6 components ε_{ij} (see above). Fixed volume (we are interested in deformation changing only shape) $\Rightarrow$ 5 independent components. Thus, 5 different slip systems are necessary in order to easily realize any small deformation (by each crystal in polycrystalline material) without cracking.

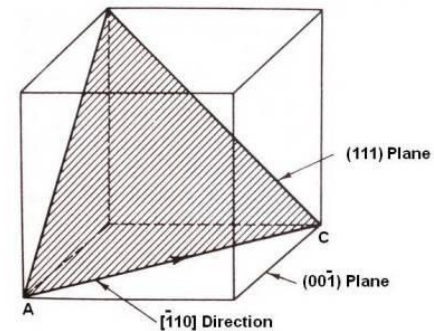
Relationship of ductility and structure

Von Mises criterion for ductile material: 5 different slip systems.

Structure hcp: 1 slip plane (close packed)
× 3 slip directions = 3 slip
systems $\Rightarrow$ brittle



Structure fcc: 4 slip planes (close packed {111})
× 3 slip directions = 12 slip
systems $\Rightarrow$ ductile
(e.g. γ -Fe, austenite)



Structure bcc: 48 slips systems, but (i) too many - they interfere
and (ii) slip planes are not close packed $\Rightarrow$
compared to fcc relatively brittle (e.g α -Fe, ferrite)

Relationship of ductility and structure

The aforementioned criterion is consistent e.g. with Poisson's ratio ν . In the table for selected transition metals, including

- four with the highest ν (Au, Nb, Pd, Pt)

(easily deform)

⇔ predominantly fcc

- four with the lowest ν (Zn, Os, Y, Cr)

(do not deform, rather crack)

⇔ predominantly hcp

symbol	ν	structure
Au	0.44	fcc
Nb	0.4	bcc
Pd	0.39	fcc
Pt	0.38	fcc
...	...	...
Ag	0.37	fcc
...	...	...
Cu	0.34	fcc
...	...	...
Fe	0.29	bcc
...	...	...
Zn	0.25	hcp
Os	0.25	hcp
Y	0.24	hcp
Cr	0.21	bcc

Relationship of ductility and poetry

Au, Ag, Cu combine non-reactivity (note the full d-orbital) with deformability (fcc structure, and weak covalent bonds - again note the full d-orbital), therefore good for craftsmen

Relatively harder iron is used differently



Rudyard Kipling



Cold Iron

Gold is for the mistress, silver for the maid,
Copper for the craftsman cunning at his trade.
"Good!" said the Baron, sitting in his hall,
"But Iron, Cold Iron, is master of them all."

Stříbro je pro děvčátko, zlato je pro paní,
měď, ta je pro umělce, jenž zná se v tepání
"Dobrá," řekl si baron, v své tvrzi zakopán,
"ale železo, chladné železo, je všeho světa pán."

symbol	ν	structure
Au	0.44	fcc
Nb	0.4	bcc
Pd	0.39	fcc
Pt	0.38	fcc
...	...	...
Ag	0.37	fcc
...	...	...
Cu	0.34	fcc
...	...	...
Fe	0.29	bcc
...	...	...
Zn	0.25	hcp
Os	0.25	hcp
Y	0.24	hcp
Cr	0.21	bcc

Speed of sound

Let's start with derivation of Newton's formula (developed for gas; see the next slide for solids - but the principle is the same)

Pressure wave passes through the cube in figure for $dt = dx/v$, for this time the forces acting on the front and the back face are different.

Resulting force is $dF = -dPdydz$,
mass of cube is $dm = \rho dx dy dz$

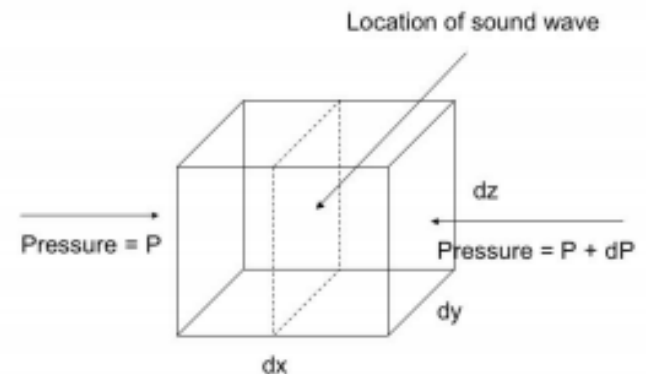


acceleration is $dv = dF \cdot dt / dm = -dP / (\rho v)$

Continuity equation $\rho v = \text{konst.} \Rightarrow \rho dv + v d\rho = 0 \Rightarrow dv = -v d\rho / \rho$



$$v^2 = dP / d\rho$$



Speed of sound (more specifically)

In the case of gas (and liquid) the stress (pressure P) is isotropic. The resulting deformation (stress-strain relationship) is therefore described by the bulk modulus $B = -V.dP/dV$ (complementary to the aforementioned definition B via dE). Liquid has some B , in the case of isothermic gas $B = P$.

$$P \text{ (gas)} = B \text{ (liquid)} = -V.dP/dV$$

$$\text{utilize } \rho.V = \text{konst.} \Rightarrow V/dV = \rho/d\rho$$

$$P \text{ (gas)} = B \text{ (liquid)} = \rho.dP/d\rho$$

$$\text{substitute to } v^2 = dP/d\rho \text{ (previous slide)}$$

$$v^2 = B/\rho$$

In the case of solid, the isotropic pressure P is replaced by anisotropic stress σ (stress tensor σ), and the bulk modulus B is replaced in the formula by another elastic modulus M :

$$v^2 = M/\rho$$

Speed of sound (more specifically)

$$v^2 = B/\rho$$

In the case of solid, the isotropic pressure P is replaced by anisotropic stress σ (stress tensor σ), and the bulk modulus B is replaced in the formula by another elastic modulus M :

$$v^2 = M/\rho$$

Shear wave:

$$M = G$$

Longitudinal wave in 1D case:

$$M = E$$

Longitudinal wave in 3D case:

$$M = \sigma_1/\varepsilon_1 \text{ for } \varepsilon_{2-6} = 0$$

(see next slide)

Important for elastic moduli measurements (not by indentation)

Speed of sound (more specifically)

Longitudinal wave in 3D case ($\sigma_1/\varepsilon_1 = ?$ for $\varepsilon_{2-6} = 0$)

From Hooke's law applied to isotropic materials, or basically from definition of E and ν

$$(\sigma_1 - \nu\sigma_2 - \nu\sigma_3)/E = \varepsilon_1$$

$$(-\nu\sigma_1 + \sigma_2 - \nu\sigma_3)/E = \varepsilon_2 = 0$$

$$(-\nu\sigma_1 - \nu\sigma_2 + \sigma_3)/E = \varepsilon_3 = 0$$

$$\begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ 2\varepsilon_{23} \\ 2\varepsilon_{13} \\ 2\varepsilon_{12} \end{bmatrix} = \begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ \gamma_{23} \\ \gamma_{13} \\ \gamma_{12} \end{bmatrix} = \frac{1}{E} \begin{bmatrix} 1 & -\nu & -\nu & 0 & 0 & 0 \\ -\nu & 1 & -\nu & 0 & 0 & 0 \\ -\nu & -\nu & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(1+\nu) & 0 & 0 \\ 0 & 0 & 0 & 0 & 2(1+\nu) & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(1+\nu) \end{bmatrix} \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{bmatrix}$$

↓ (solution is quick due to obvious symmetry $\sigma_2 = \sigma_3$)

$$\sigma_2 = \sigma_3 = \sigma_1 \nu / (1 - \nu)$$

↓ (after substituting to the first equation)

$$\sigma_1/\varepsilon_1 = E(1-\nu)/(1-\nu-2\nu^2) \text{ (or } E \text{ in the 1D case - thin rod - where } \nu \text{ has no role)}$$

↓ (using relationships between elastic moduli above)

$$\sigma_1/\varepsilon_1 = \mathbf{B+4/3G} \text{ (usually in this form: so called longitudinal modulus)}$$

Speed of sound (summary)

Starting point $v^2 = dP/d\rho = M/\rho$

Isothermal gas:

$$PV = \text{const.} \Rightarrow PdV = -VdP \Rightarrow v^2 = dP/d\rho = P/\rho$$

Adiabatic gas (Laplace's correction of Newton):

$$PV^\kappa = \text{const.} \Rightarrow \kappa PdV = -VdP \Rightarrow v^2 = dP/d\rho = \kappa P/\rho$$

Solids, longitudinal wave in 1D rod (thinner than wavelength):

$$v^2 = E/\rho$$

Solids, longitudinal wave in 3D:

$$v^2 = (B + 4/3 G)/\rho$$

Solids, shear wave

$$v^2 = G/\rho$$

Liquid

$$v^2 = B/\rho \quad \text{see isotherm. gas (where } P = B) \text{ or solid with } G = 0$$

Speed of sound

Adiabatic gas (Laplace's correction of Newton):

$$PV^\kappa = \text{const.} \Rightarrow \kappa P dV = -V dP \Rightarrow v^2 = dP/d\rho = \kappa P/\rho$$

Crosscheck against the expectation based on thermodynamics:

equipartition theorem

$$3k_B T/2 = mv^2/2 \text{ (per atom)} \Leftrightarrow 3RT/2 = Mv^2/2 \text{ (per mole)}$$

in parallel, there is the equation of state

$$PV = nRT \Leftrightarrow PM = \rho RT$$

↓

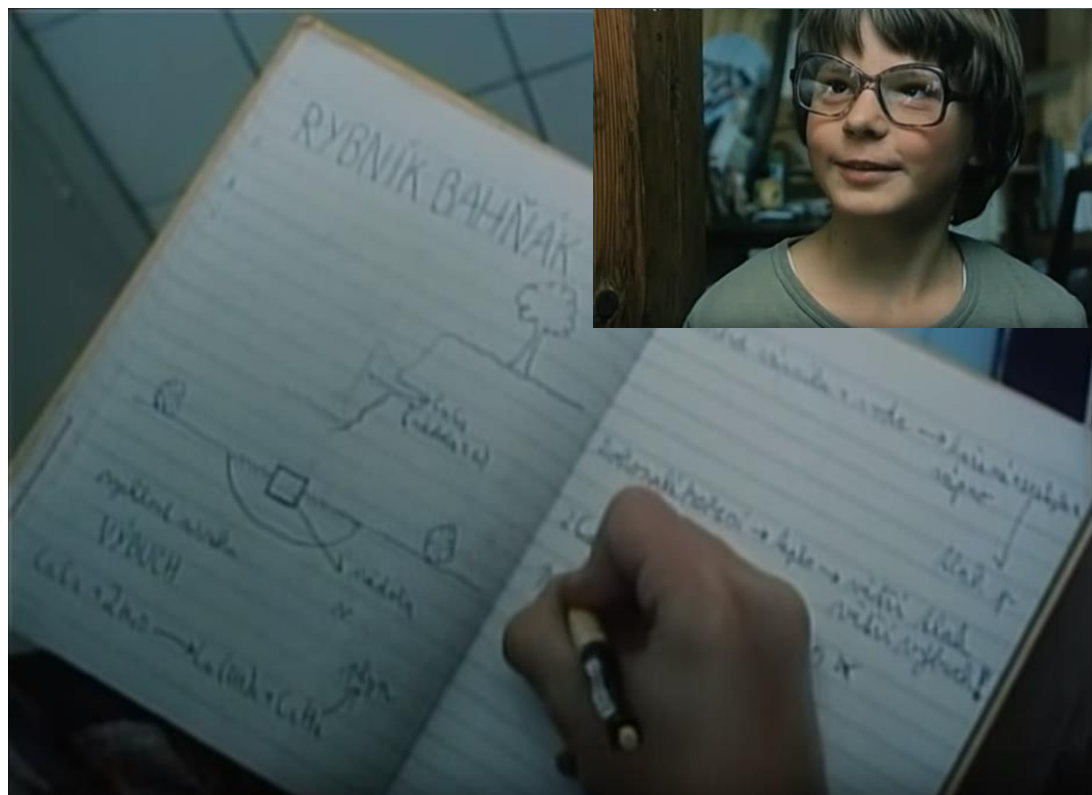
$$v^2 = 3RT/M = 3P/\rho$$

As expected, the speed of sound
is on the same order as the speed of molecules

Speed of sound (exp.)

Water: $B = 2.2 \text{ GPa}$, $\rho = 1000 \text{ kg/m}^3 \Rightarrow v = \sqrt{B\rho} = 1500 \text{ ms}^{-1}$

Value which a hero - young physicist - of a movie *Explosion at 5 pm* tried to check by throwing calcium carbide to water
($\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$)



Lost in translation

screenshots from the movie *Explosion at 5 pm*
(by the book *Explosion at 6 pm* ...
so the camera had enough light)

"We exaggerated the load a bit.
But I am not chemist, I am physicist"

Earthquake

Solids, longitudinal wave (p-wave)

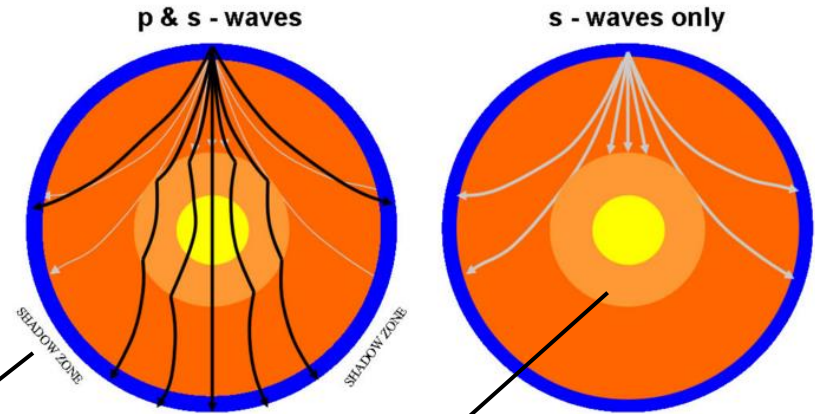
$$v^2 = (B + 4/3G)/\rho$$

Solids, shear wave (s-wave)

$$v^2 = G/\rho$$

Liquid

$$v^2 = B/\rho$$



In addition to surface waves (which do most of destruction), p- and s-waves travel from the epicenter through the Earth:

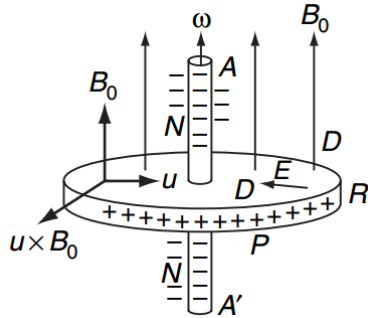
- dead angles (shadow zone) $\Rightarrow$ **Earth core dimensions**
- region where we register longitudinal waves only (shear wave cannot travel in a liquid with $G = 0$)
 $\Rightarrow$ **outer part of the core is liquid**

Why is it good that the outer part of the Earth core is liquid: Geodynamo

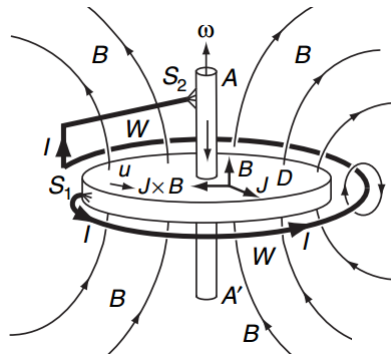
Although the Earth core is mostly of Fe and Ni, it cannot constitute a permanent magnet ($T > T_C$, Ohmic decay)

However, it can constitute a self-consistent dynamo:

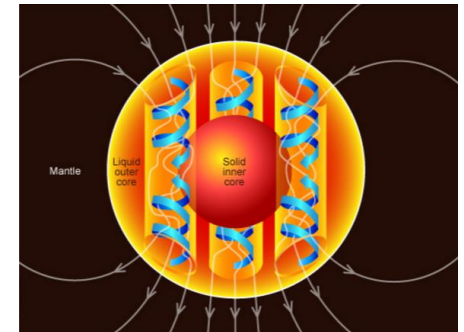
- liquid state of outer core allows flows of conductive material
- inner core is a source of energy or them (e.g. latent heat)
- Earth rotation arranges all flows in the same direction



conductive disc rotates in mag. field $B_0 \Rightarrow$ separation of + and - charge



regions of + and - charge can be connected by conductor $\Rightarrow$ current creates mag. field B replacing B_0

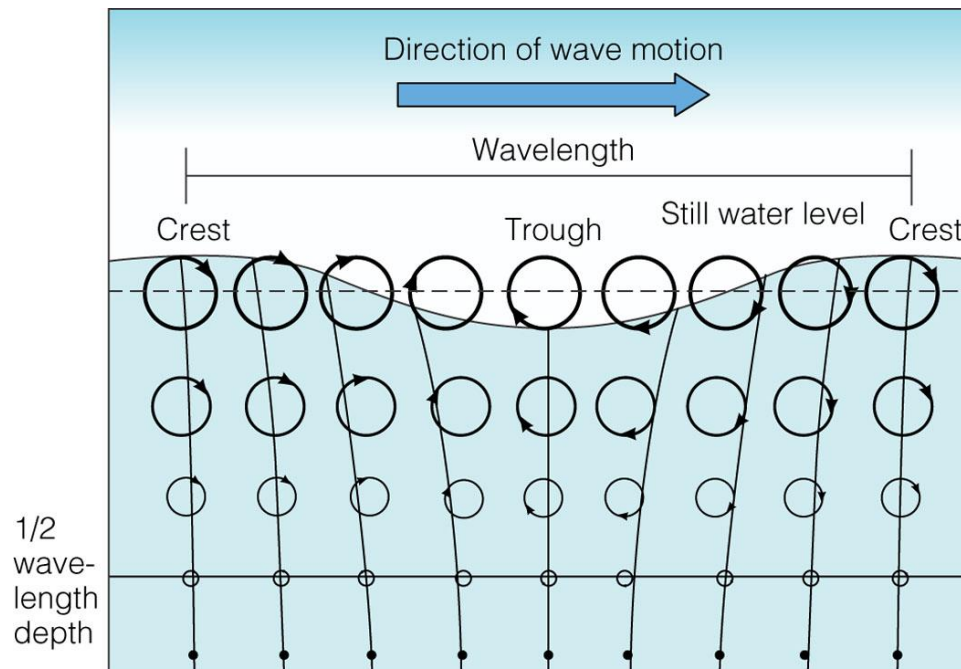


the movable conductive medium in the Earth is not metal disc, but elements of molten metal outer core

Surface waves

As shown above, only longitudinal waves can transmit through a liquid, transmission of transverse waves is prevented by $G = 0$.

All of that is valid for a bulk of the liquid. Surface waves (also called gravitational waves) are a different topic.



10) Optical properties

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

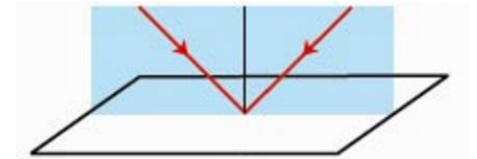
Polarized light

Interaction of light with matter depends on polarization



Thus, the stuff below is valid for fully polarized light
(superposition of two linearly polarized components
with fixed phase shift)

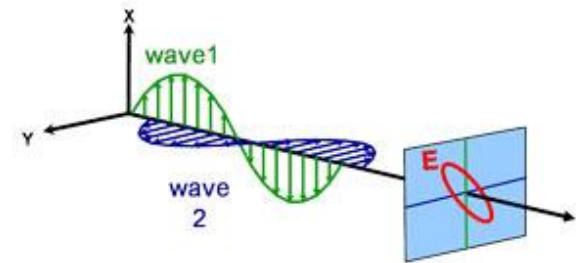
Introduce **plane of incidence**: plane
(perpendicular to surface) which contains
both the incident and the reflected beam



How to express the light polarization?

Ratio of amplitudes and phase shift of

- '**p**' component (in plane of incidence) and
- '**s**' component (perpendicular to plane of incidence)

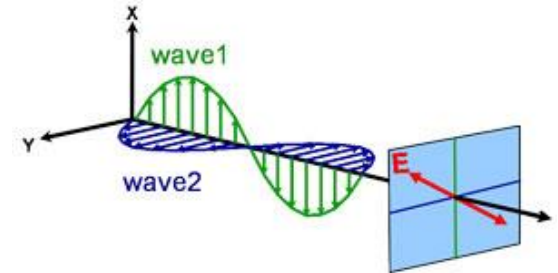


Polarized light

Which kinds of polarization exist?

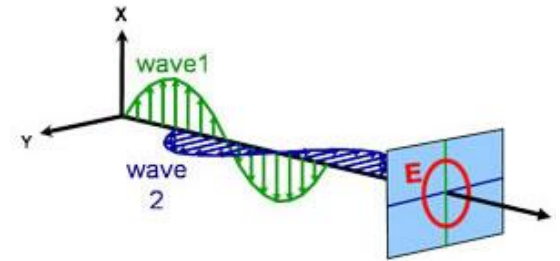
(1) **linear**

(phase shift 0° independently
of the ratio of amplitudes)



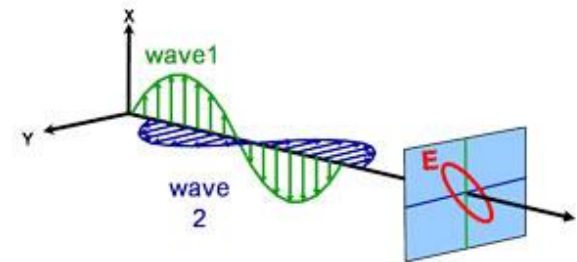
(2) **circular**

(phase shift 90° and the same
amplitudes)



(3) **elliptic**

(general case; therefore the term
ellipsometry)



Optical constants

Relevant quantities for the interaction of light with boundary
(all of them are dimensionless) :

either complex relative permittivity $\boldsymbol{\varepsilon} = \varepsilon_1 + i\varepsilon_2$

(the word 'relative' is often omitted in this context)

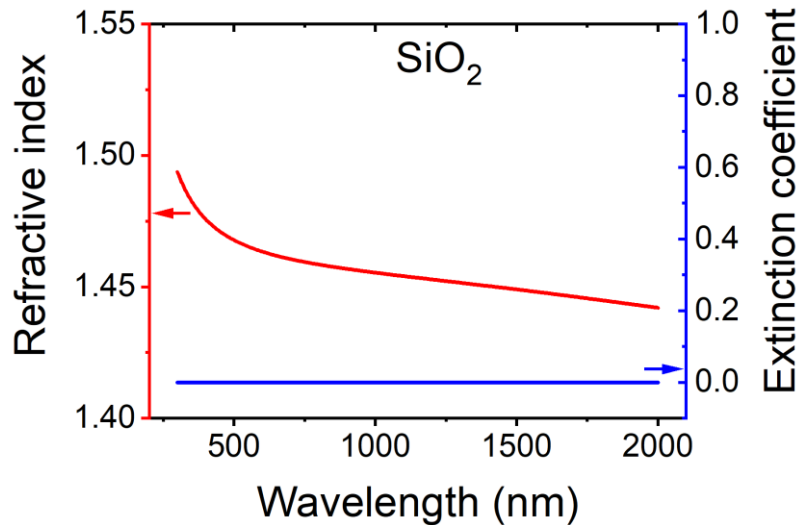
or complex refractive index $\boldsymbol{n} = n + ik$

where $\boldsymbol{\varepsilon} = \varepsilon_1 + i\varepsilon_2 = \boldsymbol{n}^2 = (n+ik)^2$

real refractive index n and extinction coefficient k are called
optical constants (but depend on the wavelength)

Optical constants

dependence on wavelength

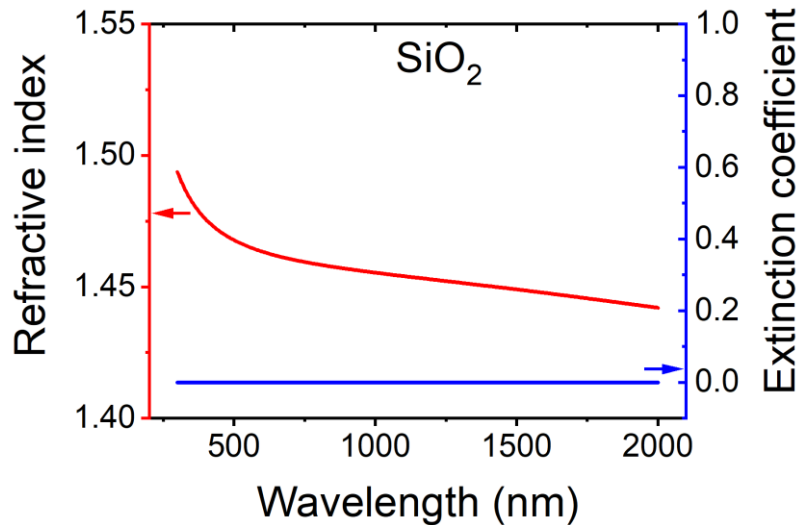


for $E < E_g$ (band gap) ideally
 $k=0$ and n monotonically
decreases with λ

therefore, value for a single
wavelength (often $\lambda=550$ nm)
has a high information content

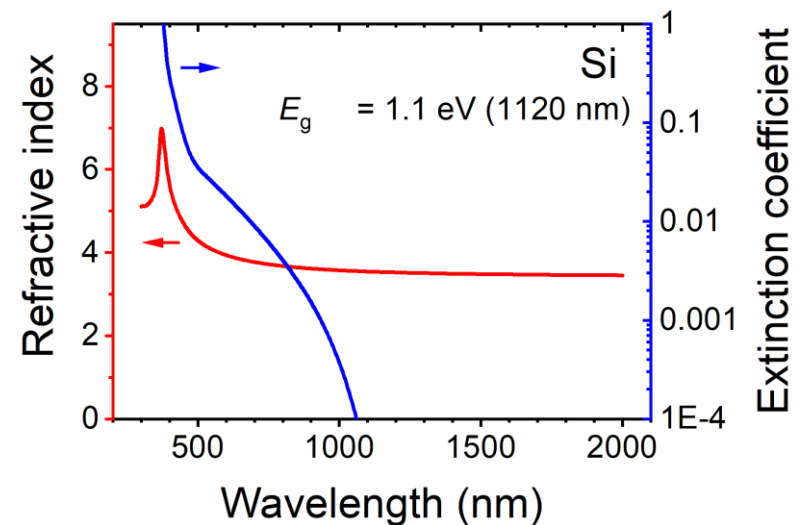
Optical constants

dependence on wavelength



for $E < E_g$ (band gap) ideally $k=0$ and n monotonically decreases with λ

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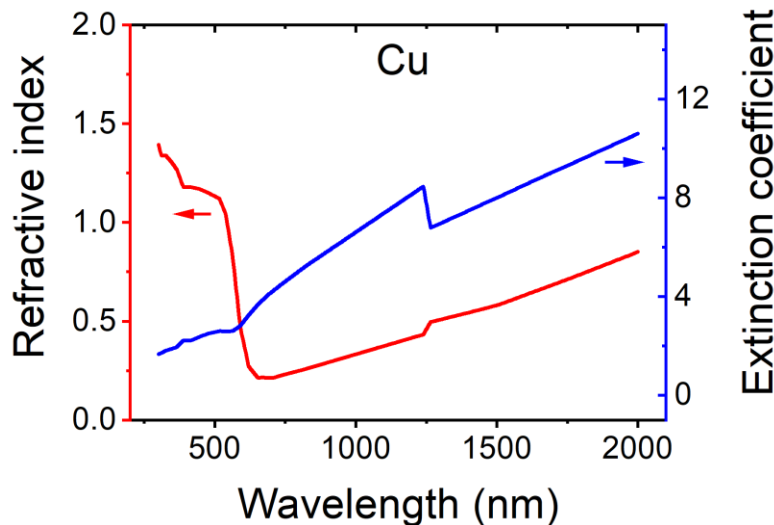
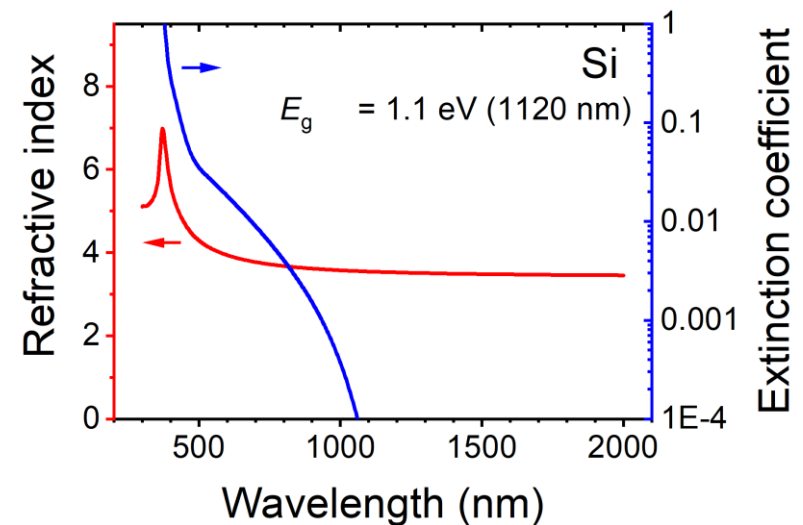
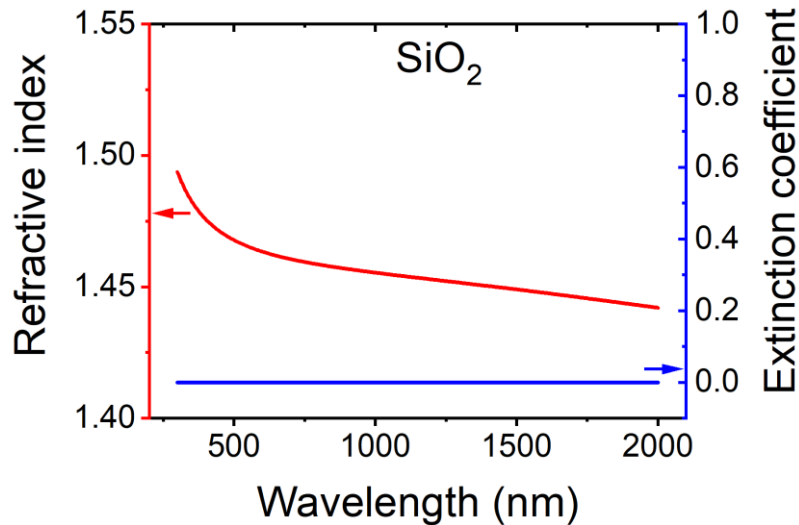


generally it does not

generally it has not: for example, 550 nm can be close to the band gap edge

Optical constants

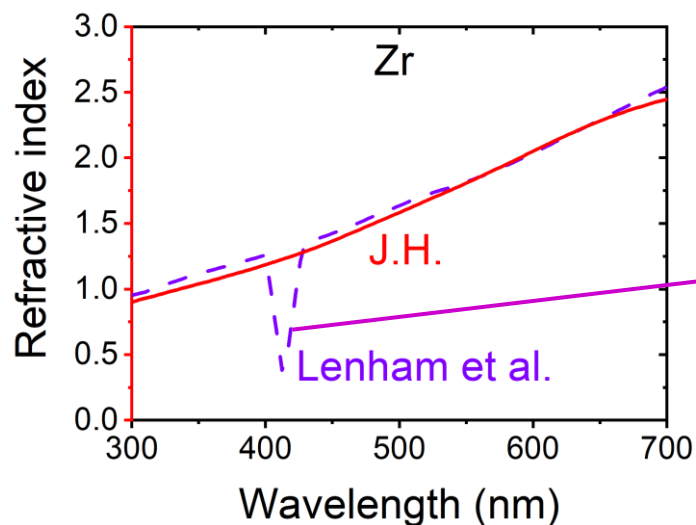
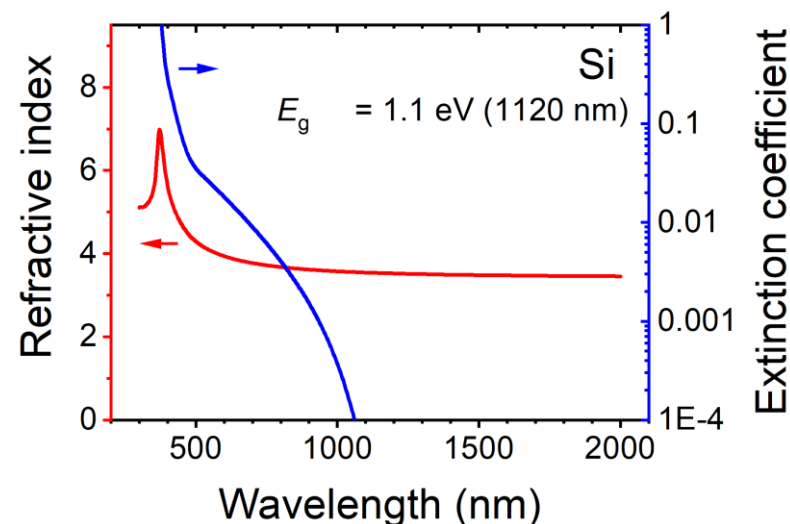
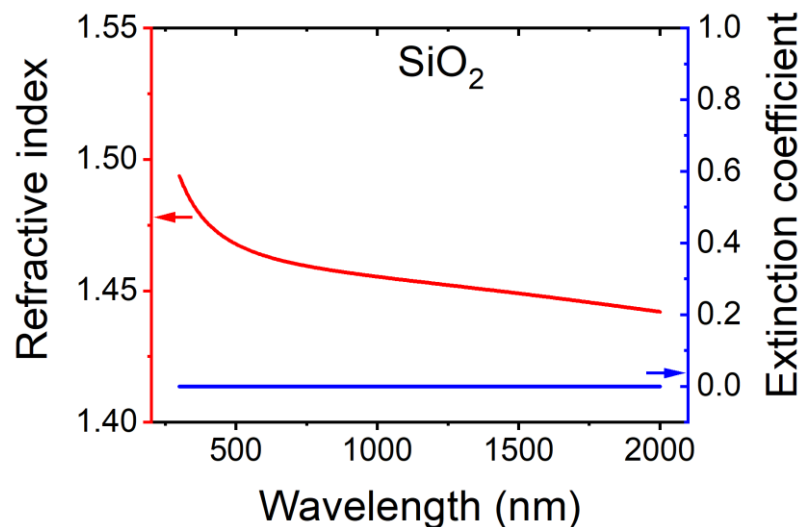
dependence on wavelength



for metals $E > E_g = 0$ everywhere
 $\Rightarrow$ the dependencies are
unpredictable without
a more detailed calculation

Optical constants

dependence on wavelength



not all optical constants
are in the databases
correctly ...

Optical constants

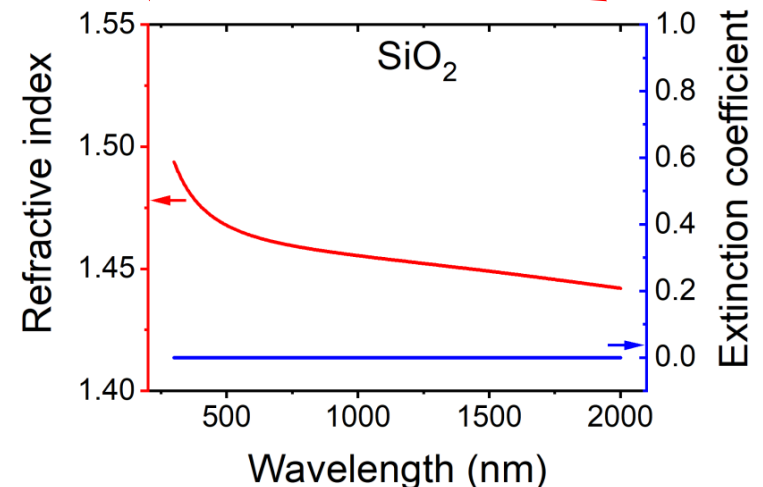
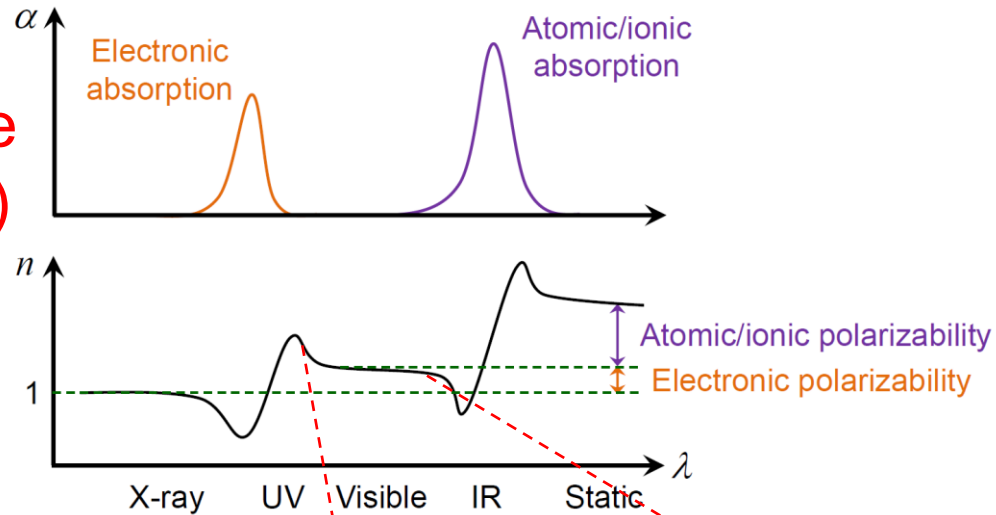
dependence on wavelength in wider range

For low λ ($\approx 10^{15}$ Hz; $E < E_g$)
electronic excitation take place
(crucial for us; previous slides)

For higher λ ($\approx 10^{12}$ Hz)
bond vibrations take place
(details in chapter 3)

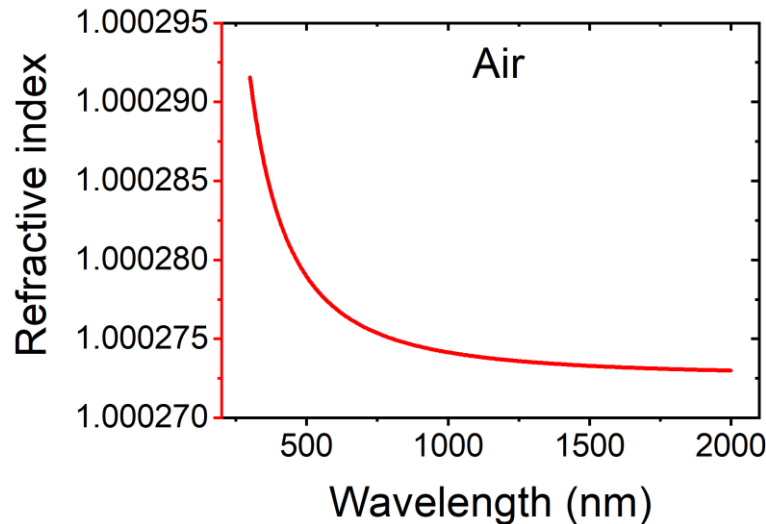
For very high λ ($\approx 10^6$ Hz) polarization
of whole material (not only that of
electron cloud) takes place if it is
possible: ionic and dipole relaxation

Increasing λ leads to increasing
absorption by free charge carriers,
if they are present (chapter 5,
further details below)



Optical constants

dependence on wavelength - green flash



similar dependence like that given for n of wide band gap materials is valid also for **n of atmosphere** (before corrections due to T , water vapour, etc.)



green light refracts more than red and yellow, and in the moment of sunrise / sunset it is the only one which makes it above the horizon (**green flash**)

Optical constants

dependence on wavelength - green flash



Well known phenomenon,
from engravings in
Jules Verne books
(Le rayon vert, 1882) ...



... to photos from wikipedia

Optical constants

dependence on wavelength - green flash

Lost in translation



„Je to Clorinda,“ řekl s pohnutím Olivier Sinclair, a po krátké napjaté pauze, už klidněji dodal: „a poněvadž má zaměřeno na východ Staffy k přístání, popluje uvnitř a nebude rušit naše pozorování.“

Byla to opravdu Clorinda, která obeplula ostrov Mull na jihu, aby opět zakotvila v malé zátoce Clam Shell.

Všichni znovu upřeli svůj pohled na západní obzor.

Slunce klesalo už s rychlostí, která se zdála zvětšovat, čím víc se blížilo k moři. Na vodní hladině se chvěl široký stříbrný pruh vyslaný kotoučem, jehož jas bodal do očí. Z odstínu starého zlata přešel k žluté třešňové barvy. Před přivřenými očima se objevovaly rudé kosočtverce a žluté kruhy, které se křížily jako prchavé barvy kaleidoskopu. Lehké vlnité rýhy narysovaly ten druh ocasu vlasatice, který odraz světla vytváří na povrchu vod. Bylo to jako chomáč stříbrných cetek, ale jeho lesk bledl čím více se blížil ke břehu.

Ani mráček, ani mlha, ani pára, třeba jen sebemenší, nebyly vidět po celém ohvodě obzoru. Nic nerušilo čistotu této kruhové čáry, kterou by ani kružítka nenarysovalo jemněji na bílém papíru.

Všichni stáli bez hnutí, dojatí víc, než se dalo tušit, a pohlíželi na sluneční kouli, která se šikmo pohybovala k obzoru, sestoupila ještě a pak na okamžik stanula, jako by zavěšená nad propastí.

Znetvoření, deformace kotouče způsobená lomem paprsků, stávala se víc a víc patrná. Kotouč teď připomínal svou podobou etruské vázy plných boků, jejichž dno je ponořeno do vody.

Nehylo pochyb, že přírodní úkaz se dostaví co nevidět. Nic už nemůže porušit tento krásný západ zářícího nebeského tělesa! Nic už nezastíní poslední zelený paprsek!!

Slunce brzy zmizelo na půl pod vodorovnou čárou. Zářivé paprsky, vystřelené zlatými šípky, dotýkaly se nejkrajnějších skalin ostrova Staffy.

Strmé břehy Mullu a hřeben Ban Moru v pozadí zrudly jako by zaplanuly ohněm.

Konečně zbýval už jen tenoučký úsek nejvrchnějšího oblouku nad mořskou hladinou.

„Zelený paprsek! Zelený paprsek!“ jedním hlasem zvolali bratři Melvillovi, Bessi i Partridge, jejichž oči po čtvrt vteřiny zíraly na tuto neporovnatelnou zelenou barvu.

Avšak Olivier a Helena neviděli ten vzácný výjev, který se konečně ukázal po tolika marných pozorováních...

V okamžicích, kdy slunce vrhlo svůj poslední paprsek do prostoru, se setkaly jejich pohledy a oba se zapomněli ve svém pozorování...

Helena viděla černý paprsek vycházející z očí mladého muže, Olivier modrý paprsek vycházející z očí mladé ženy!

Slunce zmizelo docela, ani Olivier, ani Helena neviděli zelený paprsek.

Optical constants

physical meaning and possible values

Real refractive index n

- phase velocity of light in a material $v_f = c/n$
- it is possible $n < 1 \Rightarrow v_f > c$ (theory of relativity is ok with that: the speed of information transfer is not phase velocity $\omega(k)/k$, but group velocity [velocity of wave packets] $d\omega(k)/dk$)
- it is possible $n < 0$ (metamaterials with a periodic structure [shorter period than the wavelength])

Extinction coefficient k

- absorption by layer of a thickness d is given by factor $e^{-\alpha d}$ where absorption coefficient $\alpha = 4\pi k/\lambda$ (i.e. for given k the absorption does not depend on thickness, but on a ratio of thickness and wavelength)

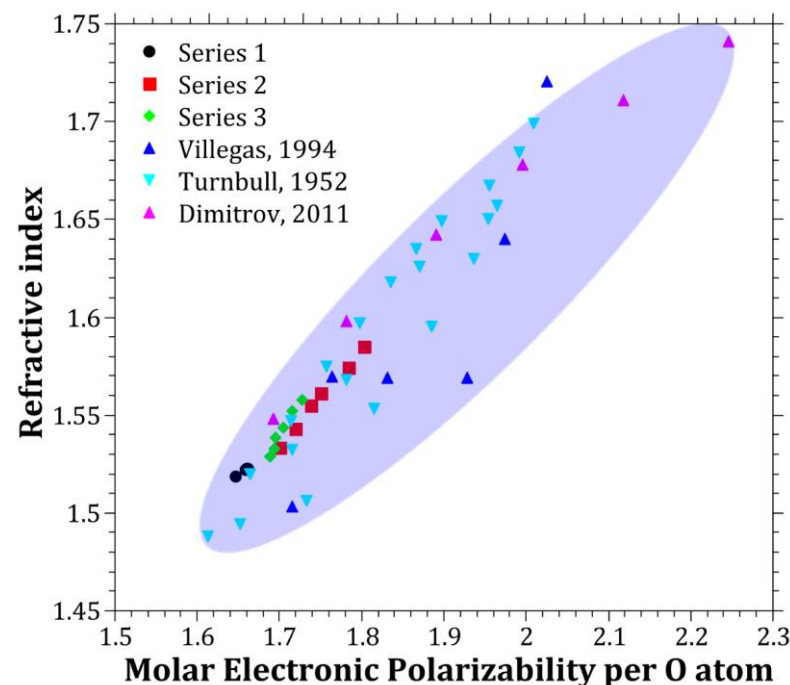
Optical constants

physical meaning and possible values

The cause of slowing the light ($v_f = c/n$), and in turn refractive index, is the atomic polarizability (recall meaning of permittivity).

At a given number of electrons, the polarizability increases with the size of atom (ion).

The transition of electrons from metallic cations to oxygen anions in ionic metal oxides increases the polarizability of O^{2-} and vice versa. However, highly polarizable cations (Ba^{2+} , Pb^{2+}) exist as well.



[S. Karlsson et al., Opt. Mater. Express 6, 1198 (2016)]

Surface plasmon resonance

As mentioned above, $\varepsilon_1 + i\varepsilon_2 = (n+ik)^2$

Real part of the permittivity $\varepsilon_1 = n^2 - k^2$ can be negative

Possible consequence is a **surface plasmon**:
electromagnetic wave (collectively oscillating surface electrons)
travelling along boundary of materials with $\varepsilon_1 < 0$ and $\varepsilon_1 > 0$
(boundary between some metals and dielectric or air)

Collective excitation of electrons, similar to a collective
excitation of atoms, i.e. phonon (chapter 3)

Surface plasmon resonance:

maximum absorption of p-polarized light - its energy
is obtained by this wave, at a resonance condition

$\varepsilon_{1_metal}(\lambda) = -\varepsilon_{1_dielectric}(\lambda)$, and for proper angle of incidence
(always such which corresponds to total internal reflection)

Localised surface plasmon resonance

Surface plasmon resonance:

maximum absorption of p-polarized light - its energy is obtained by this wave, at a resonance condition

$\varepsilon_{1_metal}(\lambda) = -\varepsilon_{1_dielectric}(\lambda)$, and for proper angle of incidence (always such which corresponds to total internal reflection)

Localized surface plasmon resonance:

metal nanoparticles instead of a flat metal surface, in the small particle limit $d \ll \lambda$ the resonance takes place for

$(\varepsilon_{1_metal}(\lambda) + 2\varepsilon_{1_dielectric}(\lambda))^2 + \varepsilon_{2_metal}(\lambda)^2 = 0$, i.e. for $\varepsilon_{1_metal}(\lambda) = -2\varepsilon_{1_dielectric}(\lambda)$ and as low ε_{2_metal} as possible

More general for of the first condition

$$\varepsilon_{1_metal}(\lambda) = -([m+1]/m)\varepsilon_{1_dielectric}(\lambda)$$

where $m = 1$ for dipole resonance, 2 for quadrupole, etc.

Localised surface plasmon resonance

Lycurgus cup (year ≈ 300)

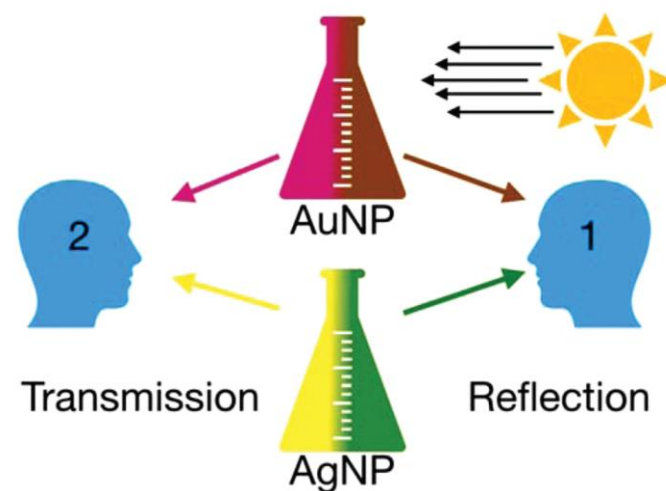
Glass + nanoparticles of silver (330 ppm) and gold (40 ppm)

Size of nanoparticles ≈ 70 nm

color in reflection

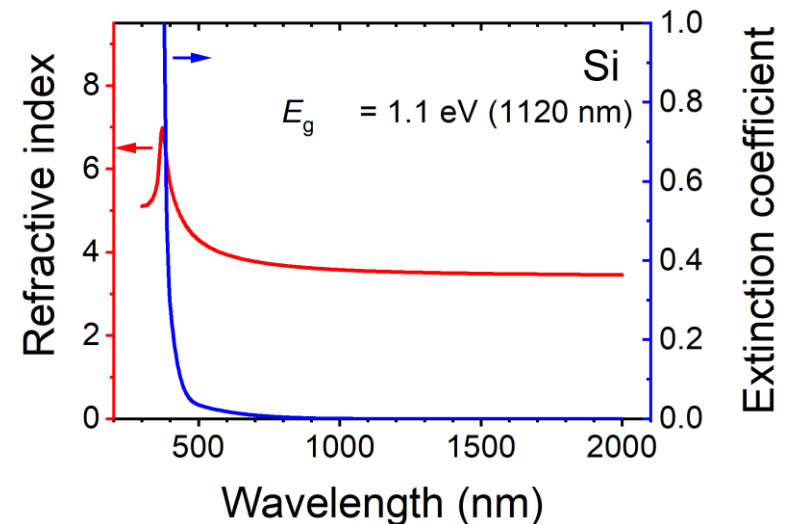
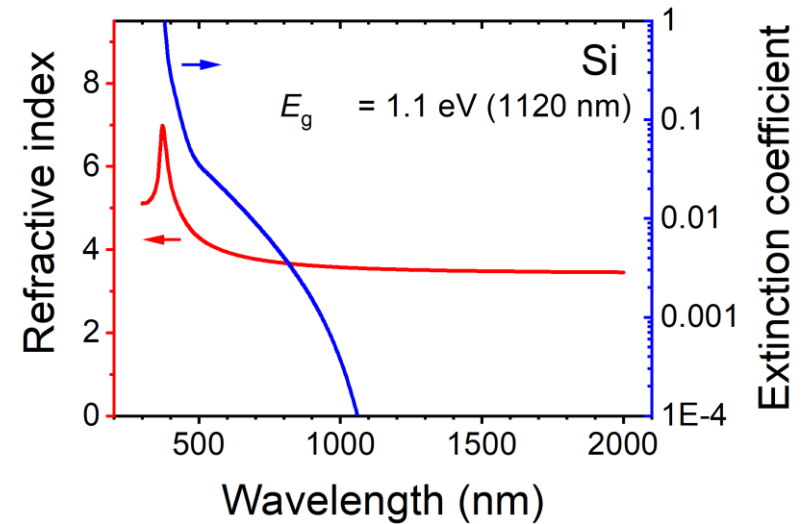


color in transmission



Optical constants

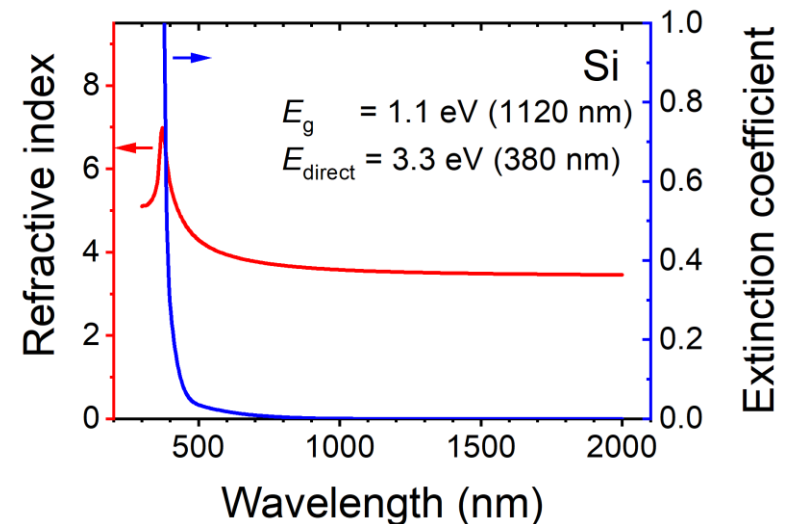
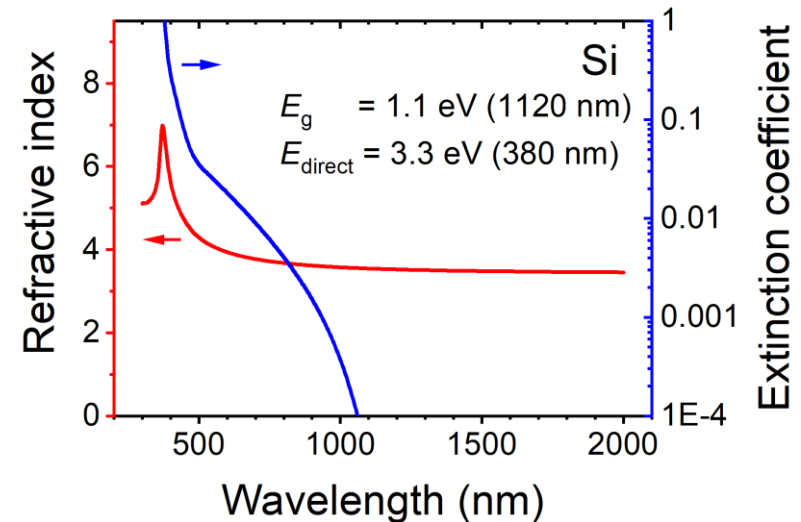
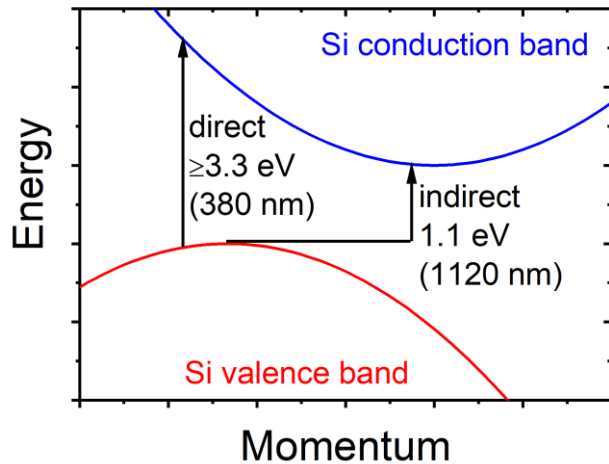
role of band gap



Extinction coefficient is >0
below **1100 nm**, but steeply
increases below **400 nm**

Optical constants

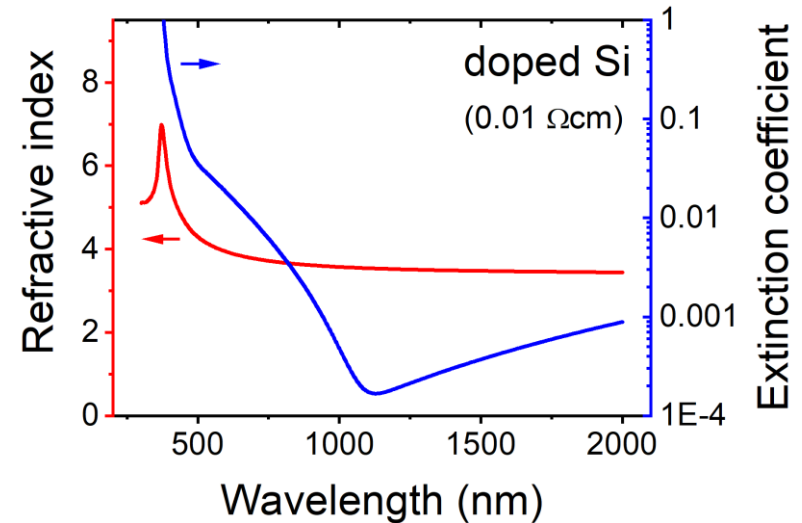
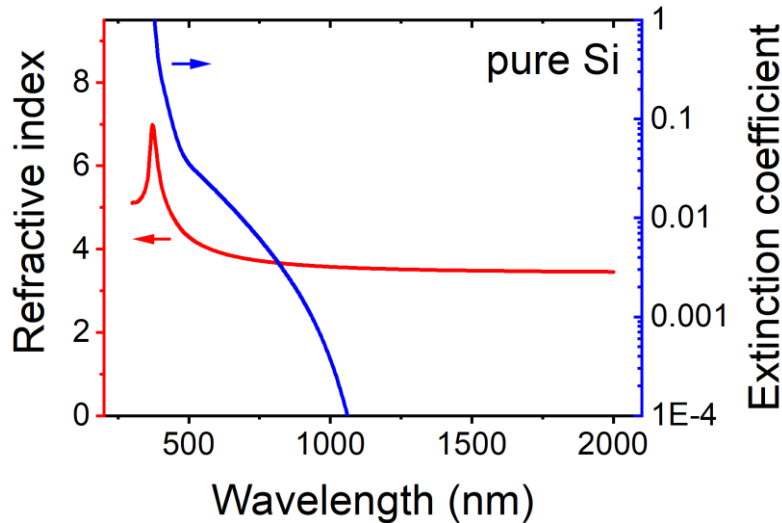
role of band gap



Extinction coefficient is >0 below **1100 nm**, but steeply increases below **400 nm** due to increasing probability of transitions - no change of momentum (phonon) required (details in chapter 6)

Optical constants

dependence on doping



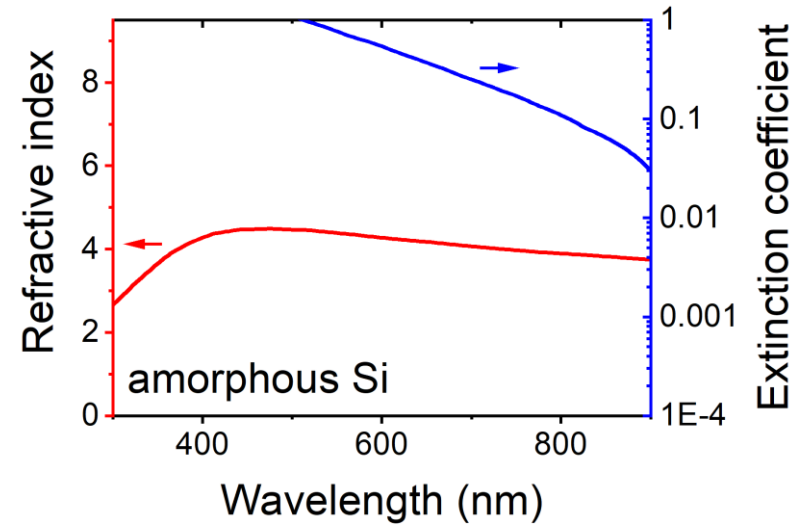
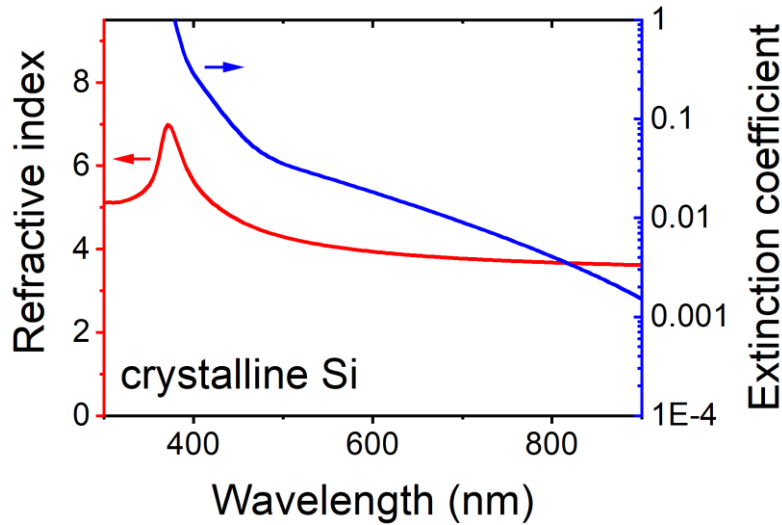
Dependence on the concentration of free charge carriers:
decrease transmittance for long wavelengths (low energies)

details / equations in chapter 5

$$(\varepsilon_2 = 2nk \text{ [at almost constant } n] \cong \hbar^3 \sigma_{dc} / \varepsilon_0 \tau^2 E^3)$$

Optical constants

dependence on crystallinity



Dependence not only on composition and crystal system, but also on size of crystals

Optical constants

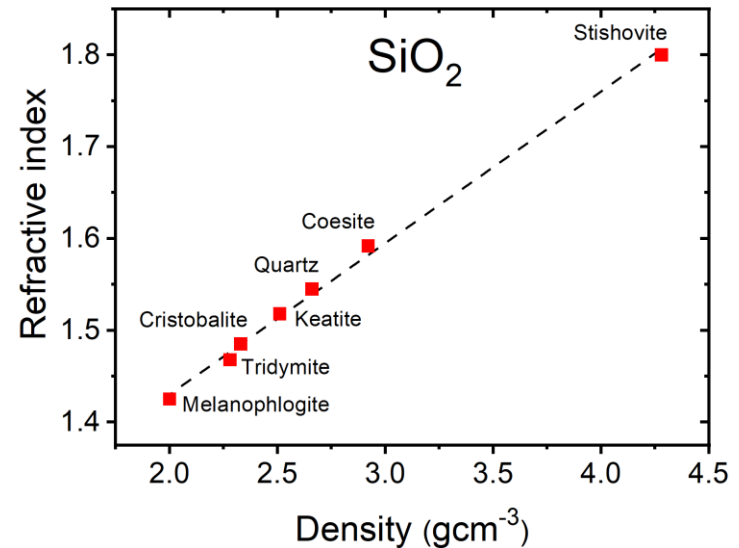
dependence on density

for **given composition** of a material,
the **dependence of refractive index
on density is almost linear**
in the transparent ($E < E_g$) range

quantification: Lorentz-Lorenz
(Clausius-Mossotti) relationship

$$(\varepsilon - 1)/(\varepsilon + 2) = 4\pi N\alpha/3$$

- N is density of polarizable particles
- α is their polarizability (dipole moment $p = \alpha E$)
- α is for historical reasons often given in m^3 (the product $N\alpha$, polarizability per volume, is then really dimensionless), in SI it is necessary to divide the right side by $4\pi\varepsilon_0$.



Optical constants

dependence on density

for **given composition** of a material,
the **dependence of refractive index
on density is almost linear**
in the transparent ($E < E_g$) range

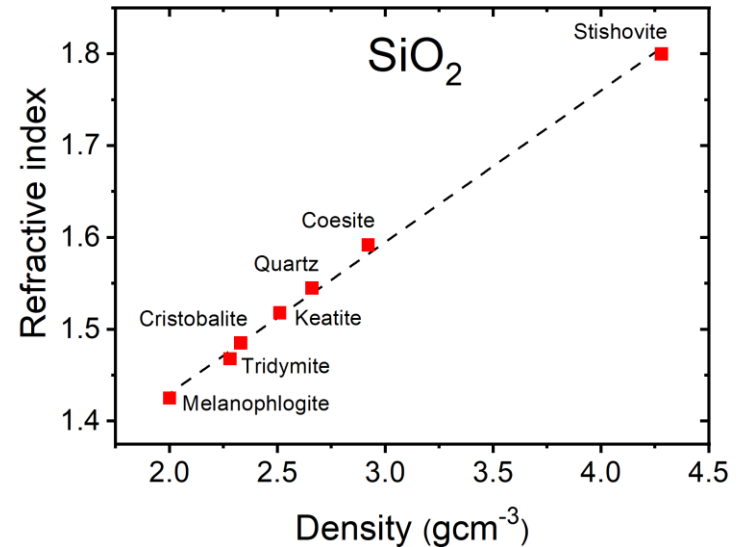
quantification: Lorentz-Lorenz
(Clausius-Mossotti) relationship

$$(\varepsilon - 1)/(\varepsilon + 2) = 4\pi N\alpha/3$$

$\varepsilon = n^2$ ($k = 0$ - note "in the transparent range") and
 $n = n_0 + x$ where $x \ll n_0 \Rightarrow$

$$(\varepsilon - 1)/(\varepsilon + 2) = (n^2 - 1)/(n^2 + 2) \approx (n_0^2 - 1)/(n_0^2 + 2) + 6n_0x/(n_0^2 + 2)^2$$

(mentioned & shown linear dependence) ←

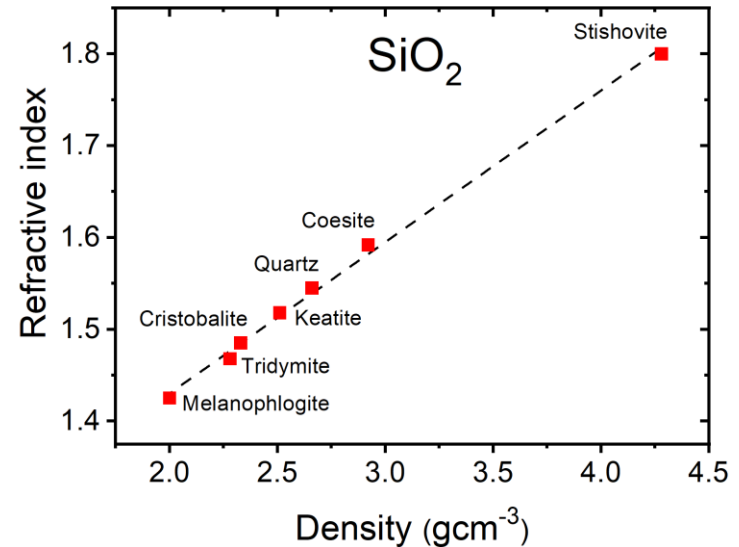


Optical constants

dependence on density

for **given composition** of a material,
the **dependence of refractive index
on density is almost linear**
in the transparent ($E < E_g$) range

higher density and refractive index
also correspond to narrower band gap
(examples instead of equations)



Example 1: SiO₂ (density and n in the figure)

quartz $E_g = 10.1$ eV

stishovite $E_g = 8.9$ eV

Example 2: TiO₂

rutile 4.2 gcm⁻³, $n = 2.71$, $E_g = 3.0$ eV

anatase 3.9 gcm⁻³, $n = 2.52$, $E_g = 3.2$ eV

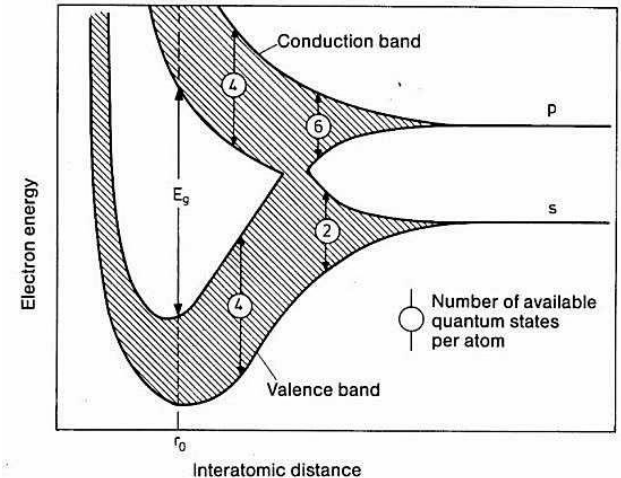
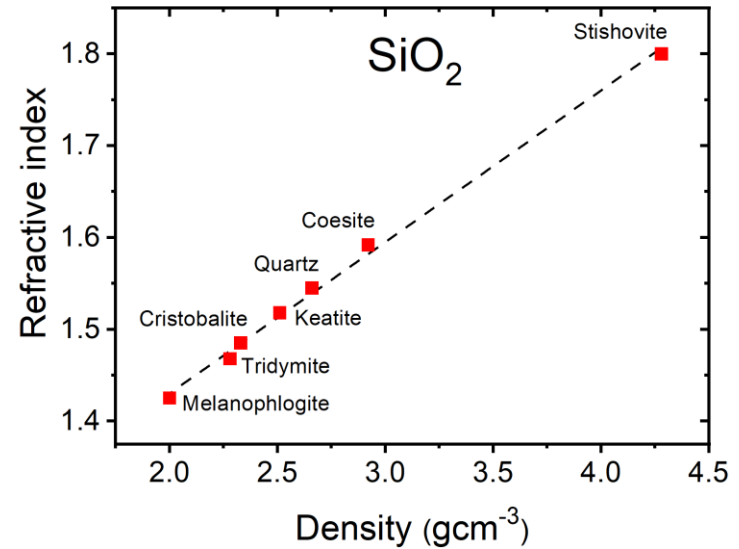
Optical constants

dependence on density

for **given composition** of a material,
the **dependence of refractive index
on density is almost linear**
in the transparent ($E < E_g$) range

higher density and refractive index
also correspond to narrower band gap

so much about different phases of
the same material (local E minima),
in a case of compressing a single phase
the dependence of E_g (figure) and n on
density is non-monotonic



Polarization catastrophe

3-4 slides above there is the equation $(\varepsilon-1)/(\varepsilon+2) = 4\pi N\alpha/3$

The right side can smoothly change (most naturally: due to the dependence of $N\alpha$ on temperature) ... what if it equals 1?

Nobody cares that this leads to **infinite permittivity**

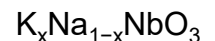
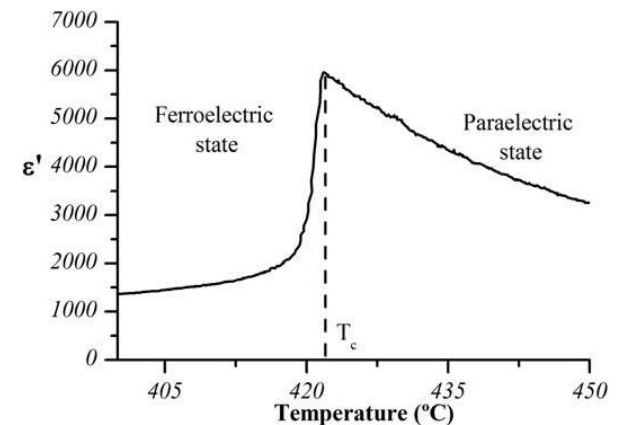
($\Leftrightarrow$ non-zero polarization at zero external field)?

Polarization catastrophe

3-4 slides above there is the equation $(\epsilon-1)/(\epsilon+2) = 4\pi N\alpha/3$

The right side can smoothly change (most naturally: due to the dependence of $N\alpha$ on temperature) ... what if it equals 1? Yes, this leads to infinite permittivity. In praxis (higher order corrections, temperature fluctuations) "only" extremely high.

Random ionic displacement leads to high electrostatic forces (higher than the elastic forces trying to restore the equilibrium position), consequently the displacement becomes permanent (new equilibrium position is found) and the material changes its permanent dipole moment (characterizing its ferroelectricity) $\Rightarrow$ **phase transition**.



Polarization catastrophe

3-4 slides above there is the equation $(\varepsilon-1)/(\varepsilon+2) = 4\pi N\alpha/3$

The right side can smoothly change (most naturally: due to the dependence of $N\alpha$ on temperature) ... what if it equals 1? Yes, this leads to infinite permittivity. In praxis (higher order corrections, temperature fluctuations) "only" extremely high.

Note also the parallel between ferro- electricity and magnetism
infinite rel. permittivity during ferroelectric transformation



infinite susceptibility during ferromagnetic transformation

$$\varepsilon \sim 1/(T-T_C) \text{ for } T > T_C$$



$$\chi \sim 1/(T-T_C) \text{ for } T > T_C \text{ (Curie-Weiss law)}$$

the term Curie temperature, T_C , is also used in both cases

Interaction of light with boundary

Fresnel coefficients for the amplitude of reflected light

r_p : (complex) Fresnel reflection coefficient for p-component

r_s : (complex) Fresnel reflection coefficient for s-component

for intensity (instead of amplitude): R_p , R_s

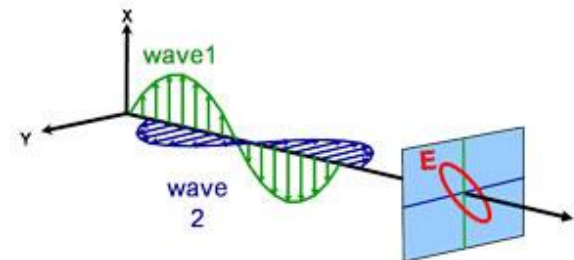
Fresnel equations

$$r_p = (\mathbf{n}_1 \cos \alpha_2 - \mathbf{n}_2 \cos \alpha_1) / (\mathbf{n}_1 \cos \alpha_2 + \mathbf{n}_2 \cos \alpha_1)$$

$$r_s = (\mathbf{n}_1 \cos \alpha_1 - \mathbf{n}_2 \cos \alpha_2) / (\mathbf{n}_1 \cos \alpha_1 + \mathbf{n}_2 \cos \alpha_2)$$

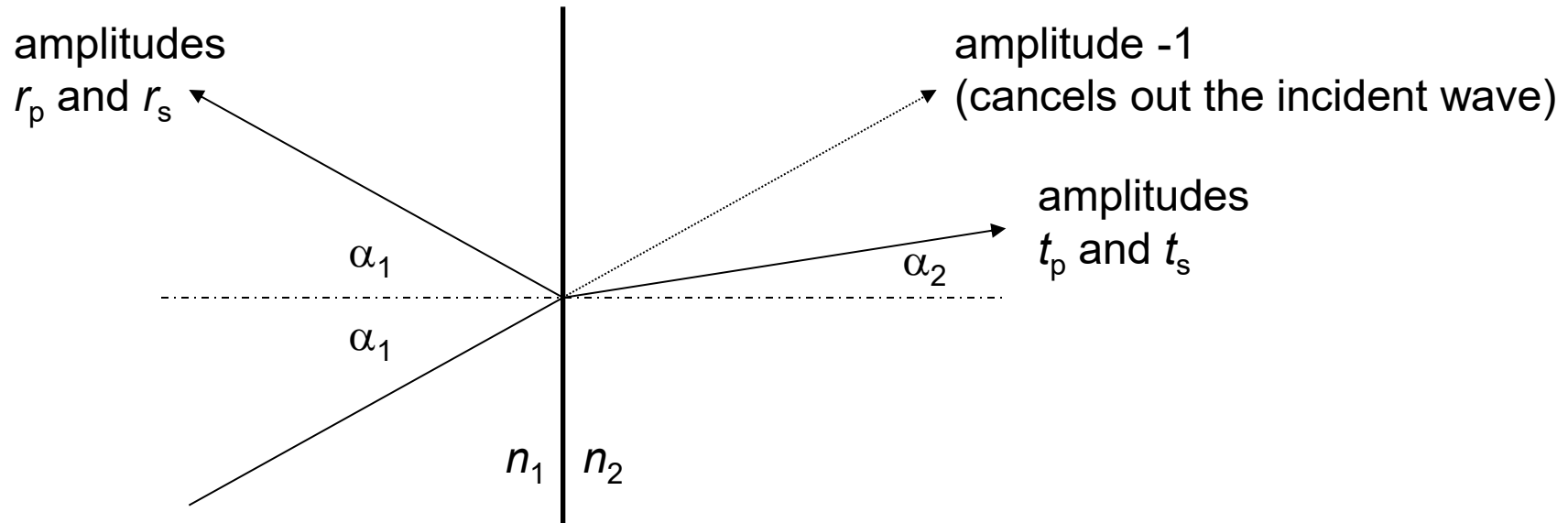
where α_1 is angle of incidence and $n_1 \sin \alpha_1 = n_2 \sin \alpha_2$

Where are they coming from?



Where are the Fresnel eq. coming from

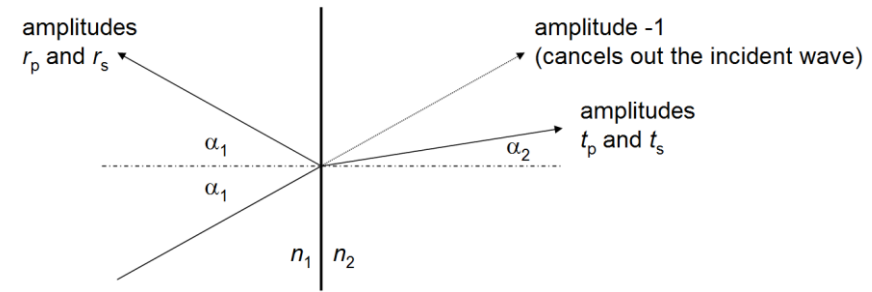
Charge oscillations at the boundary are responsible for three new beams (normal to the direction of oscillations): two really newly observed, and one which cancels out the incident beam



Where are the Fresnel eq. coming from

$$r_s / t_s = r_p / [t_p \cdot \cos(\alpha_1 + \alpha_2)]$$

Only part of oscillations in the incident plane which caused the transmitting beam cause also the reflected beam ($\Rightarrow \cos$). Oscillations normal to the incident plane do not have this problem - they are normal to all beams.



$$t_s = t_p \cdot \cos(\alpha_1 - \alpha_2)$$

Same reason for cos (except that now the transmitting beam is projected to the direction of the incident one, not reflected one).

$$r_s^2 + t_s^2 = 1 \quad \text{a} \quad r_p^2 + t_p^2 = 1$$

Law of energy conservation

$\Rightarrow$ 4 equations for 4 variables r_s, t_s, r_p, t_p

(including Snell law 5 equations for 5 variables including α_2)

Did we capture also total reflection?

Fresnel equations

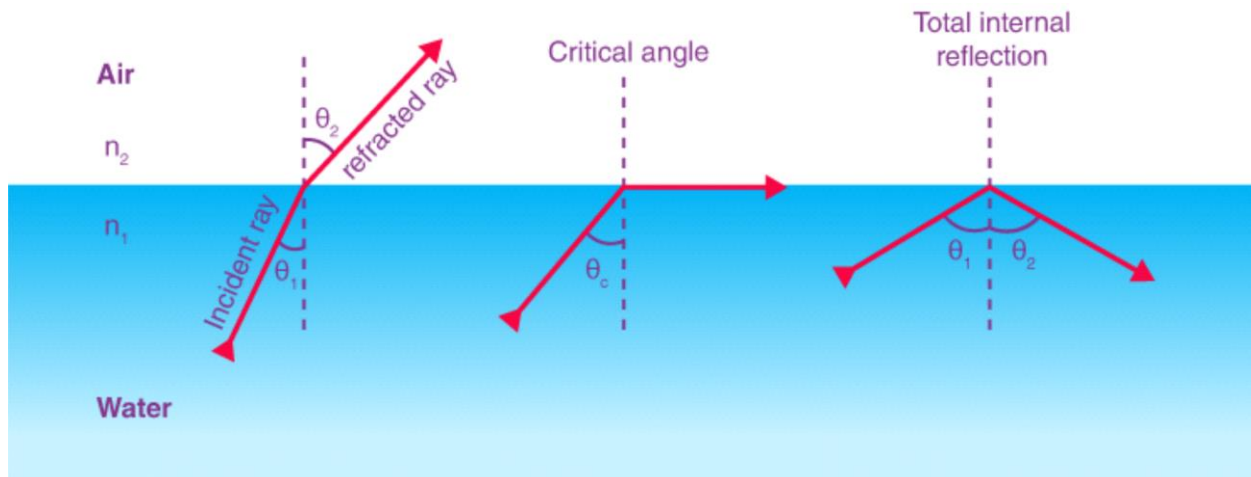
$$r_p = (\mathbf{n}_1 \cos \alpha_2 - \mathbf{n}_2 \cos \alpha_1) / (\mathbf{n}_1 \cos \alpha_2 + \mathbf{n}_2 \cos \alpha_1)$$

$$r_s = (\mathbf{n}_1 \cos \alpha_1 - \mathbf{n}_2 \cos \alpha_2) / (\mathbf{n}_1 \cos \alpha_1 + \mathbf{n}_2 \cos \alpha_2)$$

Snell law

$\sin \alpha_2 = (n_1/n_2) \sin \alpha_1$ can be > 1

(or even complex for complex $\mathbf{n}_{1,2}$, making the transfer matrix formalism - see the second half of this chapter - more practical)



Did we capture also total reflection?

Fresnel equations

$$r_p = (n_1 \cos \alpha_2 - n_2 \cos \alpha_1) / (n_1 \cos \alpha_2 + n_2 \cos \alpha_1)$$

$$r_s = (n_1 \cos \alpha_1 - n_2 \cos \alpha_2) / (n_1 \cos \alpha_1 + n_2 \cos \alpha_2)$$

Snell law

$$\sin \alpha_2 = (n_1/n_2) \sin \alpha_1 \text{ can be } > 1$$

No problem

the F. equations do not include α_2 but $\cos \alpha_2$, which is still calculable, only imaginary: $\cos \alpha_2 = \sqrt{1 - \sin^2 \alpha_2} = i\sqrt{\sin^2 \alpha_2 - 1}$

Fresnel equations

$$r_p = (-n_2 \cos \alpha_1 + i n_1 \sqrt{\sin^2 \alpha_2 - 1}) / (n_2 \cos \alpha_1 + i n_1 \sqrt{\sin^2 \alpha_2 - 1})$$

$$r_s = (n_1 \cos \alpha_1 - i n_2 \sqrt{\sin^2 \alpha_2 - 1}) / (n_1 \cos \alpha_1 + i n_2 \sqrt{\sin^2 \alpha_2 - 1})$$

indeed, for real refractive indices $|r_p| = |r_s| = 1$

Interaction of light with boundary

Fresnel coefficients for the amplitude of reflected light

r_p : (complex) Fresnel reflection coefficient for p-component

r_s : (complex) Fresnel reflection coefficient for s-component

for intensity (instead of amplitude): R_p , R_s

Fresnel equations

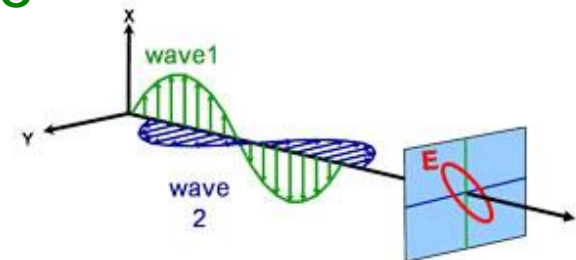
$$r_p = (\mathbf{n}_1 \cos \alpha_2 - \mathbf{n}_2 \cos \alpha_1) / (\mathbf{n}_1 \cos \alpha_2 + \mathbf{n}_2 \cos \alpha_1)$$

$$r_s = (\mathbf{n}_1 \cos \alpha_1 - \mathbf{n}_2 \cos \alpha_2) / (\mathbf{n}_1 \cos \alpha_1 + \mathbf{n}_2 \cos \alpha_2)$$

where α_1 is angle of incidence and $n_1 \sin \alpha_1 = n_2 \sin \alpha_2$

How to express the change of polarization after reflection?

using quantities Ψ and Δ : $\rho = r_p / r_s = \tan \Psi \cdot e^{i\Delta}$



Why are metals shiny

($\Leftrightarrow$ why do they have high reflectance)

Without knowledge of Fresnel equations:

free charge carriers do not let EM field inside material
(Faraday's cage)



EM field has to approach zero at the surface



incident and reflected wave must cancel out



reflected wave must have the same amplitude (and opposite phase) as the incident one



reflectance $R = |r|^2$ equals (in praxis is close to) 1

Why are metals shiny

($\Leftrightarrow$ why do they have high reflectance)

Agreement with Fresnel equations

$$r_p = (\mathbf{n}_1 \cos \alpha_2 - \mathbf{n}_2 \cos \alpha_1) / (\mathbf{n}_1 \cos \alpha_2 + \mathbf{n}_2 \cos \alpha_1)$$

$$r_s = (\mathbf{n}_1 \cos \alpha_1 - \mathbf{n}_2 \cos \alpha_2) / (\mathbf{n}_1 \cos \alpha_1 + \mathbf{n}_2 \cos \alpha_2)$$

Very low real part $\mathbf{n}_2$ (e.g. silver - see the figure) $\Rightarrow$ numerator and denominator differ especially in the sign of the imaginary part $\Rightarrow$ their absolute values almost do not differ at all

Extremal ($\Rightarrow$ simple) case

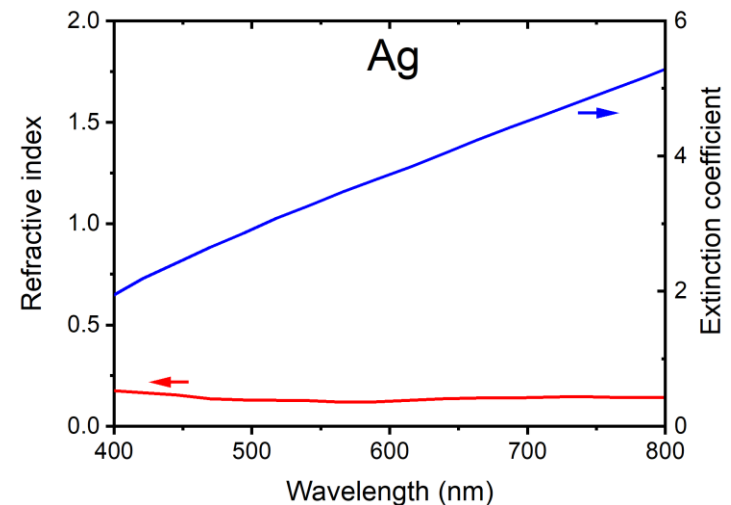
$$n_1 = 1, n_2 = 0+ik, \alpha_1 = \alpha_2 = 0$$

$\Downarrow$

$$r_p = r_s = (1-ik) / (1+ik)$$

$\Downarrow$

$$R_p = |r_p|^2 = R_s = |r_s|^2 = 1$$

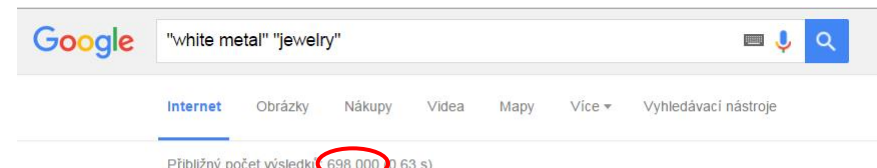
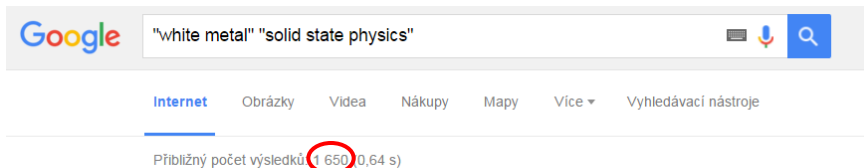
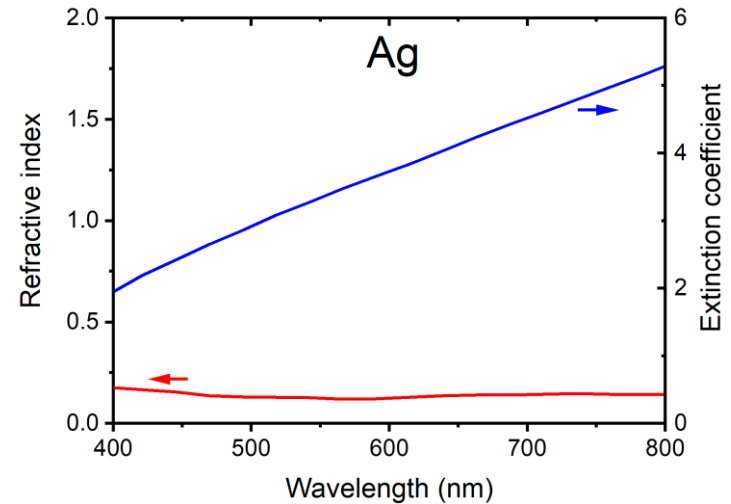


Why are metals shiny

($\Leftrightarrow$ why do they have high reflectance)

Metals like silver exhibit the same reflectance of all wavelengths (because all of them are close to 1), these metals are therefore **white**.

It looks like most people are not interested because of physics ...

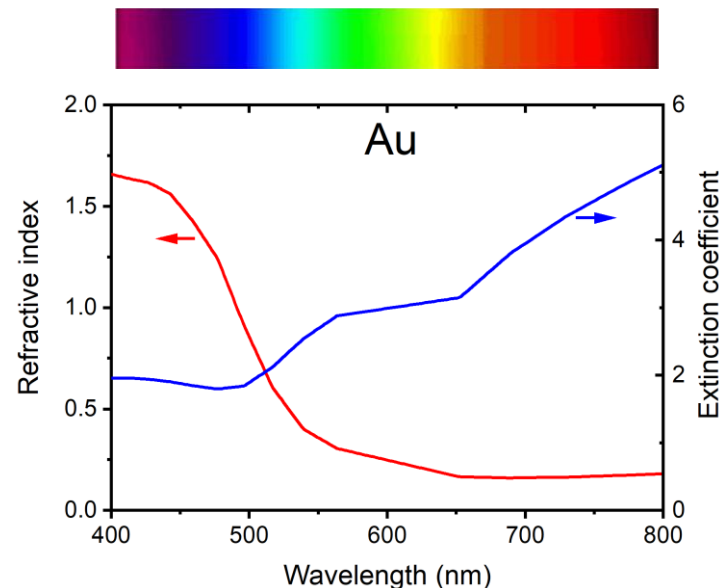


let alone searching for "white metal" "women"

Why is gold golden

Because here $k \gg n$ is valid only in a part of visible (between green and red, i.e. around yellow)

In the rest of visible spectrum $k > n$ holds (plasma frequency is in UV), but only just

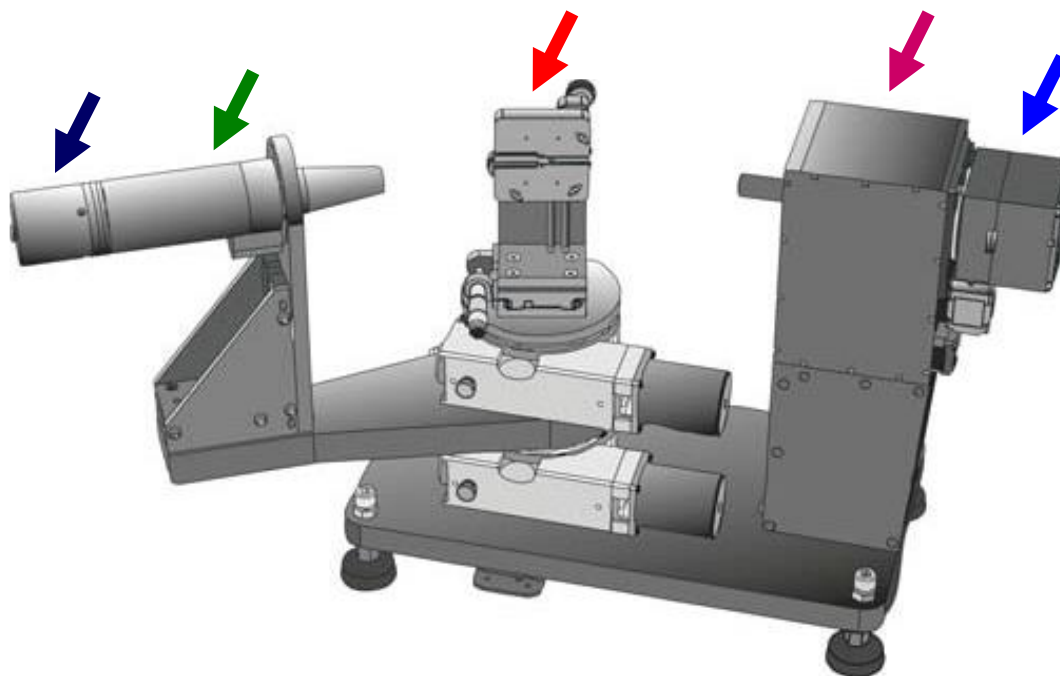


Construction of ellipsometer

example for J.A. Woollam VASE

Reminder: it measures change of polarization in terms of Ψ and Δ : $\rho = r_p / r_s = \tan \Psi \cdot e^{i\Delta}$

Monochromator → **Polarizer** → **Autoretarder** (changes phase shift of the p and s component) → **Sample** → **Analyzer** → **Detector**



Processing of raw data

bulk material

How to convert $\rho = r_p / r_s$ to n and k for bulk material?

in an ideal case (no roughness, no surface oxidation),
it can be done directly, by inverting the Fresnel equations:

$$r_p (n_1=1, n_2=n, \alpha_1), r_s (n_1=1, n_2=n, \alpha_1)$$



$$\epsilon = n^2 = (n+ik)^2 = \sin^2 \alpha_1 [1 + \tan^2 \alpha_1 (1-\rho)/(1+\rho)]$$

Processing of raw data

thin films

How to convert $\rho = r_p / r_s$ to n and k for (multi)layers?

choice of optical model (number and character of layers)
followed by iterative process minimizing the difference between

(1) $\Psi(\lambda)$ and $\Delta(\lambda)$ measured and

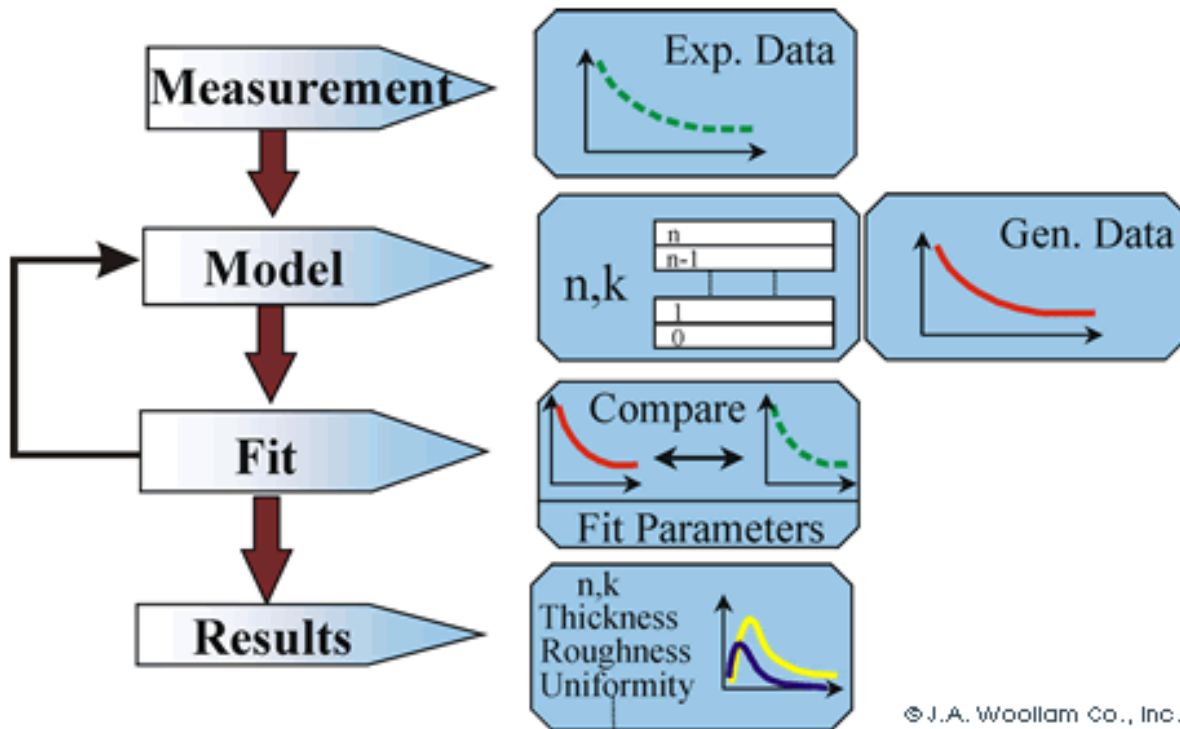
(2) $\Psi(\lambda)$ and $\Delta(\lambda)$ calculated from Fresnel equations for
parameters estimated for each layer of the optical model:
 $n(\lambda)$, $k(\lambda)$, thickness, etc.

Processing of raw data

thin films

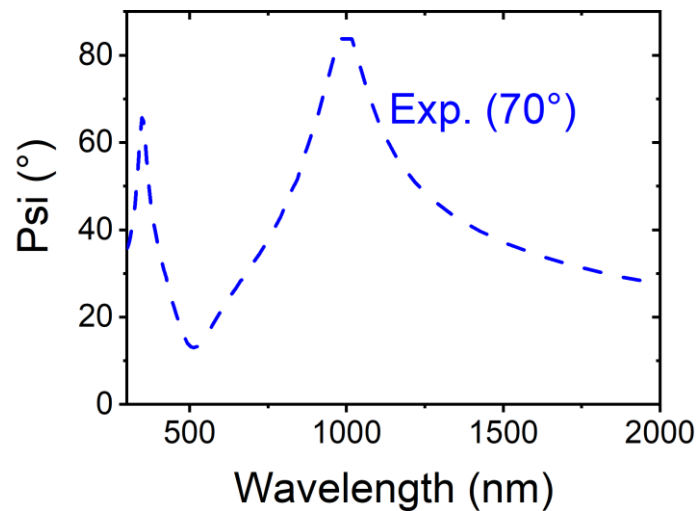
How to convert $\rho = r_p / r_s$ to n and k for (multi)layers?

choice of optical model (number and character of layers)
followed by iterative process



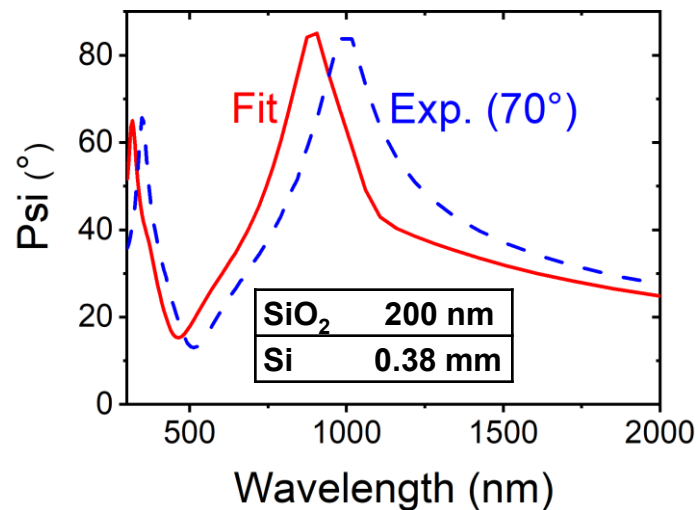
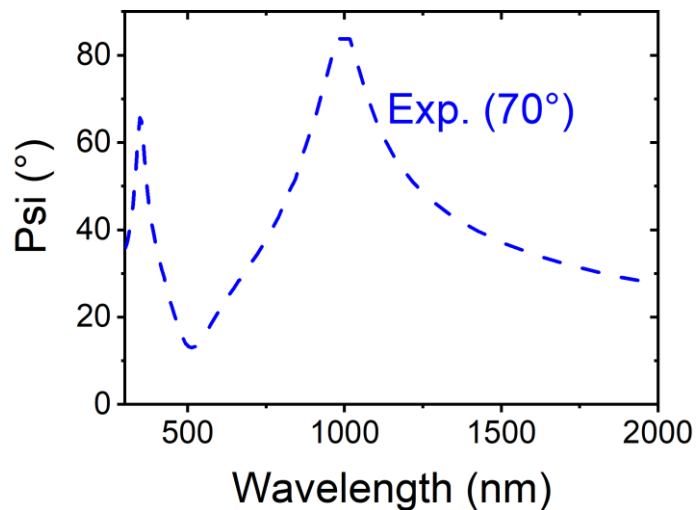
Processing of raw data

example (Si oxidation)



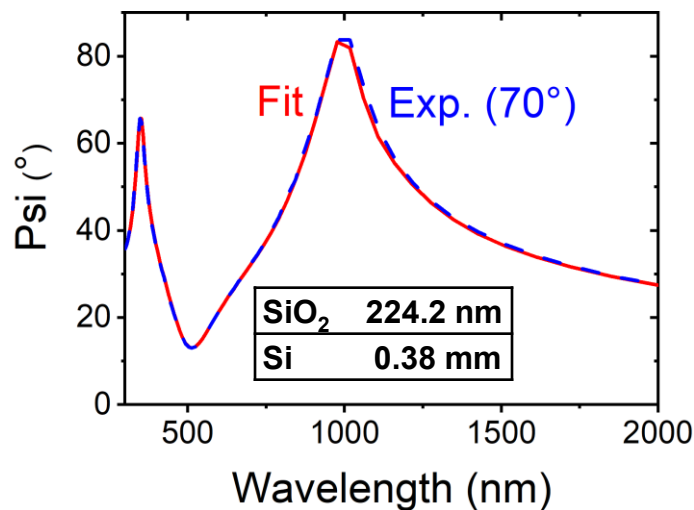
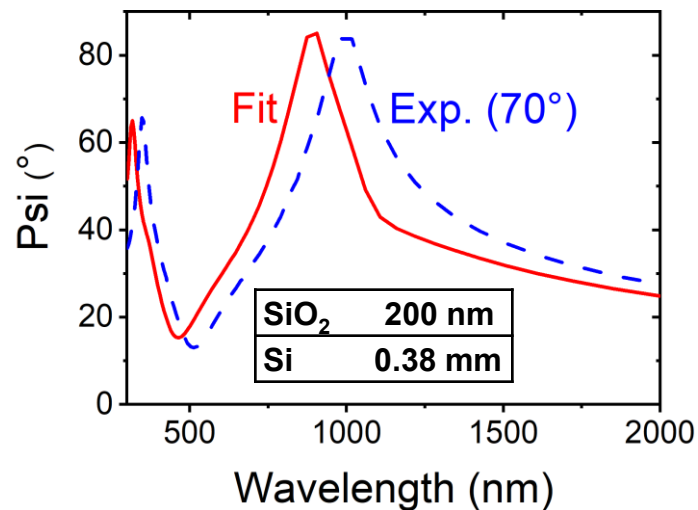
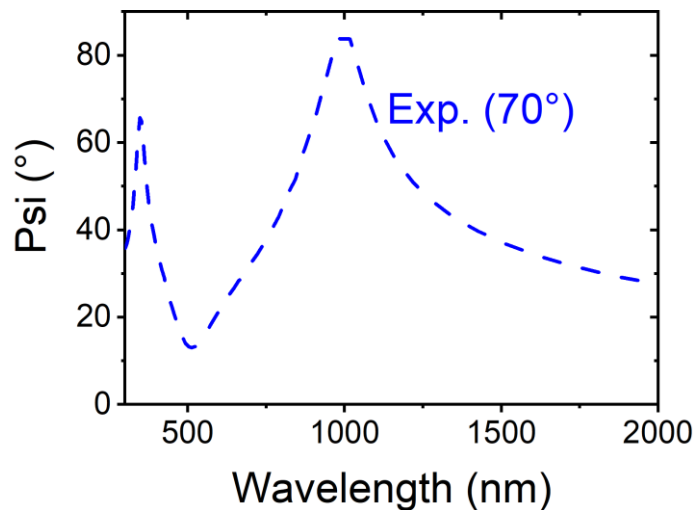
Processing of raw data

example (Si oxidation)



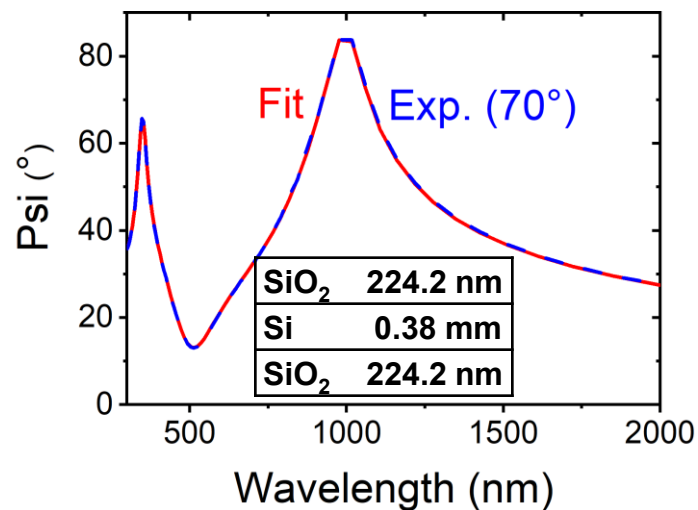
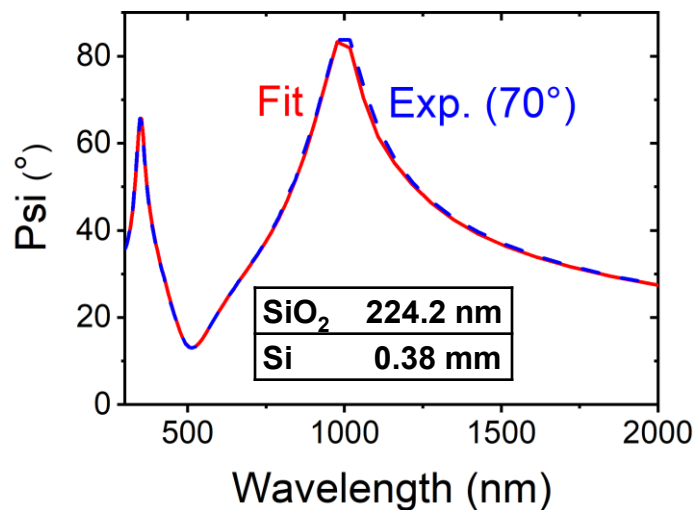
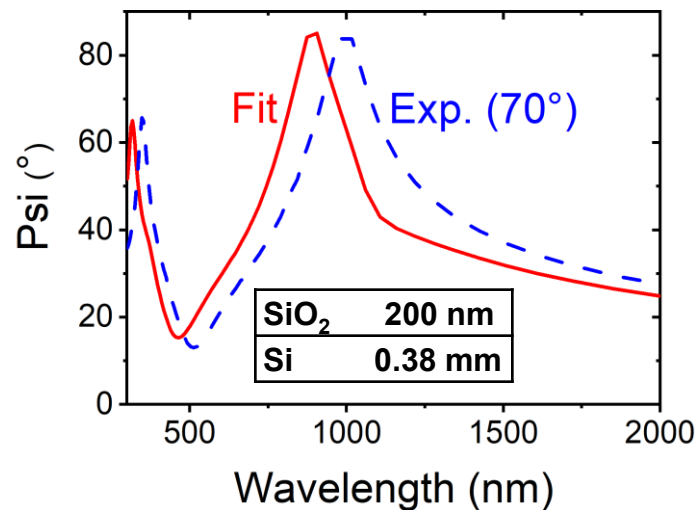
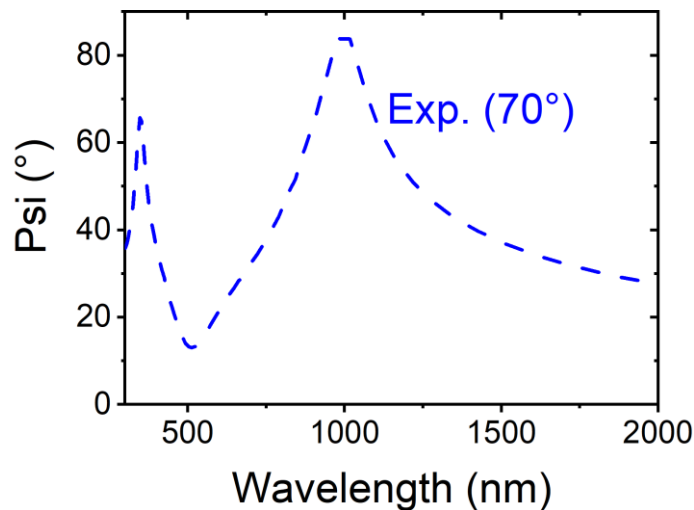
Processing of raw data

example (Si oxidation)



Processing of raw data

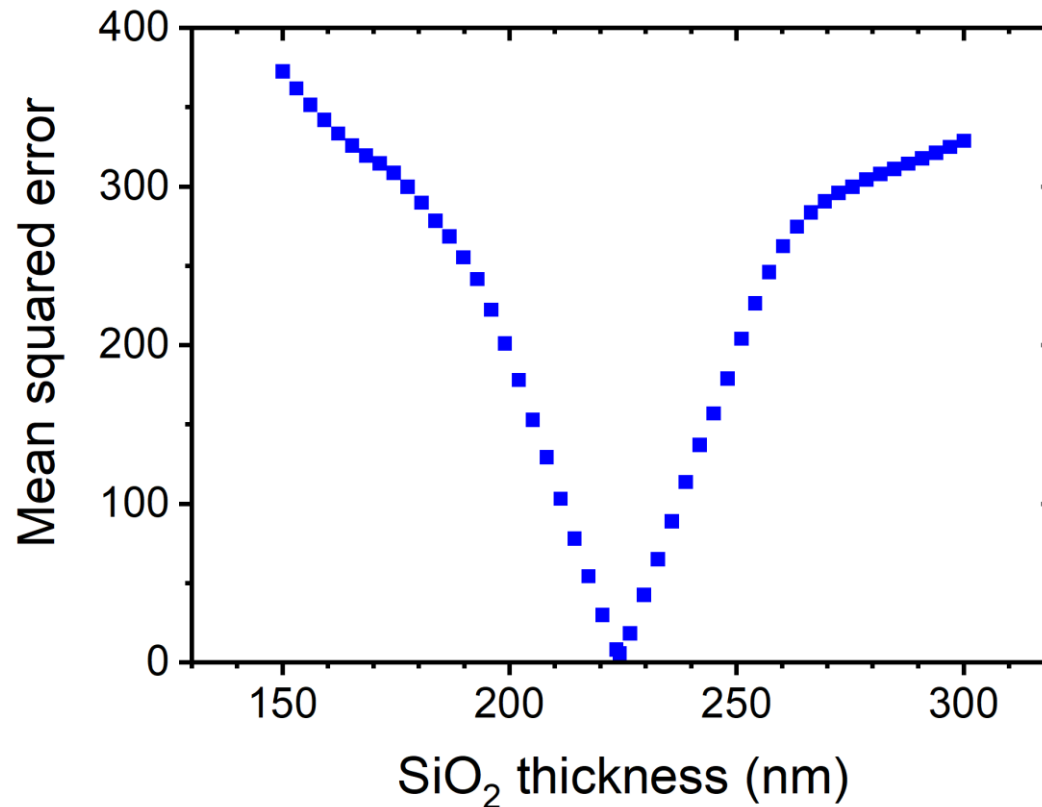
example (Si oxidation)



Processing of raw data

example (Si oxidation)

"uniqueness fit" : dependence of the difference between measured and fitted data on the SiO_2 thickness



SiO ₂	224.2 nm
Si	0.38 mm
SiO ₂	224.2 nm

Dispersion relations

motivation

Problem (measurement at N wavelengths, transparent mat.):

$2N+1$ variables for each layer: $N \times n$, $N \times k$, thickness

... but only ...

$2N$ equations for each incident angle: $N \times \Psi$, $N \times \Delta$

Solution 1: measure at more incident angles

(3 angles $\Rightarrow$ $6N$ equations, still $2N+1$ variables)

It helps and people do that, but it is not that simple:

- data for different angles are not really independent (similarity of the equations increases the role of exactness / noise)
- sensitivity is high mainly around the Brewster angle ($r_p = 0$)
- there are more variables than $2N+1$ for multilayers

Dispersion relations

motivation

Problem (measurement at N wavelengths, transparent mat.):

$2N+1$ variables for each layer: $N \times n$, $N \times k$, thickness

... but only ...

$2N$ equations for each incident angle: $N \times \Psi$, $N \times \Delta$

Solution 2: dispersion relations $n(\lambda)$ a $k(\lambda)$
[or $n(E)$ and $k(E)$ or $\varepsilon_{1,2}(\lambda)$ or $\varepsilon_{1,2}(E)$]

This really helps:

- replacement of $2N$ variables by few param. of these relations
- parameters can have interesting physical meaning
- noise in the raw data does not affect fitted data

Dispersion relations

selected examples

Cauchy (transparent materials - wide band gap)

$$n = A_n + B/\lambda^2 + C/\lambda^4$$

$$k = A_k e^{B_k(E-E_g)} \text{ (Urbach tail, only } A_k \text{ and } B_k \text{ are fitted: } E_g \text{ is not independent)}$$

Lorentz (metals)

$$\varepsilon = ABE_n / (E_n^2 - E^2 - iBE)$$

Drude (free charge carriers)

$$\varepsilon = AB / (-E^2 - iBE)$$

Drude (equivalent form which contains resistivity)

$$\varepsilon = -\hbar^2 / [\varepsilon_0 \rho (\tau E^2 + i\hbar E)] \text{ where } \rho = m^* / nq^2 \tau = 1 / q\mu n$$

Dispersion relations

selected examples

Tauc - Lorentz

(materials with band gap)

$$\varepsilon_2 = ABE_n E^{-1} (E-E_g)^2 / [(E^2 - E_n^2)^2 + B^2 E^2]$$

$$\varepsilon_2 = 0 \text{ (but why not to include Urbach tail, see Cody-Lorentz)}$$

$$E \geq E_g$$

$$E < E_g$$

Cody - Lorentz

(materials with band gap)

$$\varepsilon_2 = \underbrace{ABE_n E / [(E^2 - E_n^2)^2 + B^2 E^2]}_{\text{Lorentz term, } L(E)} \underbrace{(E-E_g)^2 / [(E-E_g)^2 + E_p^2]}_{\text{Cody term, } G(E)} \quad E \geq E_g + E_t$$

$$\varepsilon_2 = L(E_g + E_t) G(E_g + E_t) \underbrace{(E_g + E_t)/E \exp[(E-E_g-E_t)/E_u]}_{\text{(Urbach tail)}} \quad E < E_g + E_t$$

Gaussian

(bond vibrations in IR [alternative to Lorentz])

$$\varepsilon_2 = A \exp[-(E/\sigma - E_n/\sigma)^2] - A \exp[-(E/\sigma + E_n/\sigma)^2]$$

why only ε_2 : in all case ε_1 from the Kramers-Kronig relations
(see below)

Dispersion relations

Cody-Lorentz in more detail

Tauc - Lorentz

(materials with band gap)

$$\varepsilon_2 = ABE_n E^{-1} (E-E_g)^2 / [(E^2 - E_n^2)^2 + B^2 E^2]$$

$$\varepsilon_2 = 0 \text{ (but why not to include Urbach tail, see Cody-Lorentz)}$$

$$E \geq E_g$$

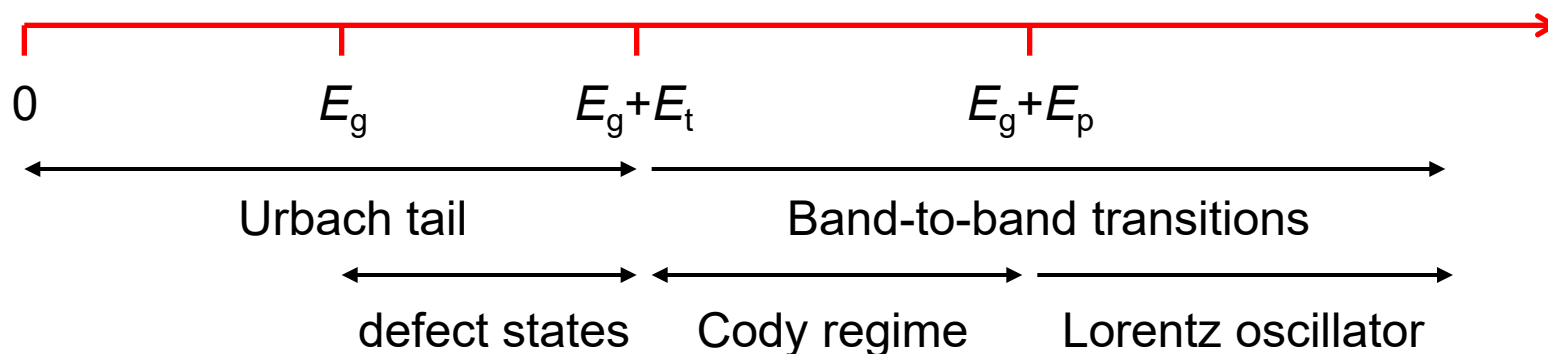
$$E < E_g$$

Cody - Lorentz

(materials with band gap)

$$\varepsilon_2 = \underbrace{ABE_n E / [(E^2 - E_n^2)^2 + B^2 E^2]}_{\text{Lorentz term, } L(E)} \underbrace{(E-E_g)^2 / [(E-E_g)^2 + E_p^2]}_{\text{Cody term, } G(E)} \quad E \geq E_g + E_t$$

$$\varepsilon_2 = L(E_g + E_t) G(E_g + E_t) \underbrace{(E_g + E_t)/E \exp[(E-E_g-E_t)/E_u]}_{\text{(Urbach tail)}} \quad E < E_g + E_t$$



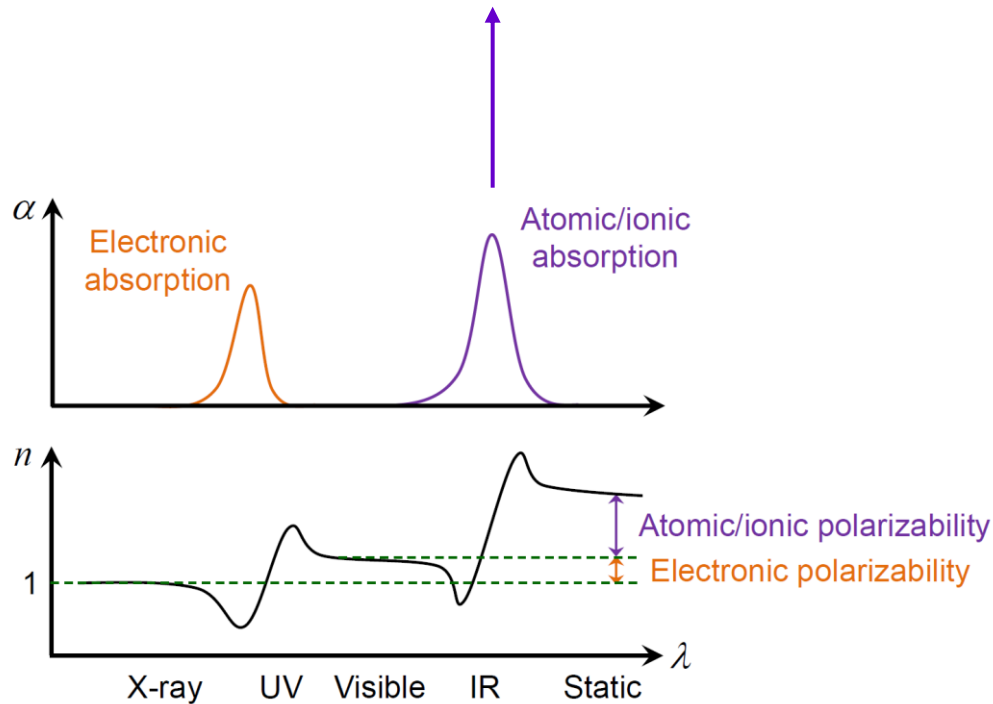
Dispersion relations

selected examples

Gaussian

(bond vibrations in IR, i.e. Atomic/ionic absorption in the figure from start of this chapter [alternative to Lorentz])

$$\varepsilon_2 = A \exp[-(E/\sigma - E_n/\sigma)^2] - A \exp[-(E/\sigma + E_n/\sigma)^2]$$



Dispersion relations

Kramers-Kronig relations for permittivity

K.-K. relations allow to calculate (except integration constant) real part of a function from its imaginary part and vice versa

$$\chi_1(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_2(\omega')}{\omega' - \omega} d\omega' \quad \chi_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_1(\omega')}{\omega' - \omega} d\omega'$$

P: Cauchy principal value (limit of integral for its limits going to ∞)

Mathematician: there are conditions for the validity of these relations (function is analytical in upper/lower half-plane, in $\pm\infty$ approaches zero like $1/|\omega|$ or faster), fulfilled by all dispersion relations above except Cauchy (which work in praxis anyway)

Physicist: it can be shown that validity of the relations is required by causality (no interaction with EM field before we turn it on, ...)

Integration constant is permittivity in ∞ (far from the frequency where the Lorentz, Cody-Lorentz, etc. oscillator is centered)

Dispersion relations

where coming from, boundaries of parameters (Lorentz)

Imagine electrons, reacting to EM field $\vec{E}$ by vibrations similarly to damped harmonic oscillators in a macroworld

$$m \cdot \frac{d^2 \vec{r}}{dt^2} + m \cdot \Gamma \cdot \frac{d\vec{r}}{dt} + m \cdot \omega_n^2 \cdot \vec{r} = -e \cdot \vec{E}$$

Solution: oscillations $\vec{r}(\omega) = \frac{1}{m} \cdot \frac{-e \cdot \vec{E}}{(\omega_n^2 - \omega^2) - i \cdot \Gamma \cdot \omega}$

with an amplitude proportional to induced polarization and in turn permittivity $\Rightarrow$ Lorentz oscillator $\varepsilon = ABE_n / (E_n^2 - E^2 - iBE)$ (damping factor Γ in frequency units, B in energy units)

Amplitude of oscillations ($\Leftrightarrow$ absolute value of ε) is maximum for $E^2 = E_n^2 - B^2/2$, this maximum exists for $B \leq E_n\sqrt{2}$

Stronger damping $B > E_n\sqrt{2}$ is not in itself unphysical, but does not correspond to the regime assumed by the Lorentz oscillator (and by corresponding software), possibility of strange results

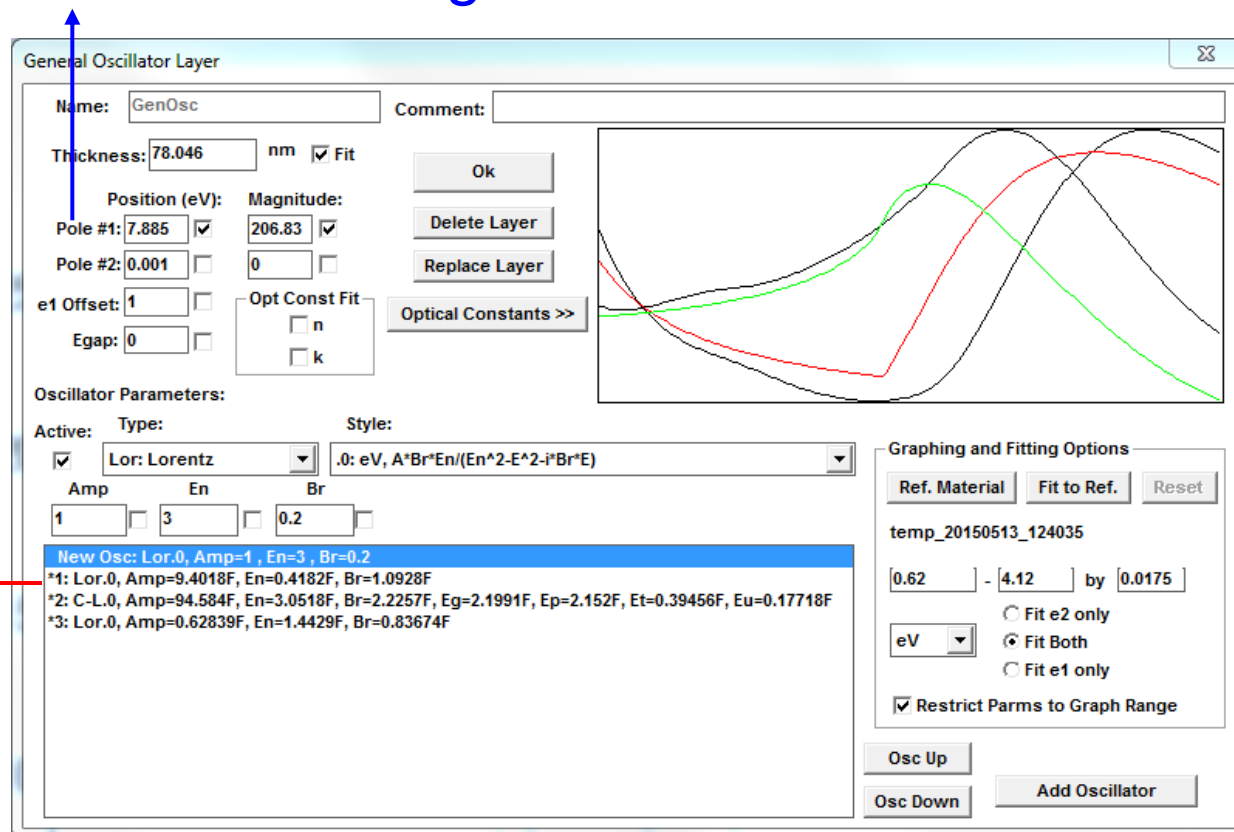
Dispersion relations

in praxis we often combine more of them

Example for VO₂: 1 Cody-Lorentz + 2 Lorentz oscillators

e1 offset or "pole oscillator" as its equivalent:

the aforementioned integration constant



Dispersion relations

in praxis we often combine more of them

Combination (in order to improve the fit) unphysically high number of oscillators (**overfitting**) is not desirable

Freeman Dyson: "I asked Fermi whether he was not impressed by the agreement between our calculated numbers and his measured numbers. He replied, "How many arbitrary parameters did you use for your calculations?" "Four." He said, "I remember my friend Johnny von Neumann used to say, **with four parameters I can fit an elephant**, and with five I can make him wiggle his trunk." With that, the conversation was over."

Dispersion relations

in praxis we often combine more of them

Freeman Dyson: "... with four parameters I can fit an elephant, and with five I can make him wiggle his trunk."

It is really possible (if the parameters are complex numbers)

Drawing an elephant with four complex parameters

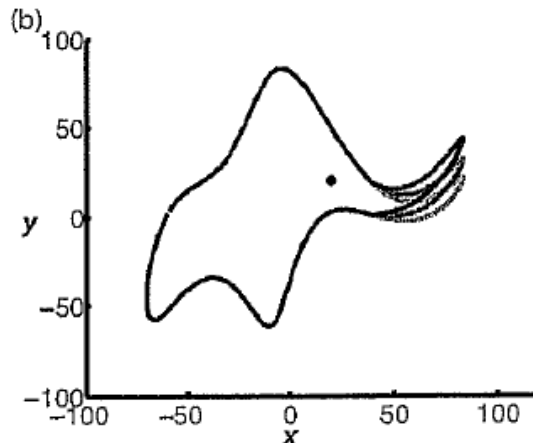
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We define four complex numbers representing the parameters needed to specify an elephantine shape. The real and imaginary parts of these complex numbers are the coefficients of a Fourier coordinate expansion, a powerful tool for reducing the data required to define shapes. © 2010 American Association of Physics Teachers.
[DOI: 10.1119/1.3254017]



Fourier series

$$x(t) = \sum_{k=0}^{\infty} (A_k^x \cos(kt) + B_k^x \sin(kt)), \quad (1)$$

$$y(t) = \sum_{k=0}^{\infty} (A_k^y \cos(kt) + B_k^y \sin(kt)), \quad (2)$$

Table I. The five complex parameters $p_1, \dots, p_5$ that encode the elephant including its wiggling trunk.

Parameter	Real part	Imaginary part
$p_1 = 50 - 30i$	$B_1^x = 50$	$B_1^y = -30$
$p_2 = 18 + 8i$	$B_2^x = 18$	$B_2^y = 8$
$p_3 = 12 - 10i$	$A_3^x = 12$	$B_3^y = -10$
$p_4 = -14 - 60i$	$A_4^x = -14$	$A_1^y = -60$
$p_5 = 40 + 20i$	Wiggle coeff. = 40	$x_{eye} = y_{eye} = 20$

Dispersion relations

in praxis we often combine more of them

Freeman Dyson: "... with four parameters I can fit an elephant,
and with five I can make him wiggle his trunk."

OK, one more quote of F. Dyson (when he got, as 15 years old,
Piaggio textbook of higher mathematics as a Christmas present)

"My idea of a joyful Christmas vacation was different. I arrived at the cottage on the coast with my precious Piaggio and did not intend to be parted from him. ... I worked my way through the problems. I started at six in the morning and stopped at ten in the evening, with short breaks for meals. I averaged fourteen hours a day. **Never have I enjoyed a vacation more.**"

Inhomogeneous materials

Mixture of several components with different optical constants can be described by **effective medium approximation**

One possible implementation: **Bruggemann equation**

$$\sum f_i \cdot [\varepsilon_i - \varepsilon] / [\varepsilon + L_i \cdot (\varepsilon_i - \varepsilon)] = 0 \quad (\text{and of course } \sum f_i = 1)$$

Depolarization factor L_i

- columnar structure / 1D inclusions: $L = 0; \varepsilon = \sum f_i \cdot \varepsilon_i$
- multilayered structure / 2D inclusions : $L = 1; 1/\varepsilon = \sum f_i / \varepsilon_i$
- randomly or. ellipsoids: $L_1 + L_2 + L_3 = 1$ (3 addends, weight 1/3)
- isotropic material / spherical incl.: $L = 1/3; \sum f_i \cdot [\varepsilon_i - \varepsilon] / [\varepsilon_i + 2\varepsilon] = 0$
(so frequent assumption that sometimes this simplified form is given as the Bruggemann equation)

Inhomogeneous materials

Maxwell-Garnett equation constitutes an alternative (leads to the same result for extremal values $L = 0$ or 1 , not in general)

Bruggemann equation for $L = 1/3$

$$\sum f_i \cdot [\varepsilon_i - \varepsilon] / [\varepsilon_i + 2\varepsilon] = 0$$

preferable when all components have similar roles

Maxwell-Garnett equation for $L = 1/3$

$$\sum f_i \cdot [\varepsilon_i - \varepsilon_m] / [\varepsilon_i + 2\varepsilon_m] = [\varepsilon - \varepsilon_m] / [\varepsilon + 2\varepsilon_m]$$

preferable when the components have different roles -
one constitutes continuous matrix (ε_m), other inclusions (ε_i)

Inhomogeneous materials

Permittivity of an inhomogeneous material is also related to its (average) polarizability, so it is not surprising that the equations resemble the Clausius-Mossoti relationship

Bruggemann equation for $L = 1/3$

$$\sum f_i \cdot [\varepsilon_i - \varepsilon] / [\varepsilon_i + 2\varepsilon] = 0$$

Maxwell-Garnett equation for $L = 1/3$

$$\sum f_i \cdot [\varepsilon_i - \varepsilon_m] / [\varepsilon_i + 2\varepsilon_m] = [\varepsilon - \varepsilon_m] / [\varepsilon + 2\varepsilon_m]$$

Clausius-Mossoti 37 slides above

$$[\varepsilon - 1] / [\varepsilon + 2] = 4\pi N \alpha / 3$$

Inhomogeneous materials

Bruggemann equation

preferable when all components have similar roles

Maxwell-Garnett equation

preferable when the components have different roles -
one constitutes continuous matrix, other inclusions

Example: 50% $n=1.500+0.000i$ + 50% $n=2.000+0.200i$

- $L=1/3$ (isotropic) : $n = 1.745+0.096i$ (Bruggemann)
 $n = 1.742+0.090i$ (Maxwell-Garnett)
- $L=0$ (columnar) : $n = 1.766+0.113i$
- $L=1$ (multilayer) : $n = 1.703+0.061i$

So not "naive" $n = 1.750+0.100i$

Hardcore description

Jones matrix, Muller matrix

Above we assumed that

- (1) the light is fully polarized, so it can be described by Jones vector of length 2 (p- and s- polarized component)
- (2) p-polarized light reflects as p-polarized, and s-polarized light reflects as s-polarized

If the first assumption is valid, but second invalid: Jones matrix 2×2 , which defines the relationship between Jones vector of the incident and reflected light, is not diagonal (in the case of polarizing optical elements we do not even want it to be)

$$\begin{pmatrix} E_p^{\text{refl}} \\ E_s^{\text{refl}} \end{pmatrix} = \begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} \begin{pmatrix} E_p^{\text{inc}} \\ E_s^{\text{inc}} \end{pmatrix} \quad \text{the second assumption above: } r_{ps} = r_{sp} = 0$$

Hardcore description

Jones matrix, Muller matrix

Above we assumed that

- (1) the light is fully polarized, so it can be described by Jones vector of length 2 (p- and s- polarized component)
- (2) p-polarized light reflects as p-polarized, and s-polarized light reflects as s-polarized

If the first assumption is also invalid: the light is described by Stokes vector of length 4, and its interaction with material / optical element is described by Muller matrix 4×4

(M_{11} gives ratio of intensities, not polarization $\Rightarrow$ ellipsometry can provide the remaining 15 components assuming $M_{11}=1$)

Ellipsometry - measurable properties

Parameters of optical model

- layer thicknesses
- roughness (microscopic)
- thickness nonuniformity (macroscopic)
- ratio of components which constitute an inhomogeneous layer

Dispersion relations $n(\lambda)$ and $k(\lambda)$

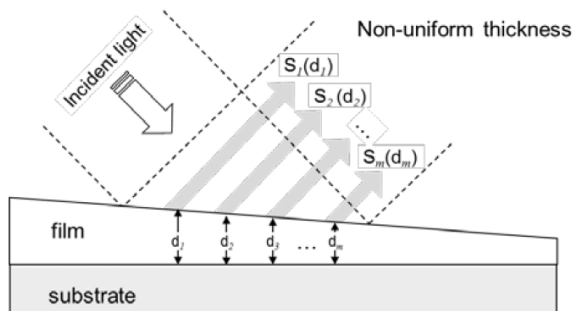
Parameters of dispersion relations

- band gap
- concentration / mobility of free charge carriers

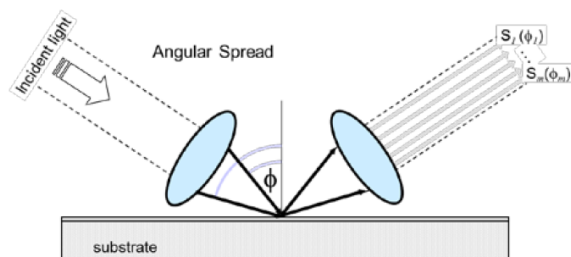
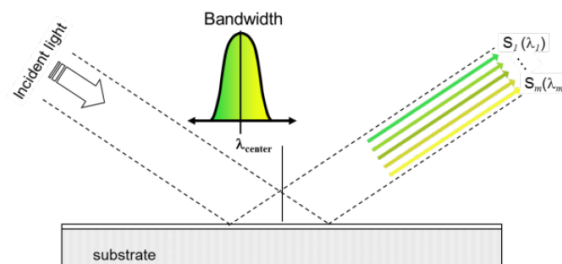
Special measurements, e.g. anisotropic materials

Ellipsometry and other optical meas.

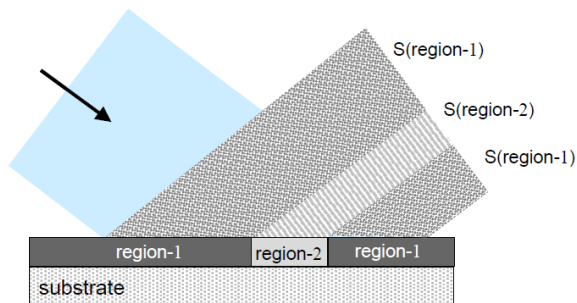
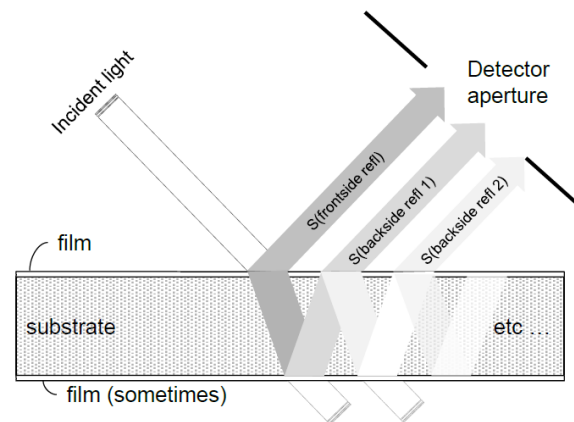
which non-idealities to take into account



b)



d)

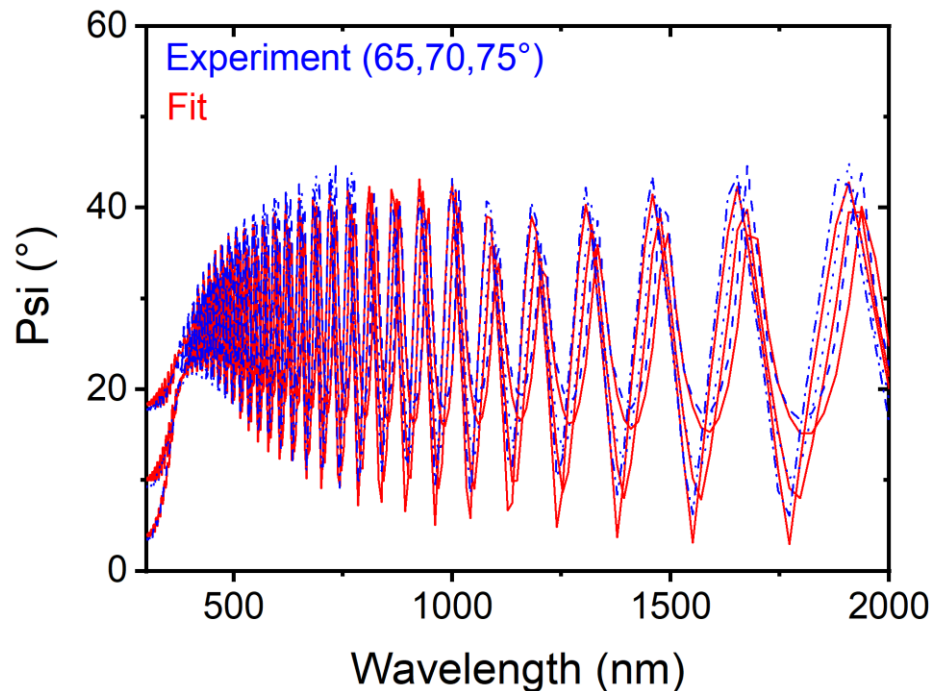


[fig. from the WVASE software manual]

Example 1 - oxidation of SiBCN

Sample before oxidation

amplitude does not change very much in transparent range
(interference on a single layer)



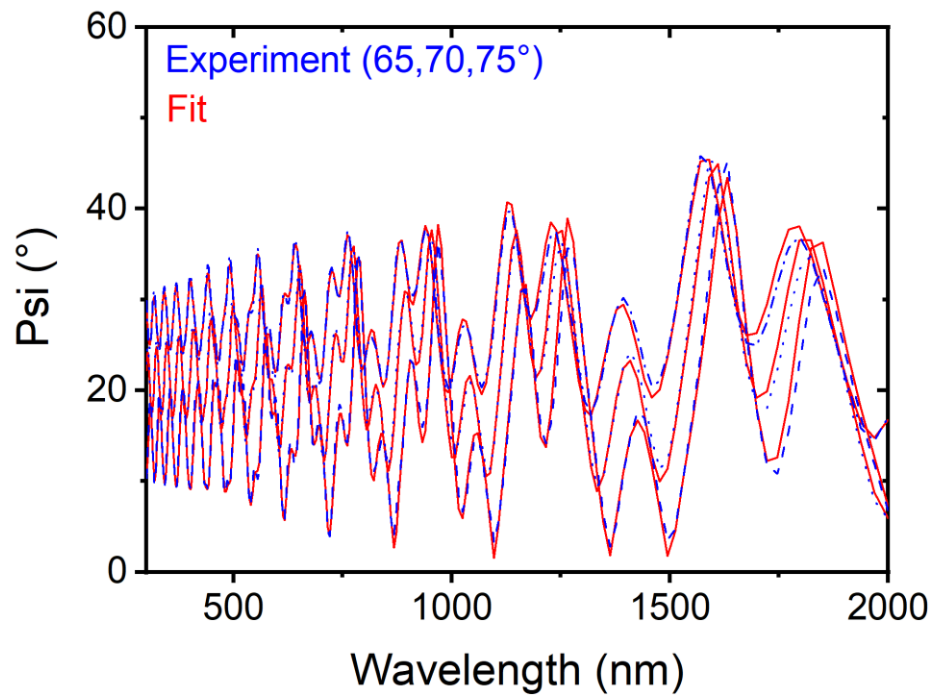
50% SiBCN + 50% void (surface roughness)	7 nm
SiBCN (Cody-Lorentz oscillator)	3775 nm
Si	0.38 mm

Example 1 - oxidation of SiBCN

Sample after oxidation (1700 °C)

variable amplitude

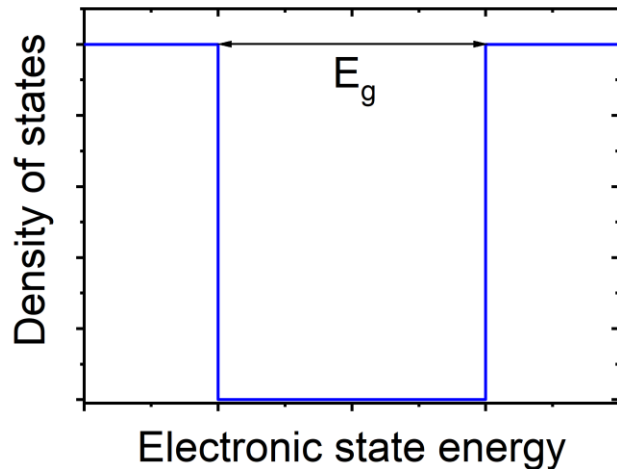
(interference on a multilayer)



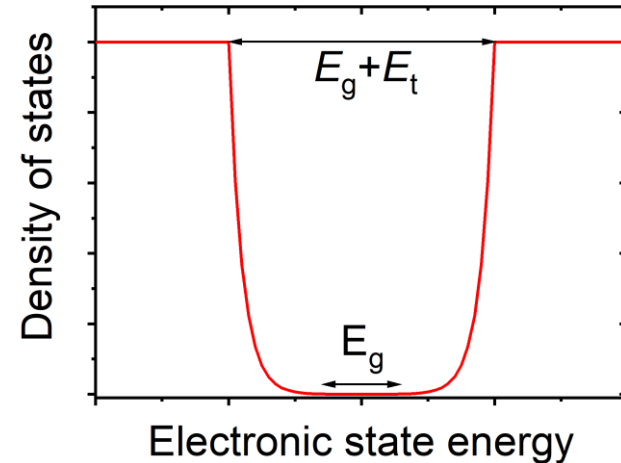
oxidized SiBCN (Cody-Lorentz oscillator)	1890 nm
non-oxidized SiBCN (Cody-Lorentz oscillator)	2340 nm
SiC	0.25 mm

Example 2 - band gap of Ta₂O₅

(Nearly) Ideal



Defect-rich



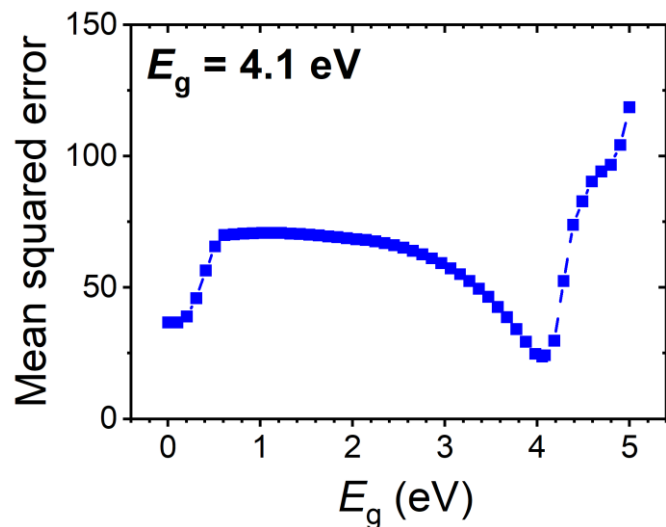
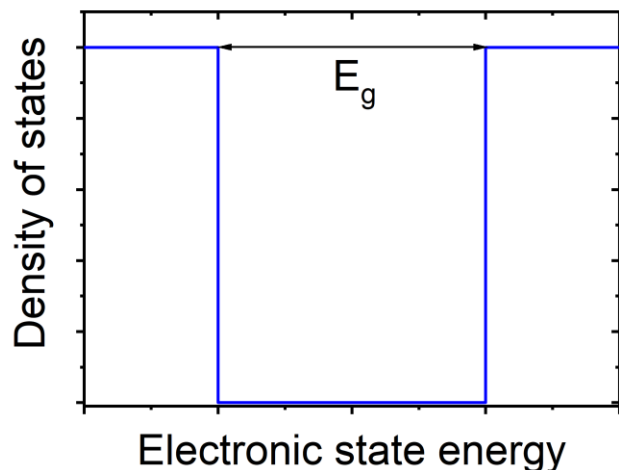
Cody - Lorentz

$$\varepsilon_2 = ABE_n E / [(E^2 - E_n^2)^2 + B^2 E^2] (E - E_g)^2 / [(E - E_g)^2 + E_p^2] \quad E \geq E_g + E_t$$

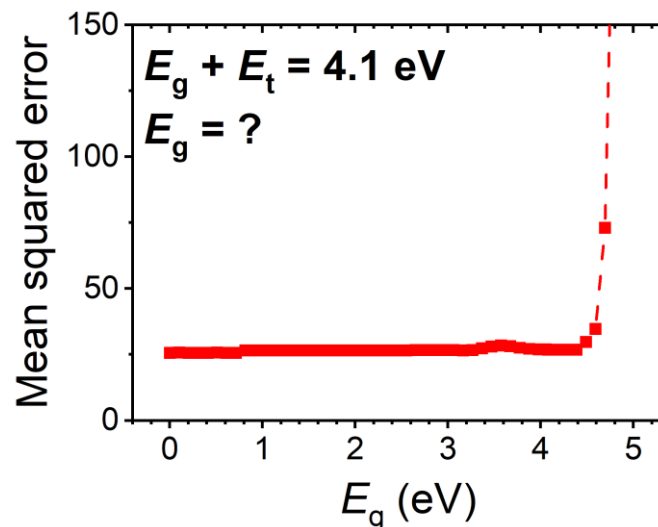
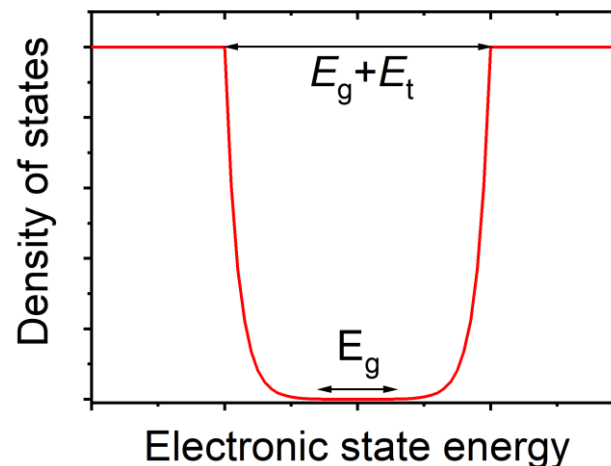
$$\varepsilon_2 = L(E_g + E_t) G(E_g + E_t) (E_g + E_t) / E \exp[(E - E_g - E_t) / E_u] \quad E < E_g + E_t$$

Example 2 - band gap of Ta_2O_5

(Nearly) Ideal

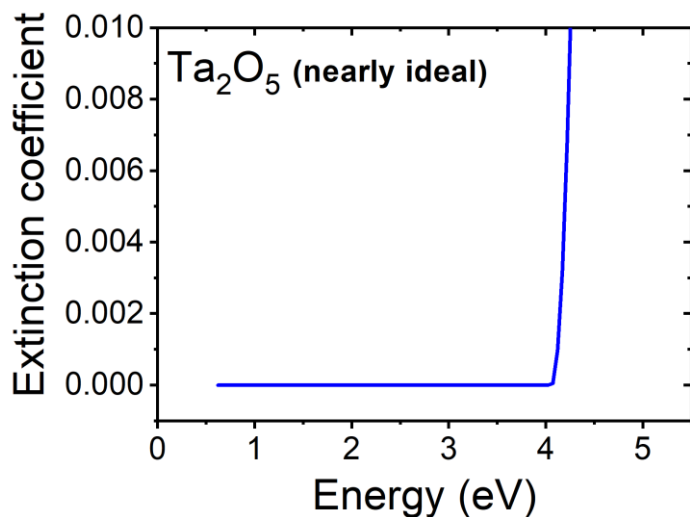
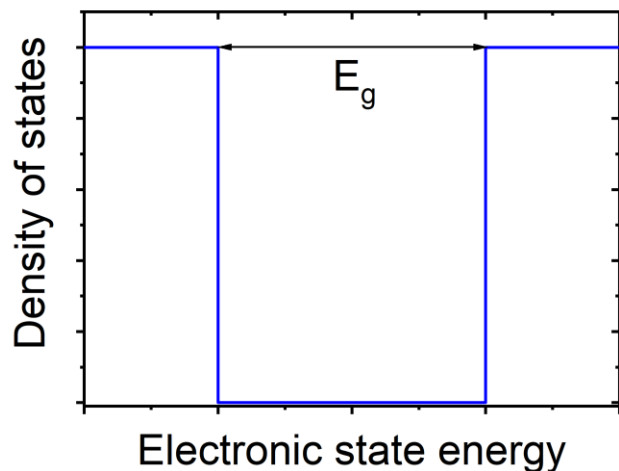


Defect-rich

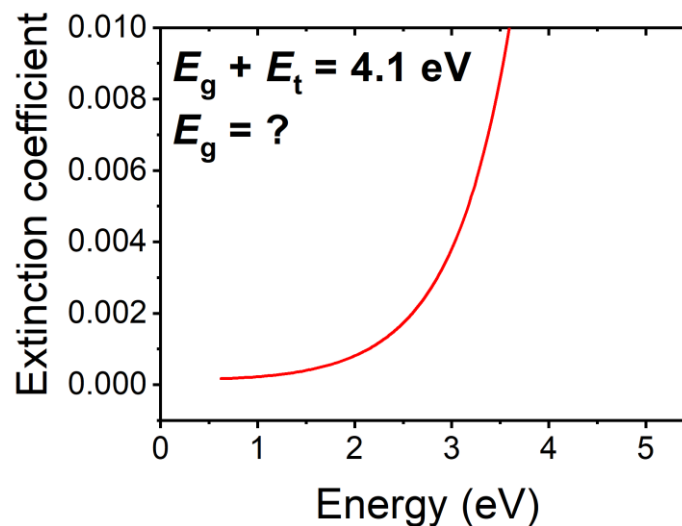
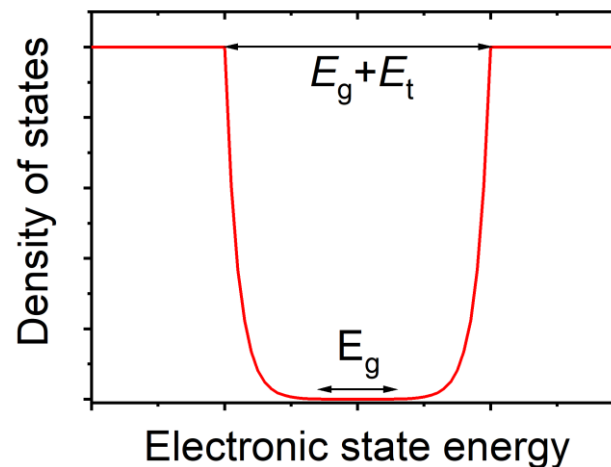


Example 2 - band gap of Ta_2O_5

(Nearly) Ideal

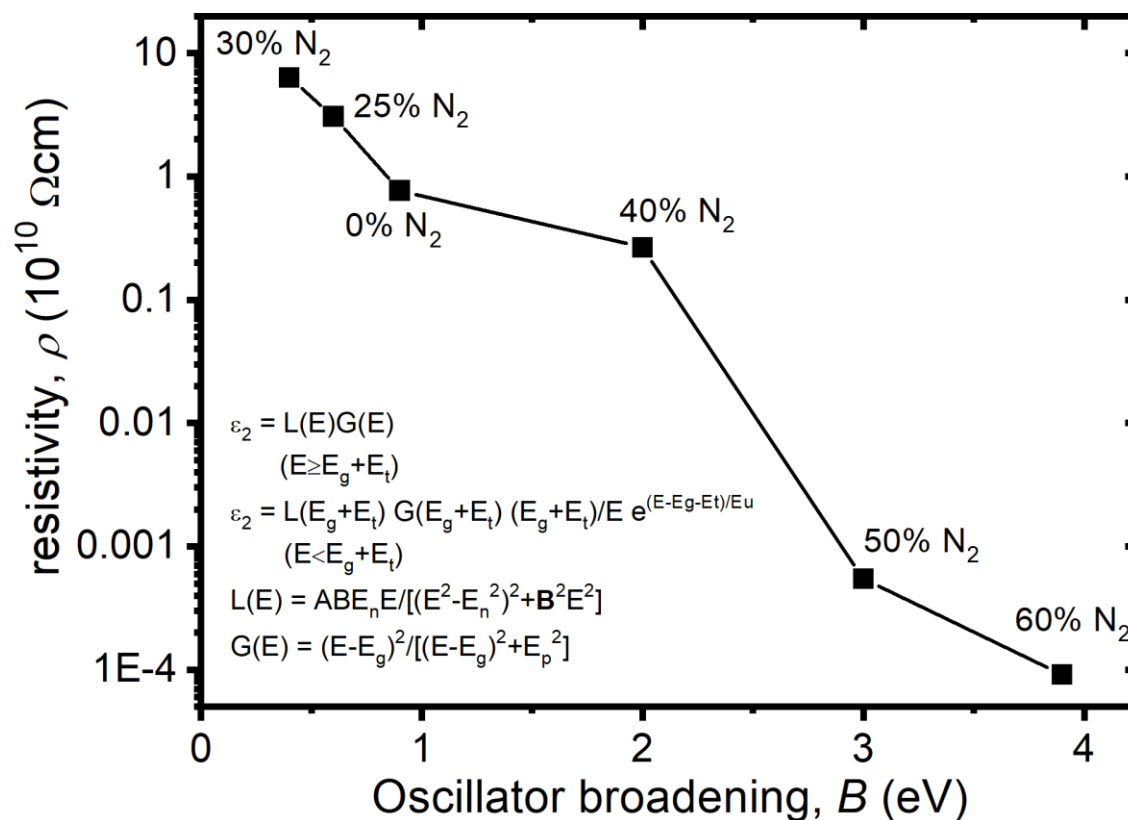


Defect-rich



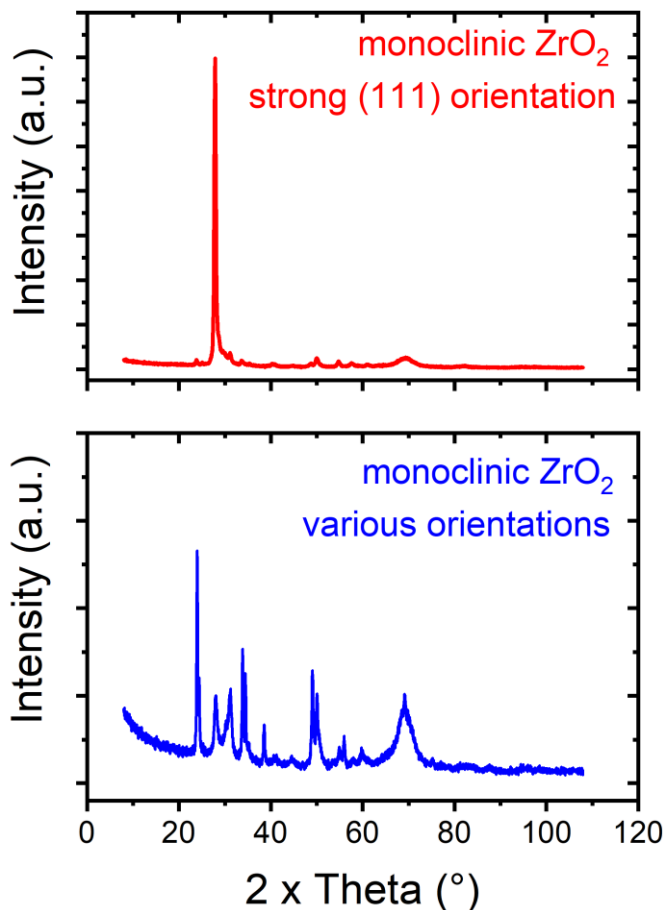
Example 3 - relationship of oscillator broadening and resistivity of TaON

O-rich TaON compositions with wide band gap:
 high $B \Rightarrow$ defects etc. $\Rightarrow$ more free charge carriers



Example 4 - anisotropy of ZrO_2

X-ray diffraction



Ellipsometry (550 nm)

in the surface plane:

$$n_x = 2.184$$

normal to the surface plane:

$$n_z = 2.157$$

in the surface plane:

$$n_x = 2.077$$

normal to the surface plane:

$$n_z = 2.072$$

Reflection of normal beam

First a reminder of Fresnel equations

$$r_p = (\mathbf{n}_1 \cos \alpha_2 - \mathbf{n}_2 \cos \alpha_1) / (\mathbf{n}_1 \cos \alpha_2 + \mathbf{n}_2 \cos \alpha_1)$$

$$r_s = (\mathbf{n}_1 \cos \alpha_1 - \mathbf{n}_2 \cos \alpha_2) / (\mathbf{n}_1 \cos \alpha_1 + \mathbf{n}_2 \cos \alpha_2)$$

where α_1 is angle of incidence and $n_1 \sin \alpha_1 = n_2 \sin \alpha_2$

For normal beam ($\alpha_1 = \alpha_2 = 0$; typical case when measuring transmittance) there is no plane of incidence, and indeed $r_p = r_s$

Reflection of normal beam

First a reminder of Fresnel equations

$$r_p = (\mathbf{n}_1 \cos \alpha_2 - \mathbf{n}_2 \cos \alpha_1) / (\mathbf{n}_1 \cos \alpha_2 + \mathbf{n}_2 \cos \alpha_1)$$

$$r_s = (\mathbf{n}_1 \cos \alpha_1 - \mathbf{n}_2 \cos \alpha_2) / (\mathbf{n}_1 \cos \alpha_1 + \mathbf{n}_2 \cos \alpha_2)$$

If we are interested in amplitude (general case)

$$r = (\mathbf{n}_1 - \mathbf{n}_2) / (\mathbf{n}_1 + \mathbf{n}_2)$$

If we are interested in amplitude (transparent media $\Leftrightarrow k_{1,2} = 0$)

$$r = (n_1 - n_2) / (n_1 + n_2) \Rightarrow \text{reflection from optically denser matter} \\ (n_2 > n_1) \text{ changes phase of } 180^\circ$$

If we are interested in amplitude (transparent layer in air)

$$r = (1 - n) / (1 + n)$$

If we are interested in intensity (transparent layer in air)

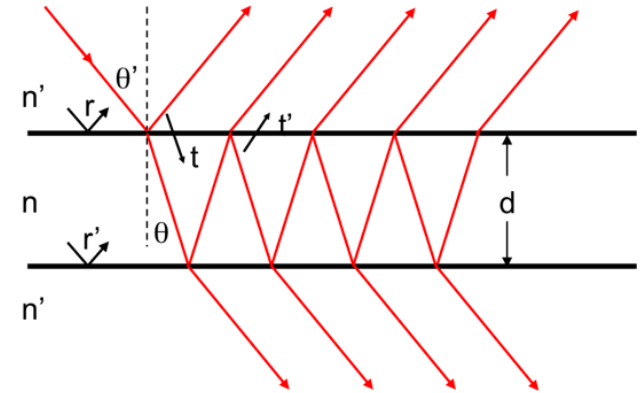
$$R = r^2 = (1 - n)^2 / (1 + n)^2$$

R and T

It is necessary to sum beams reflected from the layer frontside + beams 1 $\times$, 2 $\times$, 3 $\times$, ... reflected from the layer backside

Below: for simplicity, again a normal beam on transparent layer in air

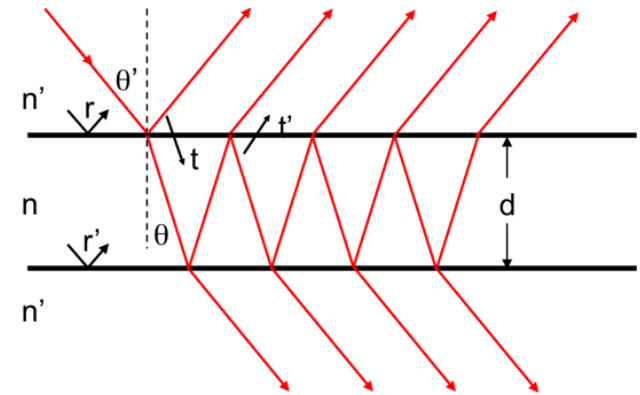
First a layer where interference does not take place (e.g. clean substrate). Why we do not observe the interference?



R and T

It is necessary to sum beams reflected from the layer frontside + beams 1 $\times$, 2 $\times$, 3 $\times$, ... reflected from the layer backside

Below: for simplicity, again a normal beam on transparent layer in air



First a layer where interference does not take place (e.g. clean substrate). Why we do not observe the interference?

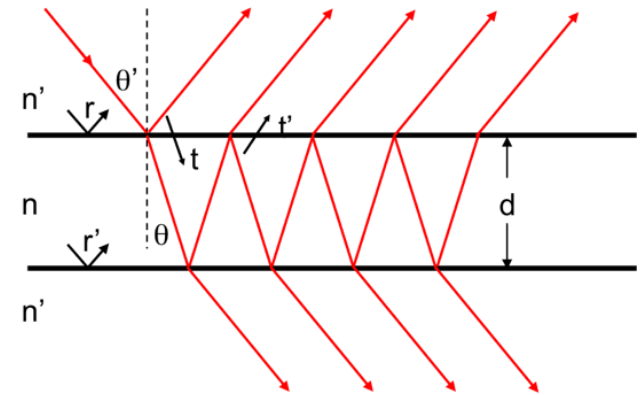
We would observe it for exact wavelengths λ . But in praxis the beam is characterized by $\lambda \pm \Delta\lambda$. If the difference between optical paths ($2\times$ thickness) is comparable with the coherence length $L \cong \lambda^2/\Delta\lambda$ (Gaussian spectrum: $L_G = \sqrt{(2\ln 2/\pi n)} \cdot \lambda^2/\Delta\lambda$) we lose the coherence and consequently also the interference.

$$\lambda = 550 \text{ nm}, \Delta\lambda = 8 \text{ nm}, n = 1.5 \Rightarrow L_G = 20 \text{ }\mu\text{m}$$

R and T

It is necessary to sum beams reflected from the layer frontside + beams 1×, 2×, 3×, ... reflected from the layer backside

Below: for simplicity, again a normal beam on transparent layer in air



Layer where interference does not take place

(so thick that the finite bandwidth of the beam is important)

⇒ we sum intensities

$$R_{\text{one_reflection}} = r^2 = (1-n)^2/(1+n)^2 \text{ (see above)}$$

$$\begin{aligned} R_{\text{total}} &= r^2 + (1-r^2) r^2 (1-r^2) + (1-r^2) r^2 r^2 r^2 (1-r^2) + \dots \\ &= 2 r^2/(1+r^2) = (n-1)^2/(n^2+1) = 8\% \text{ pro soda lime glass} \\ &\quad (n_{550} = 1.52) \end{aligned}$$

$$T_{\text{total}} = 1 - R_{\text{total}} = 2n/(n^2+1)$$

R and T

Thin film where interference does take place

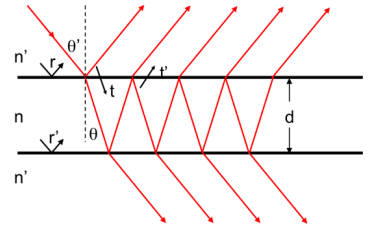
⇒ we sum amplitudes

$$|r_{\text{one_reflection}}| = |(1-n)/(1+n)| \text{ (see above)}$$

- first reflection (arrival from air) is from optically denser matter (⇒ phase changes of 180°)
- other reflections (efforts to leave the film into the air) are from optically thinner matter (⇒ phase does not change)



if all beams except the first one (reflected from the film frontside) interfere mutually constructively, they have opposite phase than the first one (and interfere destructively with it)



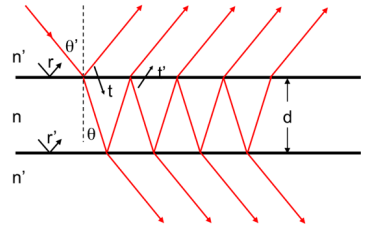
R and T

Thin film where interference does take place

⇒ we sum amplitudes

$$|r_{\text{one_reflection}}| = |(1-n)/(1+n)| \text{ (see above)}$$

if all beams except the first one (reflected from the film frontside) interfere mutually constructively, they have opposite phase than the first one (and interfere destructively with it)



Let's calculate both envelopes of the interference curve

$$\begin{aligned} r_{\text{max}} &= r + \sqrt{(1-r^2)} r \sqrt{(1-r^2)} - \sqrt{(1-r^2)} r r r \sqrt{(1-r^2)} + \dots \\ &= r + r(1-r^2)/(1+r^2) = (n^2-1)/(n^2+1) \end{aligned}$$

$$\begin{aligned} r_{\text{min}} &= r - \sqrt{(1-r^2)} r \sqrt{(1-r^2)} - \sqrt{(1-r^2)} r r r \sqrt{(1-r^2)} - \dots \\ &= r - r(1-r^2)/(1-r^2) = 0 \end{aligned}$$

$$R_{\text{max}} = r_{\text{max}}^2 = (n^2-1)^2/(n^2+1)^2, \quad T_{\text{min}} = 1-R_{\text{max}} = 4n^2/(n^2+1)^2$$

$$R_{\text{min}} = r_{\text{min}}^2 = 0, \quad T_{\text{max}} = 1-R_{\text{min}} = 1$$

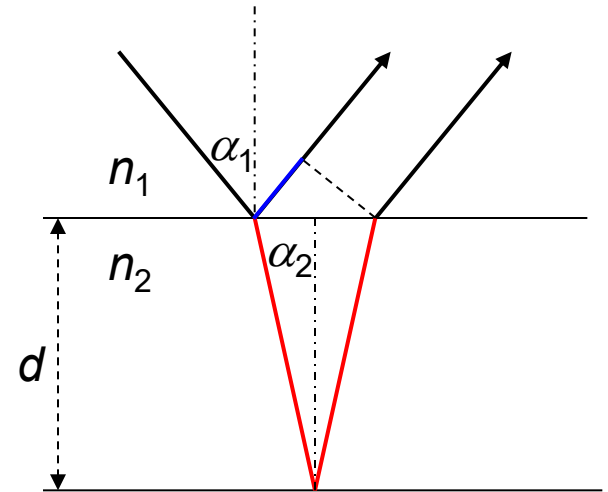
R and T

Thin film where interference does take place

What if the beam is not normal? How do we change thickness in order to preserve positions of interf. minima and maxima?

Beam reflected from the bottom boundary is delayed of $2.d.n_2/\cos\alpha_2$

Beam reflected from the top boundary is due to the lateral shift $2.d.\operatorname{tg}\alpha_2$ delayed of $2.d.n_1.\operatorname{tg}\alpha_2.\sin\alpha_1$
= (see the Snell law) $2.d.n_2.\operatorname{tg}\alpha_2.\sin\alpha_2$

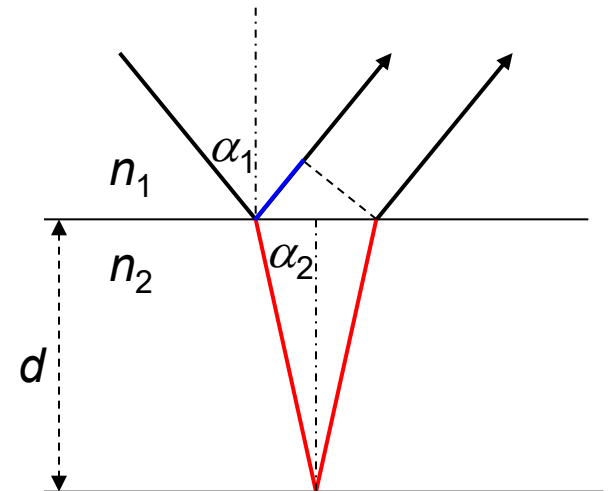


The total phase shift (let alone 180° in a case of one reflection from optically denser medium) is $2.d.n_2/\cos\alpha_2 - 2.d.n_2.\operatorname{tg}\alpha_2.\sin\alpha_2$
 $= (2.d.n_2/\cos\alpha_2).(1-\sin^2\alpha_2) = (2.d.n_2/\cos\alpha_2).\cos^2\alpha_2 = 2.d.n_2.\cos\alpha_2$

R and T

The total phase shift (let alone 180° in a case of one reflection from optically denser medium) is $2.d.n_2/\cos\alpha_2 - 2.d.n_2.\text{tg}\alpha_2.\sin\alpha_2 = (2.d.n_2/\cos\alpha_2).(1-\sin^2\alpha_2) = (2.d.n_2/\cos\alpha_2).\cos^2\alpha_2 = 2.d.n_2.\cos\alpha_2$

- $\cos\alpha_2$ in denominator (only the first summand) if we forgot to consider the lateral shift
- $\cos\alpha_2$ in numerator (both summands) after considering both shifts, i.e. **positions of interference minima and maxima are preserved for increasing layer thickness with increasing angle of incidence**



Minimum R

Thin film where interference does take place

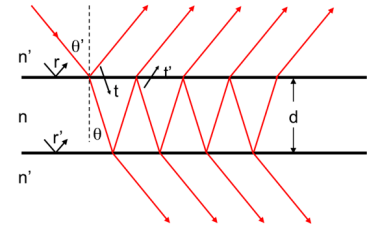
⇒ we sum amplitudes

Normal beam 3-4 slides above:

$$r_{\min} = r - r(1-r^2)/(1-r^2) = 0, \quad R_{\min} = r_{\min}^2 = 0$$

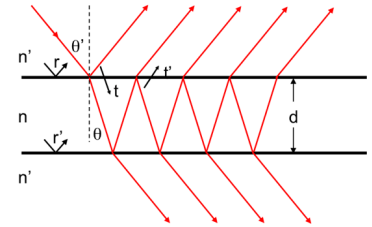
Relatively non-intuitive: if e.g. the first interaction includes reflection of 99% of the original energy ($r_{\text{one_reflection}} = \sqrt{0.99}$)

- it does not guarantee $R_{\min} \geq 0.99$
- it does not guarantee $R_{\min} \geq 0.99-0.01$
(destructive interference of intensities)
- it does not guarantee $R_{\min} \geq (\sqrt{0.99}-\sqrt{0.01})^2$
(destructive interference of amplitudes)
- indeed, $R_{\min} = 0$

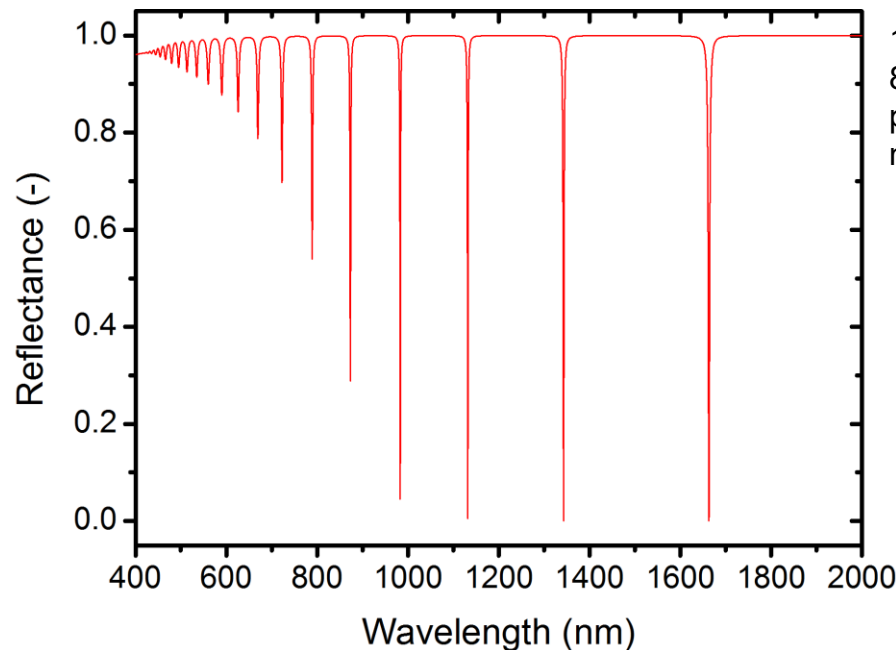


Minimum R - lossy mode resonance

Thin film where interference does take place
 $\Rightarrow$ we sum amplitudes



Almost tangential beam: *lossy mode resonance*
takes place: $R_{\min} = 0$ also here, but the minima are very sharp
(if all beams except the first one do not interfere exactly constructively, it becomes clear how weak they are)



1000 nm Si in the air
89.9° from normal
p-polarization (even sharper
minima for s-polarization)

R and T

General case (above layer n_0 , below layer n_1 , refractive index n is complex): see e.g. formulas in the cited paper Manificier et al.

A simple method for the determination of the optical constants n , k and the thickness of a weakly absorbing thin film

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Abstract We propose a new calculation following traditional methods for deducing optical constants and thickness from the fringe pattern of the transmission spectrum of a thin transparent dielectric film surrounded by non-absorbing media. The particular interest of this method, apart from its easiness, is that it makes a directly programmable calculation possible; the accuracy is of the same order as for the iteration method.

1 Introduction

The measurement of the transmission T of light through a parallel-faced dielectric film in the region of transparency is sufficient to determine the real and imaginary parts of the complex refractive index $\eta = n - ik$, as well as the thickness t . Both Hall and Ferguson (1955) and Lyashenko and Miloslavskii (1964) developed a method using successive approximations and interpolations to calculate these three quantities. We propose a similar method of analysis in the same range of applicability and precision. Our method can be distinguished from that of Lyashenko and Miloslavskii (1964) in two ways: firstly data handling, calculation and computation are easier, and secondly it gives an explicit expression for n , k , t . The accuracy for n and t will be emphasized.

2 Theory

Figure 1 represents a thin film with a complex refractive index $\eta = n - ik$, bounded by two transparent media with refractive

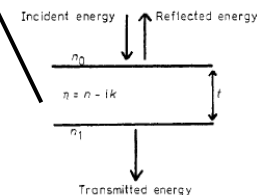


Figure 1 Reflection and transmission of light by a single film

R and T

General case (above layer n_0 , below layer n_1 , refractive index n is complex): see e.g. formulas in the cited paper Manificier et al.

For $k = 0$ and $n_0 = n_1 = 1$ again $T_{\max} = 1$ and $T_{\min} = 4n^2/(n^2+1)^2$

For zero thickness we obtain $T = T_{\max}$ ($T_{\min}$ never takes place)

It is possible to obtain $T_{\max} < T_{\min}$ (for n between n_0 and $n_1 \Rightarrow$ antireflection layer): transmittance without layer still equals $T_{\max}$, but here $T_{\max}$ is the lower envelope and $T_{\min}$ the upper envelope)

Determination of the optical constants of a thin film

indices, n_0 and n_1 . Considering a unit amplitude for the incident light, in the case of normal incidence the amplitude of the transmitted wave is given by

$$A = \frac{t_1 t_2 \exp(-2\pi i \eta t / \lambda)}{1 + r_1 r_2 \exp(-4\pi i \eta t / \lambda)} \quad (1)$$

in which t_1, t_2, r_1, r_2 are the transmission and reflection coefficients at the front and rear faces (Heavens 1965). The transmission of the layer is given by

$$T = \frac{n_1}{n_0} |A|^2. \quad (2)$$

The exact expression is given in the appendix. In the case of weak absorption (see appendix) with $k^2 \ll (n - n_0)^2$ and $k^2 \ll (n - n_1)^2$,

$$T = \frac{16n_0 n_1 n^2 \alpha}{C_1^2 + C_2^2 \alpha^2 + 2C_1 C_2 \alpha \cos(4\pi n t / \lambda)} \quad (3)$$

where $C_1 = (n + n_0)(n_1 + n)$, $C_2 = (n - n_0)(n_1 - n)$ and

$$\alpha = \exp(-4\pi k t / \lambda) = \exp(-K t). \quad (4)$$

K is the absorption coefficient of the thin film. Generally, outside the region of fundamental absorption ($h\nu > EG$; thin film gap) or of the free-carrier absorption (for higher wavelengths), the dispersion of n and k is not very large. The maxima and minima of T in equation (3) occur for

$$4\pi n t / \lambda = m\pi \quad (5)$$

where m is the order number. In the usual case ($n > n_0$, corresponding to a semiconducting film on a transparent non-absorbing substrate, $C_2 < 0$), the extreme values of the transmission are given by the formulae

$$T_{\max} = 16n_0 n_1 n^2 \alpha / (C_1 + C_2 \alpha)^2 \quad (6)$$

$$T_{\min} = 16n_0 n_1 n^2 \alpha / (C_1 - C_2 \alpha)^2. \quad (7)$$

By combining equations (6) and (7), Lyashenko and Miloslavskij (1964) developed an iterative method allowing the determination of n and α and, using (4) and (5), k and t .

We propose an important simplification of this method: we consider $T_{\min}$ and $T_{\max}$ as continuous functions of λ through $n(\lambda)$ and $\alpha(\lambda)$. These functions which are the envelopes of the maxima $T_{\max}(\lambda)$ and the minima $T_{\min}(\lambda)$ in the transmission spectrum are shown in figure 2. The ratio of equations (6) and (7) gives

$$\alpha = \frac{C_1 [1 - (T_{\max}/T_{\min})^{1/2}]}{C_2 [1 + (T_{\max}/T_{\min})^{1/2}]} \quad (8)$$

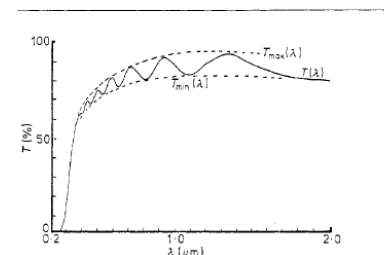


Figure 2 Typical transmission spectrum for a thin SnO_2 film of uniform thickness, $t = 0.9 \pm 0.04 \mu\text{m}$

Then, from equation (6),

$$n = [N + (N^2 - n_0^2 n_1^2)^{1/2}]^{1/2} \quad (9)$$

where

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0 n_1 \frac{T_{\max} - T_{\min}}{T_{\max} T_{\min}}.$$

Equation (9) shows that n is explicitly determined from $T_{\max}$, $T_{\min}$, n_1 and n_0 at the same wavelength.

Knowing n , we can determine α from equation (8). The thickness t of the layer can be calculated from two maxima or minima using equation (5):

$$t = \frac{M \lambda_1 \lambda_2}{2(n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1)} \quad (10)$$

where M is the number of oscillations between the two extrema ($M = 1$ between two consecutive maxima or minima); λ_1 , $n(\lambda_1)$ and λ_2 , $n(\lambda_2)$ are the corresponding wavelengths and indices of refraction. Knowing t and α we are able to calculate the extinction coefficient k from equation (4). It is worthwhile noting that expressions (8), (9) and (10) can be easily calculated using a programmable pocket calculator.

3 Precision of the method and experimental precautions

The relative error was determined using equation (11) obtained by combining equations (8) and (6):

$$\frac{n^2}{C_1 C_2} = \frac{T_{\min} T_{\max}}{4n_0 n_1 (T_{\min} - T_{\max})} \quad (11)$$

giving

$$f(n, n_0, n_1) \frac{dn}{n} = \left(\frac{dT_{\min}}{T_{\min}} \right) \left(\frac{T_{\max}}{T_{\max} - T_{\min}} \right) - \left(\frac{dT_{\max}}{T_{\max}} \right) \left(\frac{T_{\min}}{T_{\max} - T_{\min}} \right) \quad (12)$$

and

$$f(n, n_0, n_1) = \frac{2(n^2 - n_0 n_1)(n^2 + n_0 n_1)}{(n^2 - n_0^2)(n^2 - n_1^2)}.$$

We assumed: (i) that we could neglect the comparatively insignificant error in n_1 , which is usually the case for a glass substrate of known index of refraction, and (ii) that the errors for the two envelopes $T_{\max}(\lambda)$ and $T_{\min}(\lambda)$ are non-correlated. We then obtained

$$\frac{\Delta n}{n} = \frac{\Delta T}{T} \left(\frac{T_{\max} + T_{\min}}{T_{\max} - T_{\min}} \right) \frac{1}{|f(n, n_0, n_1)|} \quad (13)$$

with $\Delta T/T$ being the relative precision of measurements ($\Delta T/T = \Delta T_{\min}/T_{\min} = \Delta T_{\max}/T_{\max}$).

The function $f(n, n_0, n_1)$ has been plotted on figure 3 for $n_0 = 1$ and for two particular values of n_1 , $n_1 = 1.51$ and $n_1 = 1.6$, corresponding respectively to the two extreme values for a conventional glass substrate. Equation (12) shows that due to the presence of the ratio $(T_{\max} + T_{\min})/(T_{\max} - T_{\min})$ the accuracy is strongly affected when the amplitude of oscillations is weak. A necessary condition for a good fringe pattern is that the difference between n and n_1 should be as great as possible. Similarly, from equation (10), we obtain

$$\frac{dt}{t} = d\lambda \frac{n(\lambda_1) \lambda_2^2 - n(\lambda_2) \lambda_1^2}{\lambda_1 \lambda_2 (n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1)} + dn(\lambda_2) \frac{\lambda_1}{n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1} - dn(\lambda_1) \frac{\lambda_2}{n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1} \quad (14)$$

This can usually be simplified in the case of a weak dispersion of n ($n(\lambda_1) \approx n(\lambda_2)$, $dn(\lambda_1) \approx dn(\lambda_2)$) and leads to

$$\Delta t/t \approx \Delta \lambda (\lambda_1 + \lambda_2) / \lambda_1 \lambda_2 + \Delta n/n. \quad (15)$$

R and T - antireflection layers

Layer with n on substrate with n_1 , furthermore $k=0$ and $n_0=1$ (air): when is it most antireflective?

$$\begin{aligned} T_{\min} &= 1 \\ 16n_1n^2 &= (C_1 - C_2)^2 \\ 16n_1n^2 &= (2n^2 + 2n_1)^2 \\ 4n_1n^2 &= n^4 + 2n_1n^2 + n_1^2 \\ 0 &= n^4 - 2n_1n^2 + n_1^2 \\ 0 &= (n^2 - n_1)^2 \\ n &= \sqrt{n_1} \end{aligned}$$

Plus the interference condition, in order to be on the upper envelope represented by $T_{\min}$ (for the first order $d = \lambda/4n$)

Determination of the optical constants of a thin film

indices, n_0 and n_1 . Considering a unit amplitude for the incident light, in the case of normal incidence the amplitude of the transmitted wave is given by

$$A = \frac{t_1 t_2 \exp(-2\pi i \eta t / \lambda)}{1 + r_1 r_2 \exp(-4\pi i \eta t / \lambda)} \quad (1)$$

in which t_1, t_2, r_1, r_2 are the transmission and reflection coefficients at the front and rear faces (Heavens 1965). The transmission of the layer is given by

$$T = \frac{n_1}{n_0} |A|^2. \quad (2)$$

The exact expression is given in the appendix. In the case of weak absorption (see appendix) with $k^2 \ll (n - n_0)^2$ and $k^2 \ll (n - n_1)^2$,

$$T = \frac{16n_0n_1n^2\alpha}{C_1^2 + C_2^2\alpha^2 + 2C_1C_2\alpha \cos(4\pi n t / \lambda)} \quad (3)$$

where $C_1 = (n + n_0)(n_1 + n)$, $C_2 = (n - n_0)(n_1 - n)$ and

$$\alpha = \exp(-4\pi k t / \lambda) = \exp(-Kt). \quad (4)$$

K is the absorption coefficient of the thin film.

Generally, outside the region of fundamental absorption ($h\nu > EG$: thin film gap) or of the free-carrier absorption (for higher wavelengths), the dispersion of n and k is not very large. The maxima and minima of T in equation (3) occur for

$$4\pi n t / \lambda = m\pi \quad (5)$$

where m is the order number. In the usual case ($n > n_1$, corresponding to a semiconducting film on a transparent non-absorbing substrate, $C_2 < 0$), the extreme values of the transmission are given by the formulae

$$T_{\max} = 16n_0n_1n^2\alpha / (C_1 + C_2\alpha)^2 \quad (6)$$

$$T_{\min} = 16n_0n_1n^2\alpha / (C_1 - C_2\alpha)^2. \quad (7)$$

By combining equations (6) and (7), Lyashenko and Miloslavskii (1964) developed an iterative method allowing the determination of n and α and, using (4) and (5), k and t .

We propose an important simplification of this method: we consider $T_{\min}$ and $T_{\max}$ as continuous functions of λ through $n(\lambda)$ and $\alpha(\lambda)$. These functions which are the envelopes of the maxima $T_{\max}(\lambda)$ and the minima $T_{\min}(\lambda)$ in the transmission spectrum are shown in figure 2. The ratio of equations (6) and (7) gives

$$\alpha = \frac{C_1[1 - (T_{\max}/T_{\min})^{1/2}]}{C_2[1 + (T_{\max}/T_{\min})^{1/2}]} \quad (8)$$

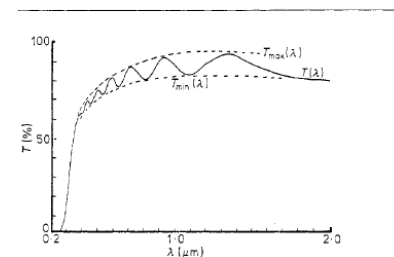


Figure 2 Typical transmission spectrum for a thin SnO_2 film of uniform thickness, $t = 0.9 \pm 0.04 \mu\text{m}$

Then, from equation (6),

$$n = [N + (N^2 - n_0^2 n_1^2)^{1/2}]^{1/2} \quad (9)$$

where

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0n_1 \frac{T_{\max} - T_{\min}}{T_{\max} + T_{\min}}.$$

Equation (9) shows that n is explicitly determined from $T_{\max}$, $T_{\min}$, n_1 and n_0 at the same wavelength.

Knowing n , we can determine α from equation (8). The thickness t of the layer can be calculated from two maxima or minima using equation (5):

$$t = \frac{M\lambda_1\lambda_2}{2(n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1)} \quad (10)$$

where M is the number of oscillations between the two extrema ($M=1$ between two consecutive maxima or minima); λ_1 , $n(\lambda_1)$ and λ_2 , $n(\lambda_2)$ are the corresponding wavelengths and indices of refraction. Knowing t and α we are able to calculate the extinction coefficient k from equation (4). It is worthwhile noting that expressions (8), (9) and (10) can be easily calculated using a programmable pocket calculator.

3 Precision of the method and experimental precautions

The relative error was determined using equation (11) obtained by combining equations (8) and (6):

$$\frac{n^2}{C_1C_2} = \frac{T_{\min}T_{\max}}{4n_0n_1(T_{\min} - T_{\max})} \quad (11)$$

giving

$$f(n, n_0, n_1) \frac{dn}{n} = \left(\frac{dT_{\min}}{T_{\min}} \right) \left(\frac{T_{\max}}{T_{\max} - T_{\min}} \right) - \left(\frac{dT_{\max}}{T_{\max}} \right) \left(\frac{T_{\min}}{T_{\max} - T_{\min}} \right) \quad (12)$$

and

$$f(n, n_0, n_1) = \frac{2(n^2 - n_0n_1)(n^2 + n_0n_1)}{(n^2 - n_0^2)(n^2 - n_1^2)}.$$

We assumed: (i) that we could neglect the comparatively insignificant error in n_1 , which is usually the case for a glass substrate of known index of refraction, and (ii) that the errors for the two envelopes $T_{\max}(\lambda)$ and $T_{\min}(\lambda)$ are non-correlated. We then obtained

$$\frac{\Delta n}{n} = \frac{\Delta T}{T} \left(\frac{T_{\max} + T_{\min}}{T_{\max} - T_{\min}} \right) \frac{1}{|f(n, n_0, n_1)|} \quad (13)$$

with $\Delta T/T$ being the relative precision of measurements ($\Delta T/T = \Delta T_{\min}/T_{\min} = \Delta T_{\max}/T_{\max}$).

The function $f(n, n_0, n_1)$ has been plotted on figure 3 for $n_0=1$ and for two particular values of n_1 , $n_1=1.51$ and $n_1=1.6$, corresponding respectively to the two extreme values for a conventional glass substrate. Equation (12) shows that due to the presence of the ratio $(T_{\max} + T_{\min})/(T_{\max} - T_{\min})$ the accuracy is strongly affected when the amplitude of oscillations is weak. A necessary condition for a good fringe pattern is that the difference between n and n_1 should be as great as possible. Similarly, from equation (10), we obtain

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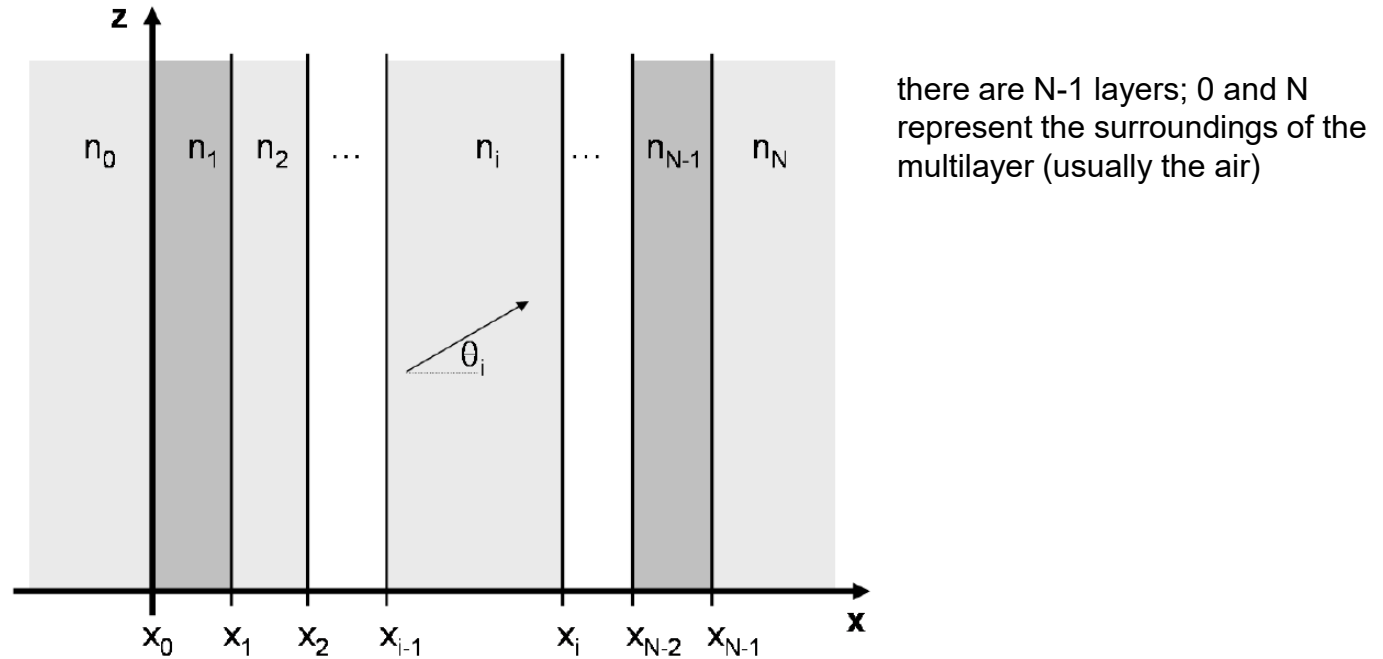
R and T

That's very nice, but the analytical sum of infinite series (8-10 slides above) is easy if there is a single homogeneous layer. But what if we want $T(R)$ of a complex multilayer? We probably do not want to analytically sum an infinite series inside an infinite series inside an infinite series

In parallel: we get sum of intensities (thick non-coherent layer) and sum of amplitudes (thin coherent layer). But what if there is a multilayer combining thin and thick layers?

Transfer matrix formalism

Effective way how to calculate the transmittance of a multilayer



Consider EM waves going forward ('F') and back ('B'):

- amplitudes constitute (for each polarization) vector of length 2
- relationship between amplitudes in front of and behind the layer is described (for each polarization) by a 2×2 matrix

Transfer matrix formalism

Effective way how to calculate the transmittance of a multilayer
Consider EM waves going forward ('F') and back ('B'):

Matrix describing transmission of EM wave trough a boundary

$$\mathbf{T}_{ij} = \frac{1}{t_{ij}} \begin{bmatrix} 1 & r_{ij} \\ r_{ij} & 1 \end{bmatrix}, \text{ i.e. } \begin{bmatrix} E_F(x_i^-) \\ E_B(x_i^-) \end{bmatrix} = \frac{1}{t_{ij}} \begin{bmatrix} 1 & r_{ij} \\ r_{ij} & 1 \end{bmatrix} \begin{bmatrix} E_F(x_i^+) \\ E_B(x_i^+) \end{bmatrix}$$

where for a normal beam $r_{ij} = (n_i - n_j)/(n_i + n_j)$ a $t_{ij} = 2n_i/(n_i + n_j)$
(see the Fresnel equations)

Transfer matrix formalism

Effective way how to calculate the transmittance of a multilayer
Consider EM waves going forward ('F') and back ('B'):

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where for a normal beam $r_{ij} = (n_i - n_j)/(n_i + n_j)$ and $t_{ij} = 2n_i/(n_i + n_j)$
(see the Fresnel equations)

Matrix describing the transmission of EM wave through a layer

$$\mathbf{T}_i = \begin{bmatrix} e^{j\Phi_i} & 0 \\ 0 & e^{-j\Phi_i} \end{bmatrix}$$

where for a normal beam $\Phi_i = 2\pi n_i d_i / \lambda$

(can be also found with minus: depending on the direction of 'x')

Transfer matrix formalism

Matrix describing transmission of EM wave through a boundary

$$\mathbf{T}_{ij} = \frac{1}{t_{ij}} \begin{bmatrix} 1 & r_{ij} \\ r_{ij} & 1 \end{bmatrix}$$

Matrix describing the transmission of EM wave through a layer

$$\mathbf{T}_i = \begin{bmatrix} e^{j\Phi_i} & 0 \\ 0 & e^{-j\Phi_i} \end{bmatrix}$$

Not to be confused with Jones matrix (which tells us how the intensity of only-reflected or only-transmitted beam is divided between both polarizations, now we divide the intensity between reflected and transmitting beam). Yes, the idea to represent the optical elements / layers by a product of matrices is similar.

Transfer matrix formalism

Matrix describing transmission of EM wave through a boundary

$$\mathbf{T}_{ij} = \frac{1}{t_{ij}} \begin{bmatrix} 1 & r_{ij} \\ r_{ij} & 1 \end{bmatrix}$$

Matrix describing the transmission of EM wave through a layer

$$\mathbf{T}_i = \begin{bmatrix} e^{j\Phi_i} & 0 \\ 0 & e^{-j\Phi_i} \end{bmatrix}$$

Matrix describing the transmission through whole multilayer

$$\begin{bmatrix} E_F(x_0^-) \\ E_B(x_0^-) \end{bmatrix} = \mathbf{T}_{0N} \begin{bmatrix} E_F(x_{N-1}^+) \\ E_B(x_{N-1}^+) \end{bmatrix} = \begin{bmatrix} T_{11}^{0N} & T_{12}^{0N} \\ T_{21}^{0N} & T_{22}^{0N} \end{bmatrix} \begin{bmatrix} E_F(x_{N-1}^+) \\ E_B(x_{N-1}^+) \end{bmatrix}$$

where $\mathbf{T}_{0N} = \mathbf{T}_{01} \mathbf{T}_1 \mathbf{T}_{12} \mathbf{T}_2 \dots \mathbf{T}_{(N-1)} \mathbf{T}_{(N-1)N}$

Transfer matrix formalism

Matrix describing the transmission through whole multilayer

$$\begin{bmatrix} E_F(x_0^-) \\ E_B(x_0^-) \end{bmatrix} = \mathbf{T}_{0N} \begin{bmatrix} E_F(x_{N-1}^+) \\ E_B(x_{N-1}^+) \end{bmatrix} = \begin{bmatrix} T_{11}^{0N} & T_{12}^{0N} \\ T_{21}^{0N} & T_{22}^{0N} \end{bmatrix} \begin{bmatrix} E_F(x_{N-1}^+) \\ E_B(x_{N-1}^+) \end{bmatrix}$$

where $\mathbf{T}_{0N} = \mathbf{T}_{01} \mathbf{T}_1 \mathbf{T}_{12} \mathbf{T}_2 \dots \mathbf{T}_{(N-1)} \mathbf{T}_{(N-1)N}$

The transmittance and reflectance of the multilayer is given by

$$r = \frac{E_B(x_0^-)}{E_F(x_0^-)} = \frac{T_{21}^{0N}}{T_{11}^{0N}}$$
$$t = \frac{E_F(x_{N-1}^+)}{E_F(x_0^-)} = \frac{1}{T_{11}^{0N}}$$

Transfer matrix formalism

Matrix describing the transmission through whole multilayer

$$\begin{bmatrix} E_F(x_0^-) \\ E_B(x_0^-) \end{bmatrix} = \mathbf{T}_{0N} \begin{bmatrix} E_F(x_{N-1}^+) \\ E_B(x_{N-1}^+) \end{bmatrix} = \begin{bmatrix} T_{11}^{0N} & T_{12}^{0N} \\ T_{21}^{0N} & T_{22}^{0N} \end{bmatrix} \begin{bmatrix} E_F(x_{N-1}^+) \\ E_B(x_{N-1}^+) \end{bmatrix}$$

where $\mathbf{T}_{0N} = \mathbf{T}_{01}\mathbf{T}_1\mathbf{T}_{12}\mathbf{T}_2\ldots\mathbf{T}_{(N-1)}\mathbf{T}_{(N-1)N}$

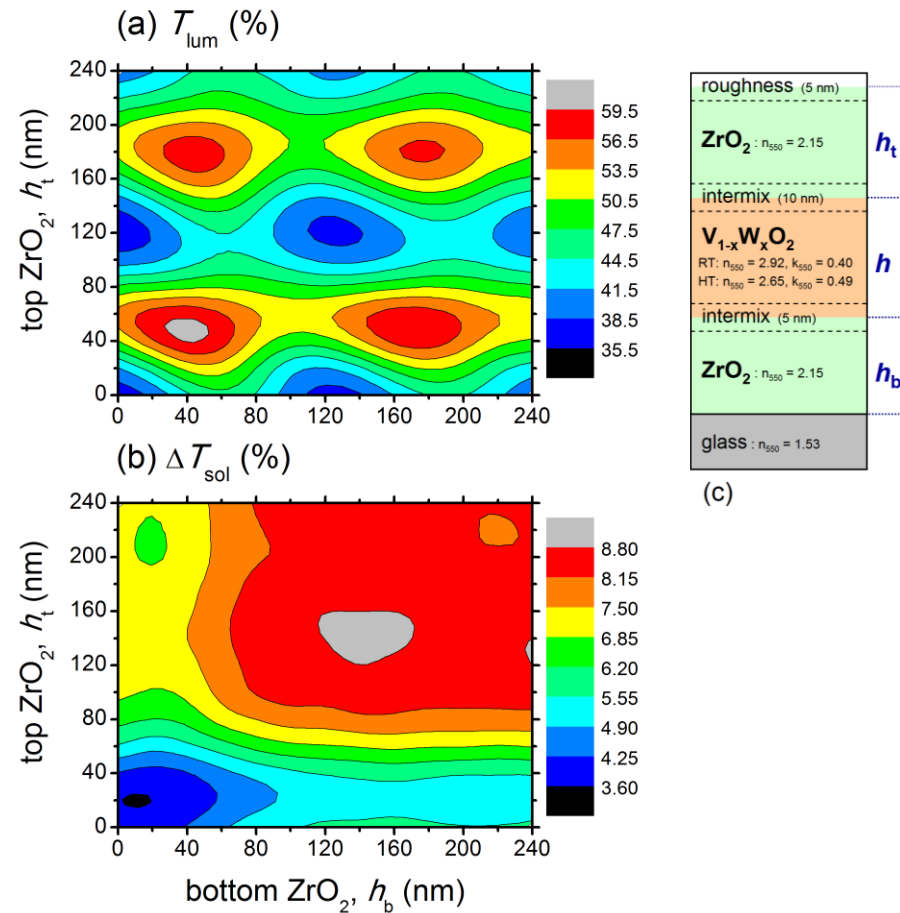
If some of the layers is thick $\Leftrightarrow$ non-coherent, e.g. layer N-1 is a glass substrate: we calculate the amplitudes for different phase shifts resulting from the transmission through the non-coherent layer (e.g.. 0° , 10° , ..., 350°) and average the corresponding intensities (squares of amplitudes)

Transfer matrix formalism

Example of usefulness:
fast optimization of
thermochromic multilayers in
a wide range of thicknesses
of individual layers

Point-by-point (with a software
calculating transmittance):
1 day for each figure like
the present one

After writing a specialized
programme utilizing the
transfer matrix formalism:
1 minute



T_{lum} = luminous transmittance

ΔT_{sol} = strength of the thermochromic effect

[J. Houska et al., Sol. Energy Mater.
Sol. Cells 191, 365 (2019)]

How to get the band gap from T

(from the absorption coefficient α)

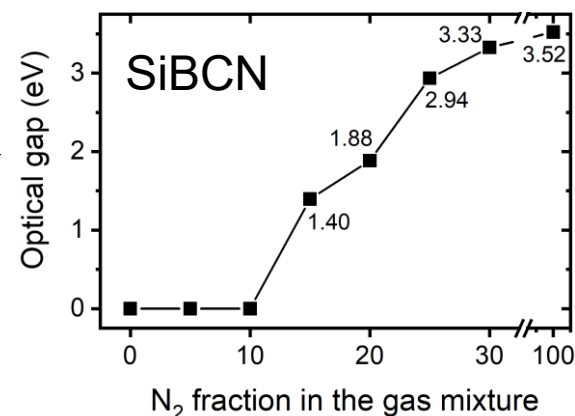
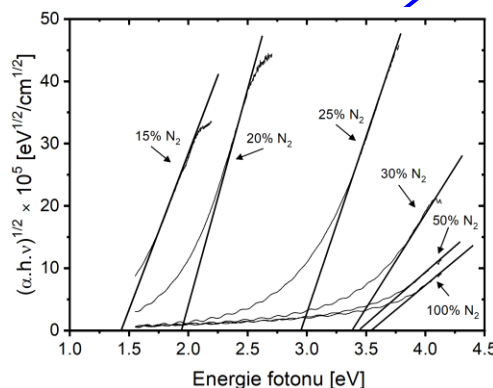
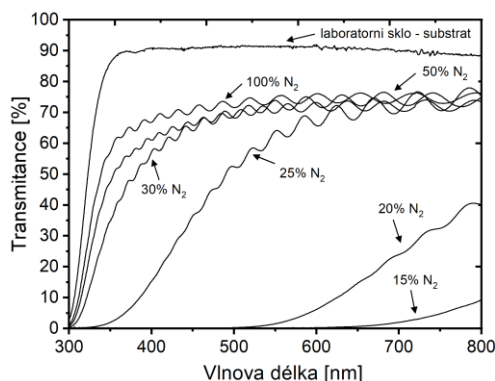
Direct band gap (direct $\times$ indirect: see above)

$\alpha \hbar \omega \sim (\hbar \omega - E_g)^{1/2}$, or $(\alpha \hbar \omega)^2 \sim \hbar \omega - E_g$ (Tauc plot)

Indirect band gap and amorphous materials

$\alpha \hbar \omega \sim (\hbar \omega - E_g)^2$, or $(\alpha \hbar \omega)^{1/2} \sim \hbar \omega - E_g$ (Tauc plot)

Optical band gap (also Tauc gap) is the intersect of tangent to the linear part of this dependence and x-axis



(More precisely $E_g - E_p$: small correction because of phonons)

[V. Petrman et al., *Acta Mater.* 59, 2341 (2011)]

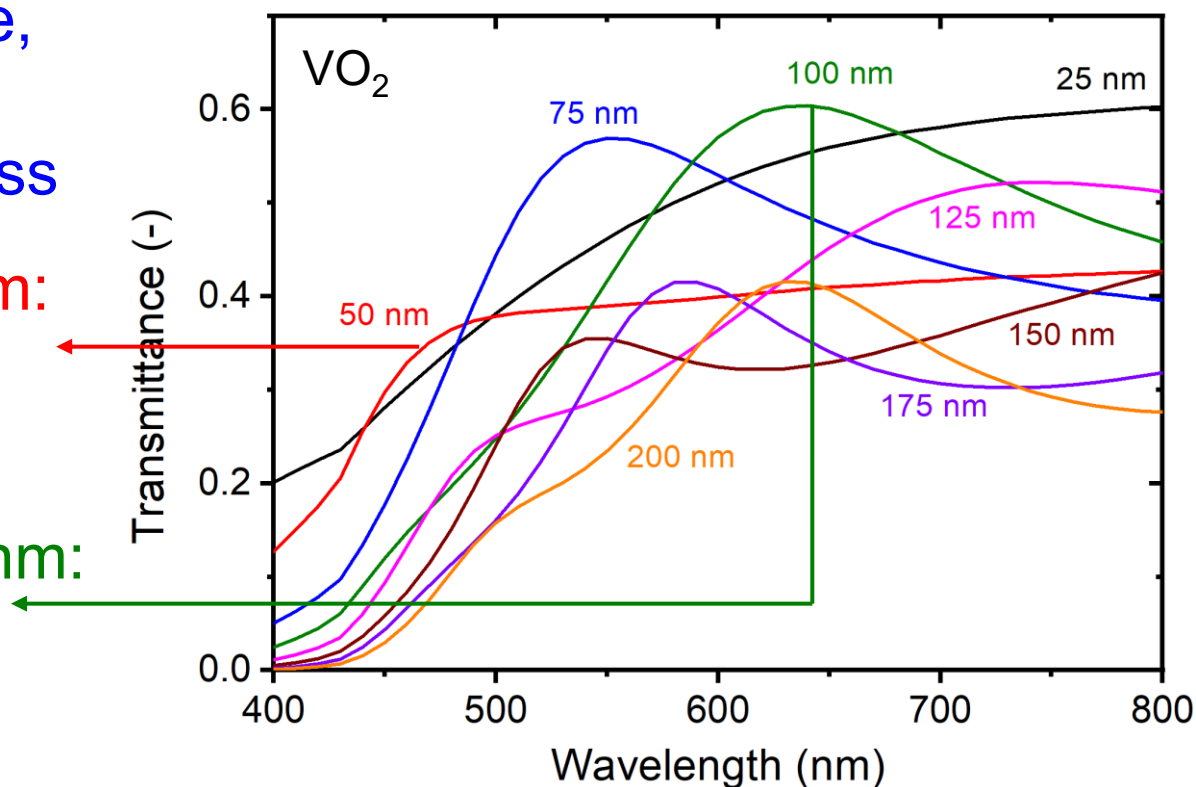
Relationship of T and bulk properties

Trivial - but not always respected - fact:
quantity which characterizes the material (independently of the thickness of layer of this material which we just deposited) is extinction or absorption coefficient, not transmittance

Due to the interference,
 T is not even
proportional to thickness

VO_2 thickness of 50 nm:
 T in the visible range
< 40%

VO_2 thickness of 100 nm:
 T in the visible range
up to > 60%



Relationship of A and bulk properties

Interference $\Rightarrow$ non-monotonic dependence of T and R on d .

Minima of T correspond to maxima of R and vice versa.

Absorption, $A = 1 - T - R$, is less affected by interference (not at all for layer without substrate) $\Rightarrow$ monotonic dependence on d .

Derivation for normal beam on a layer in air

(like 19-21 slides above, but now for non-zero k)

$$R_{\text{one_reflection}} = R' = |n+ik-1|^2/|n+ik+1|^2$$

$$A_{\text{one_passage}} = A' = (1 - e^{-4\pi kd/\lambda})$$

$$A = (1-R')[A' + R'(1-A')A' + R'^2(1-A')^2A' + \dots]$$

$$= (1-R')A'/(1-R'+R'A') \quad (\text{approaching } A' \text{ for low } k)$$

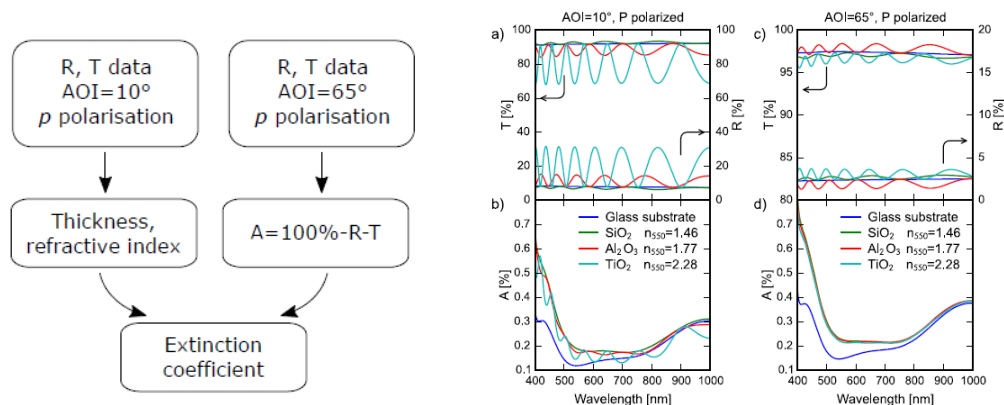
Thus, k can be evaluated not only from ellipsometry but also spectrophotometry: not from T but $A = 1 - T - R$. T and R have to be measured under the same angle, but not necessarily zero.

Relationship of A and bulk properties

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$10^\circ \Rightarrow$ interference strongly affects T and $R \Rightarrow d, n$

65° close to Brewster angle $\Rightarrow$ interference affects A even less than in other cases $\Rightarrow$ exact k

[R. Vernhes et al., Optics Express 23, 28501 (2015)]

Relation of optical properties (in IR) and static dielectric constant ε_{dc}

This slide is valid independently of the source of the raw data:
IR ellipsometry or IR transmittance/reflectance (FTIR)

In order to obtain $\varepsilon(\omega) = n^2(\omega)$, it is enough to fit **sum**
of Gauss or Lorentz oscillators (see above)

However, it is also possible to fit **product** containing
frequencies of longitudinal and transverse waves ω_L , ω_T

$$\varepsilon(\omega) = \varepsilon(\infty) \prod_{j=1-N} (\omega_{Lj}^2 - \omega^2 - iB_{Lj}\omega) / (\omega_{Tj}^2 - \omega^2 - iB_{Tj}\omega)$$

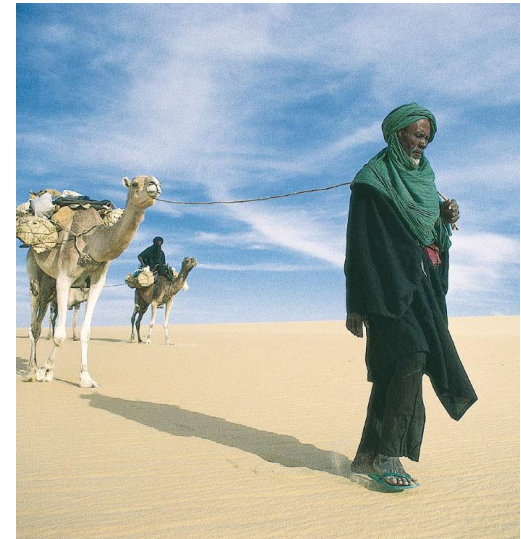
Therefore $\varepsilon_{dc} = \varepsilon(0) = \varepsilon(\infty) \prod_{j=1-N} (\omega_{Lj}^2 / \omega_{Tj}^2)$
(Lyddane-Sachs-Teller relationship)

Relation of reflectance and fashion

White color = high reflectance of all wavelengths. As expected, we find it e.g. on the surface of firemen suits (coated by a thin layer of Al).



So why do bedouins on hot desert dress in black? Aren't they unnecessarily hot? Do they have physical reason for that?



Relation of reflectance and fashion

So why do bedouins on hot desert dress in black? Aren't they unnecessarily hot? Do they have physical reason for that?

They do. Black textile heats more (of up to 6°C), but the loose robe does not transfer this heat to the body, but to the layer of air between the robe and the body. Warm air moves up faster (chimney effect for a proper design) and the resulting **air flow** cools the body, facilitates sweating.

Bedouins are not stupid

letters

Nature 283, 373 - 375 (24 January 1980); doi:10.1038/283373a0

Why do Bedouins wear black robes in hot deserts?

AMIRAM SHKOLNIK, C. RICHARD TAYLOR*, VIRGINIA FINCH* & ARIEH BORUT

Department of Zoology, Tel Aviv University, Tel Aviv, Israel

*Museum of Comparative Zoology, Harvard University, Cambridge, Massachusetts 02138



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7 triků, jak přežít vedro



LUCIE MÜLLEROVÁ

25. 6. 2019



V nejbližších dnech se pořádně zapotíme. Podle meteorologů nás čekají tropická vedra. V lese či ve stínu u rybníka to nemusí být nijak nepříjemné, ale jak je přežít v běžném pracovním procesu, v rozpálených ulicích a podobně? Tyhle tipy vás určitě překvapí.

Lost in translation

4. Černé oblečení? Ano, ale...

Je všeobecně známo, že **černá barva** přitahuje světlo (sluneční záření), kdežto bílá (a obecně světlejší barvy) ho odráží. Takže v černém tričku vám bude o dost větší híc než v bílém.

Jenže proč tedy v jižních zemích a arabském světě, kde je vedro vlastně pořád, chodí lidé převážně v černém oblečení? Kromě toho, že je to věcí jejich kultury, tak za určitých podmínek v něm totiž může být příjemněji! Jde o to, že jejich oblečení je volné a z materiálů, které nepřilnou k tělu. „Černá látka se sice ohřeje až o šest stupňů více, toto teplo ale volná róba nepředá přímo tělu, ale vrstvě vzduchu mezi róbou a tělem. Teplejší vzduch ale stoupá rychleji vzhůru, pro vhodný střih je to až komínový efekt, a vzniklé proudění ochlazuje povrch těla a usnadňuje pocení,“ vysvětlil Jiří Houska z katedry fyziky Fakulty aplikovaných věd západočeské univerzity v Plzni.

S našimi střihy a materiály je tedy na černé oblečení lepší zapomenout, pokud byste ale ve skříni našli třeba nějaký arabský model, rozhodně v něm vedra přečkáte lépe.

Optics of monocrystals, birefringence

Crystal is optically isotropic (does not have optical axis) $\Rightarrow$ characterized by a single refractive index n (see above)

Crystal has optical axis $\Rightarrow$ characterized by two ref. indices

- n_o (**ordinary**) for beam polarized perpendicularly to the axis
- n_e (**extraordinary**) for beam polarized in parallel to the axis

Beam coming from general direction with general polarization:

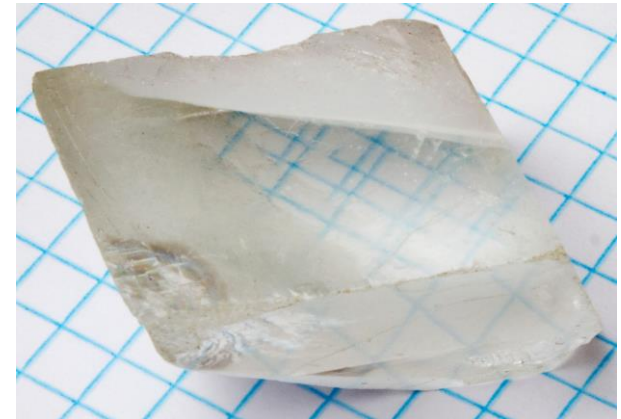
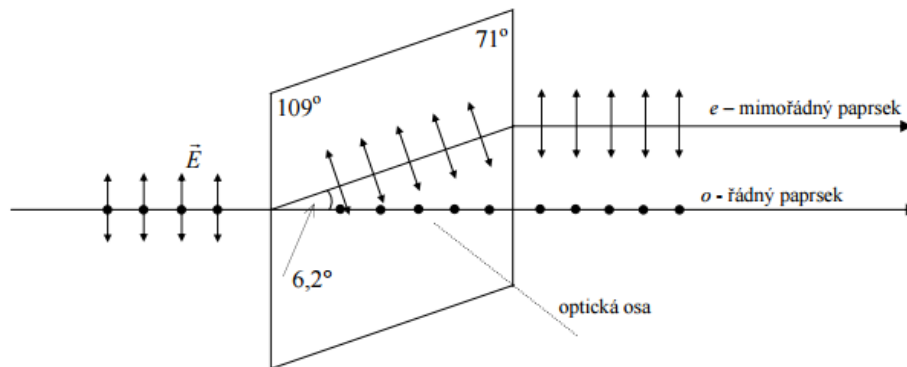
- one component is polarized perpendicularly to the axis $\Rightarrow$ controlled by the index n_o (**ordinary beam / ray**)
- the other component is polarized in some general direction $\Rightarrow$ controlled by index between n_o and n_e (**extraordinary beam**)

Consequently, the ordinary and extraordinary beam are shifted from each other, **even for a normal incidence**

Optics of monocrystals, birefringence

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calcite

Light arriving in parallel to the optical axis is an exception: fully polarized perpendicularly to the axis, i.e. only ordinary beam

Optics of monocrystals, birefringence

- one component is polarized perpendicularly to the axis $\Rightarrow$ controlled by the index n_o (**ordinary beam / ray**)
- the other component is polarized in some general direction $\Rightarrow$ controlled by index between n_o and n_e (**extraordinary beam**)

Cubic system (only this one, but contains many materials):
optically isotropic

Hexagonal, tetragonal, trigonal system:
uniaxial (one optical axis)

Orthorhombic, monoclinic, triclinic system:
biaxial (two optical axes $\Rightarrow$ both beams can be extraordinary)

Optics of monocrystals, birefringence

Examples of uniaxial materials - table from wikipedia

Material	Crystal system	n_o	n_e	Δn
calcite CaCO_3	Trigonal	1.658	1.486	-0.172
barium borate BaB_2O_4	Trigonal	1.6776	1.5534	-0.1242
lithium niobate LiNbO_3	Trigonal	2.272	2.187	-0.085
beryl $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$	Hexagonal	1.602	1.557	-0.045
tourmaline (complex silicate)	Trigonal	1.669	1.638	-0.031
ruby Al_2O_3	Trigonal	1.770	1.762	-0.008
sapphire Al_2O_3	Trigonal	1.768	1.760	-0.008
ice H_2O	Hexagonal	1.309	1.313	+0.004
magnesium fluoride MgF_2	Tetragonal	1.380	1.385	+0.006
quartz SiO_2	Trigonal	1.544	1.553	+0.009
silicon carbide SiC	Hexagonal	2.647	2.693	+0.046
zircon, low ZrSiO_4	Tetragonal	1.920	1.967	+0.047
zircon, high ZrSiO_4	Tetragonal	1.960	2.015	+0.055
rutile TiO_2	Tetragonal	2.616	2.903	+0.287

→ that's why calcite is on the photo 2 slides above

For some materials $n_o > n_e$, for other materials $n_o < n_e$

Utilization of birefringence - waveplate

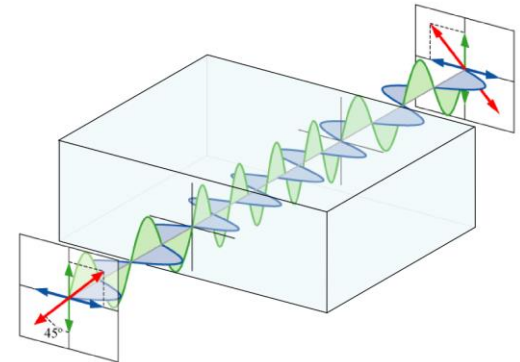
Waveplate: plate of uniaxial material, with optical axis parallel to the surface which the light is arriving on

Component polarized in parallel to the **ordinary axis** (normal to optical axis) feels ordinary refractive index n_o

Component polarized in parallel to the **extraordinary axis** (parallel to optical axis) feels extraordinary ref. index n_e

Out of these two axes, that which corresponds to lower refractive index (out of the pair n_o , n_e) is called **fast axis**

Components which feel different refractive indices travel through the plate with different velocities, i.e. their **phase shift changes** (in the figure of $\lambda/2$)

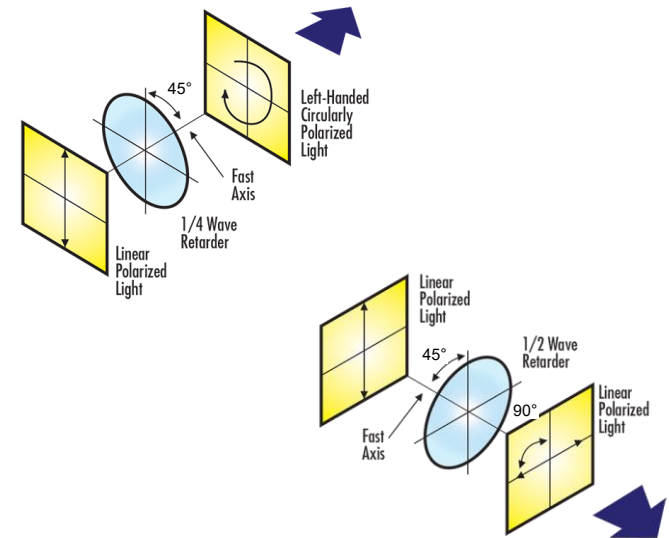


Utilization of birefringence - waveplate

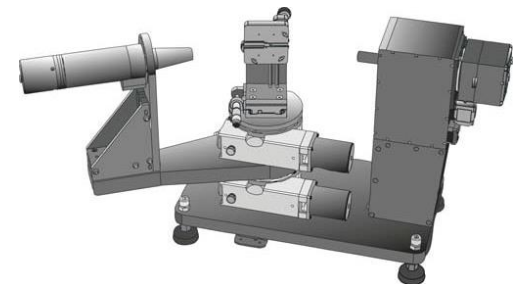
Components which feel different ref. indices travel through the plate with different velocities, i.e. **their phase shift changes**

Two frequent cases:

- shift of $\lambda/4$ (**quarter-wave plate**):
e.g. liner polarization 45° from the fast axis changes to circular
- shift of $\lambda/2$ (**half-wave plate**):
e.g. liner polarization 45° from the fast axis rotates of 90°



Application e.g. when constructing ellipsometers (first half of this chapter): setting polarization of incident light and measuring polarization of reflected light



Jones matrix

Jones matrix, defined in the first half of this chapter, is used also for description of optical elements interacting with normal beam: there is no plane of incidence, but a convention horizontal = p, vertical = s

$$\begin{pmatrix} E_p^{\text{refl}} \\ E_s^{\text{refl}} \end{pmatrix} = \begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} \begin{pmatrix} E_p^{\text{inc}} \\ E_s^{\text{inc}} \end{pmatrix}$$

Horizontal polarizer

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

Vertical polarizer

$$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

Right circular polarizer

$$\frac{1}{2} \begin{pmatrix} 1 & -i \\ i & 1 \end{pmatrix}$$

Left circular polarizer

$$\frac{1}{2} \begin{pmatrix} 1 & i \\ -i & 1 \end{pmatrix}$$

Jones matrix

Jones matrix, defined in the first half of this chapter, is used also for description of optical elements interacting with normal beam: there is no plane of incidence, but a convention horizontal = p, vertical = s

$$\begin{pmatrix} E_p^{\text{refl}} \\ E_s^{\text{refl}} \end{pmatrix} = \begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} \begin{pmatrix} E_p^{\text{inc}} \\ E_s^{\text{inc}} \end{pmatrix}$$

Quarter-wave plate (+ i for horizontal, - i from vertical fast axis)

$$\begin{pmatrix} 1 & 0 \\ 0 & i \end{pmatrix} \quad \begin{pmatrix} 1 & 0 \\ 0 & -i \end{pmatrix}$$

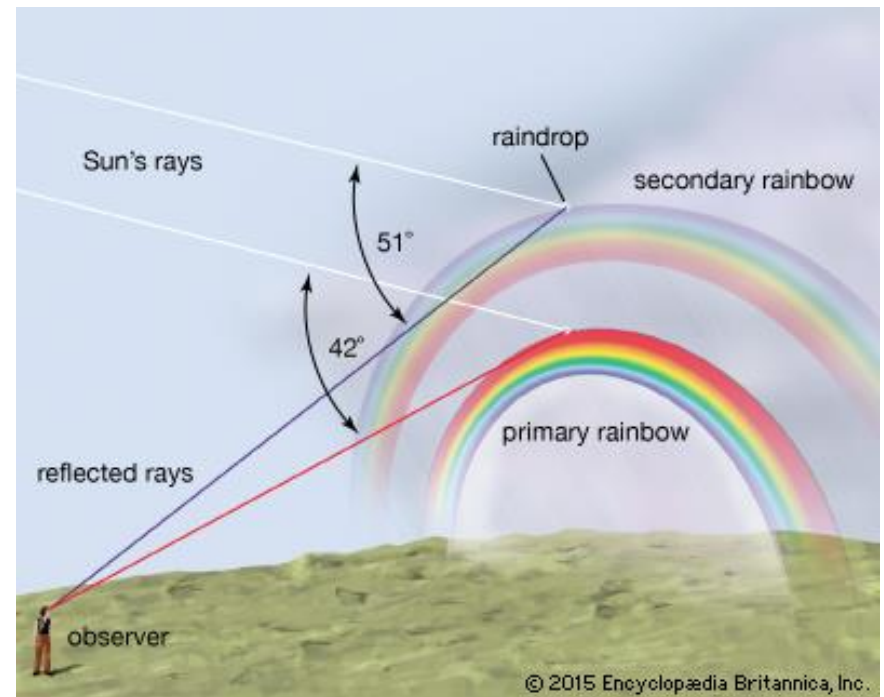
Half-wave plate (fast axis tilted of θ from horizontal)

$$\begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix}$$

Rainbow

At least one example of reflection and refraction
for the angle of incidence $\neq 90^\circ$

Why do we see the (primary) bow under the angle of 42°
from the direction of Sun rays?



Rainbow

First order rainbow: when the ray goes through a spherical drop of water with a refractive index n , it changes its direction of $180^\circ - 2\phi$. The rainbow is seen in the direction which the rays arriving to the eye are coming from, i.e. under the angle 2ϕ from the point hit by the ray without the rain.

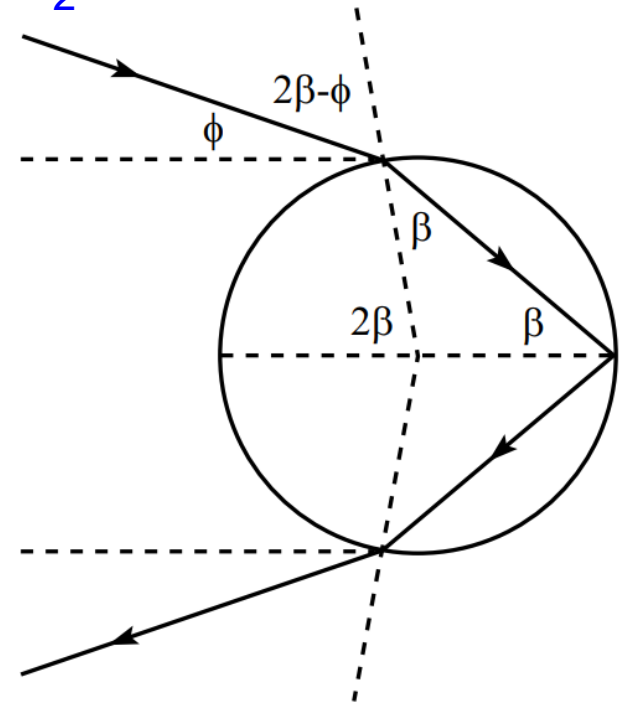
Snell law in a general form $n_1 \sin \alpha_1 = n_2 \sin \alpha_2$



$$\sin(2\beta - \phi) = n \sin \beta$$



$$\phi = 2\beta - \arcsin(n \sin \beta)$$



Rainbow

$$\sin(2\beta - \phi) = n \sin \beta \Rightarrow \phi = 2\beta - \arcsin(n \sin \beta)$$

The directions of output rays depend on the incidence angle
 $\Leftrightarrow$ on the distance of the trajectory from the drop center
(ray going through the center does not change direction at all),
but many of them are close to that corresponding to zero
derivative $\phi(\beta)$ (similar ϕ in a wide range of β)

$$\phi'(\beta) = 0$$

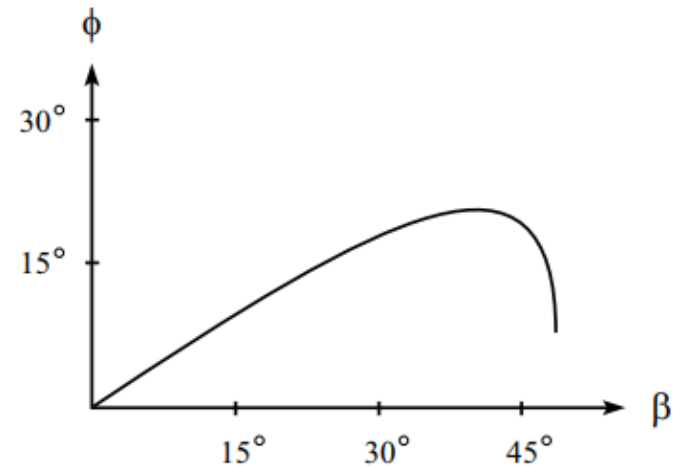


$$\sin^2(\beta_{\max}) = (4 - n^2)/3n^2$$



$$\text{(for water refr. index) } 2\phi_{\max} = 42^\circ$$

The value 42° is called "rainbow angle"
(already Roger Bacon 1214-1294)



Rainbow

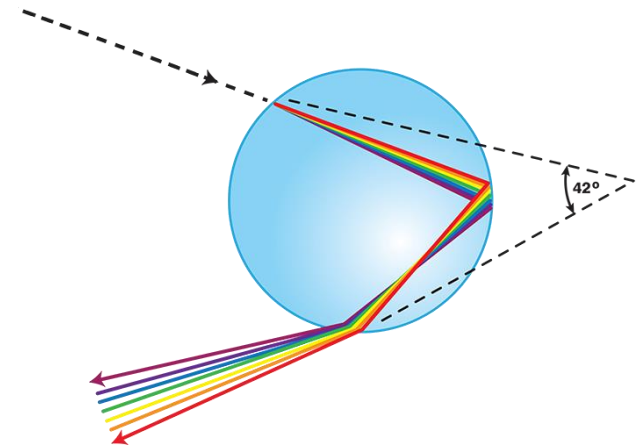
The argument above explains why the strip around 42° is **brighter**. Due to the decreasing $n(\lambda)$ it is also **colorful**.

Red end of the spectrum ($n_{\text{H}_2\text{O}}=1.332$): $2\phi_{\text{max}} = 42.2^\circ$

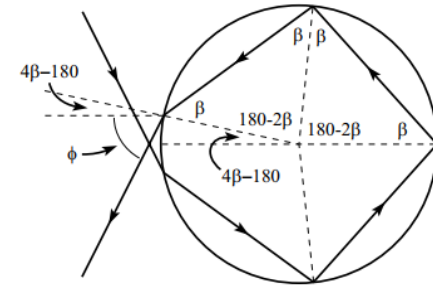
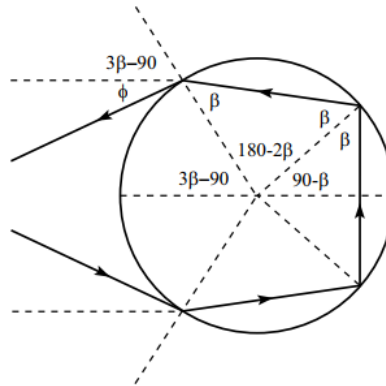
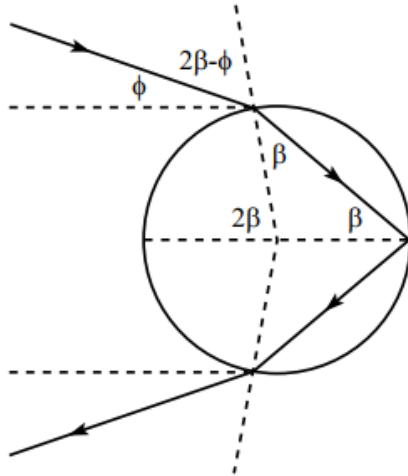
Violet end of the spectrum ($n_{\text{H}_2\text{O}}=1.344$): $2\phi_{\text{max}} = 40.5^\circ$

What the angle 42° tells us:

- the rainbow can be seen from the ground only if the Sun is at most 42° above the horizon
- whole rainbow circle can be seen from plane which has horizon at least (for horizon Sun) 42° below it



Rainbow



Rainbow **1st order**

$$n \sin \beta = \sin(2\beta - \phi)$$

$$|2\phi_{\max}| \quad 42^\circ$$

2nd order

$$\sin(3\beta - 90^\circ + \phi)$$

$$51^\circ$$

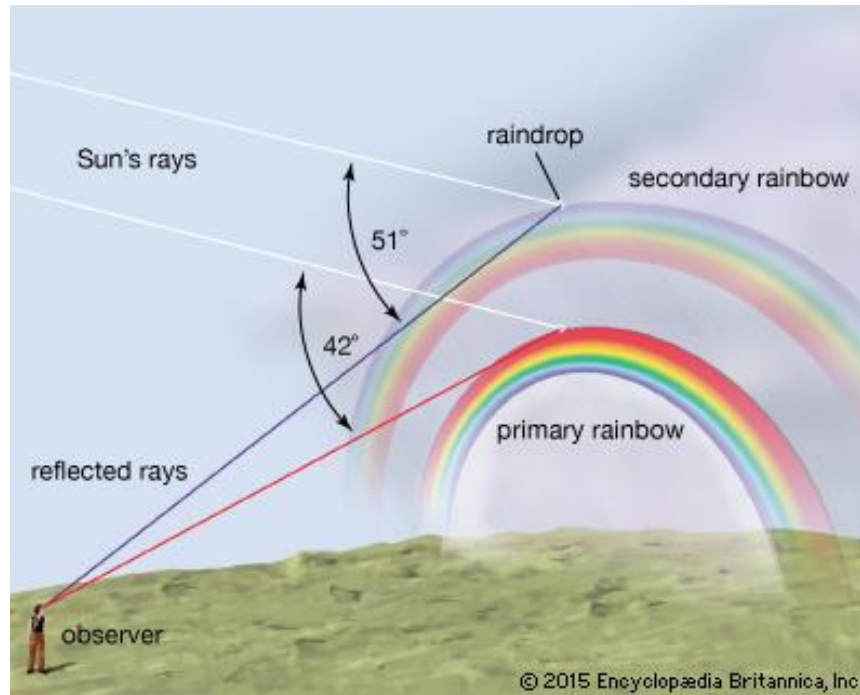
3rd order

$$\sin(4\beta - 180^\circ + \phi) \dots$$

$$138^\circ \dots$$

(upper and lower half of the drop lead to opposite signs of ϕ)

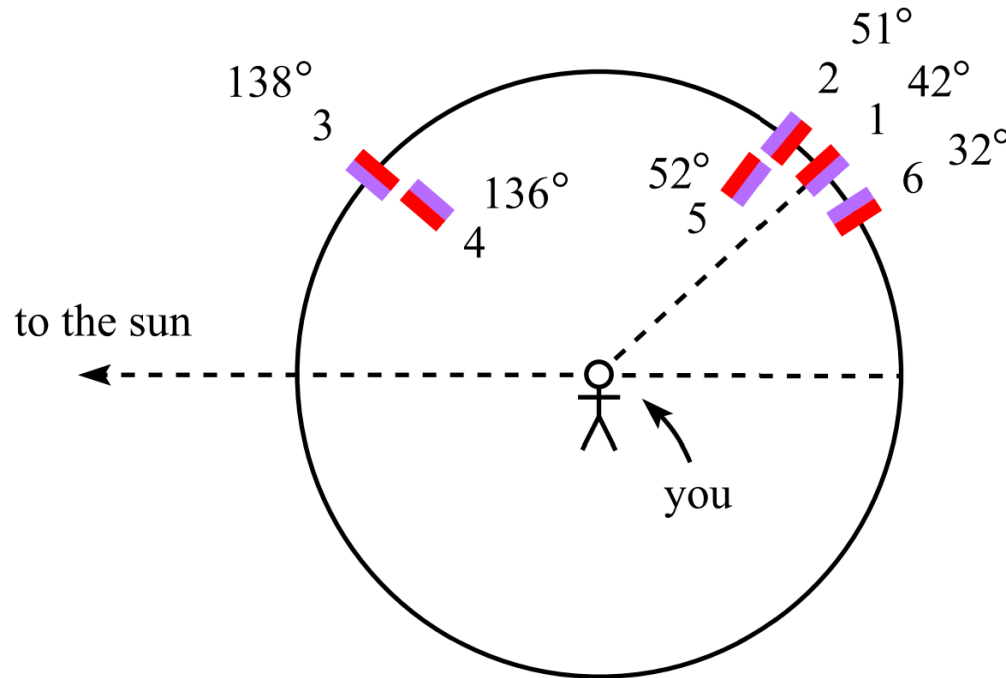
Rainbow



Intensity decreases with increasing rainbow order, because

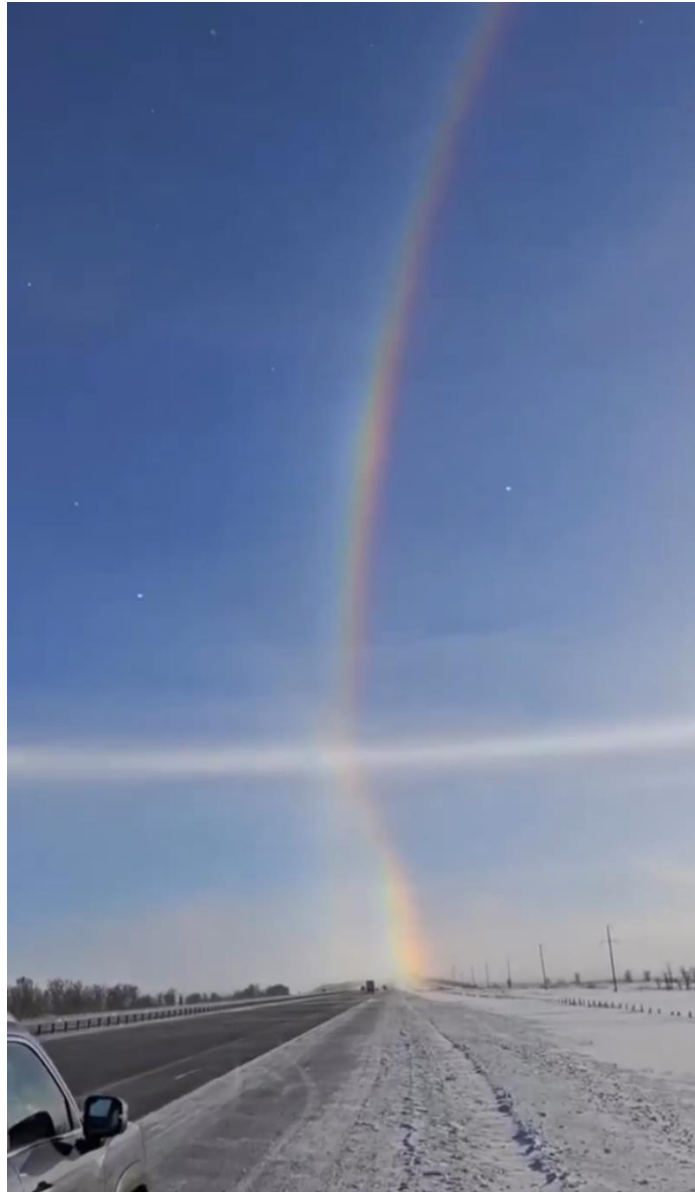
- only decreasing part of the original ray contributes to it
- $n \sin \beta_{\max}$ is gradually approaching 1, i.e. $2\phi_{\max}$ happens for almost tangent rays, and drop has low cross-section for them

Rainbow



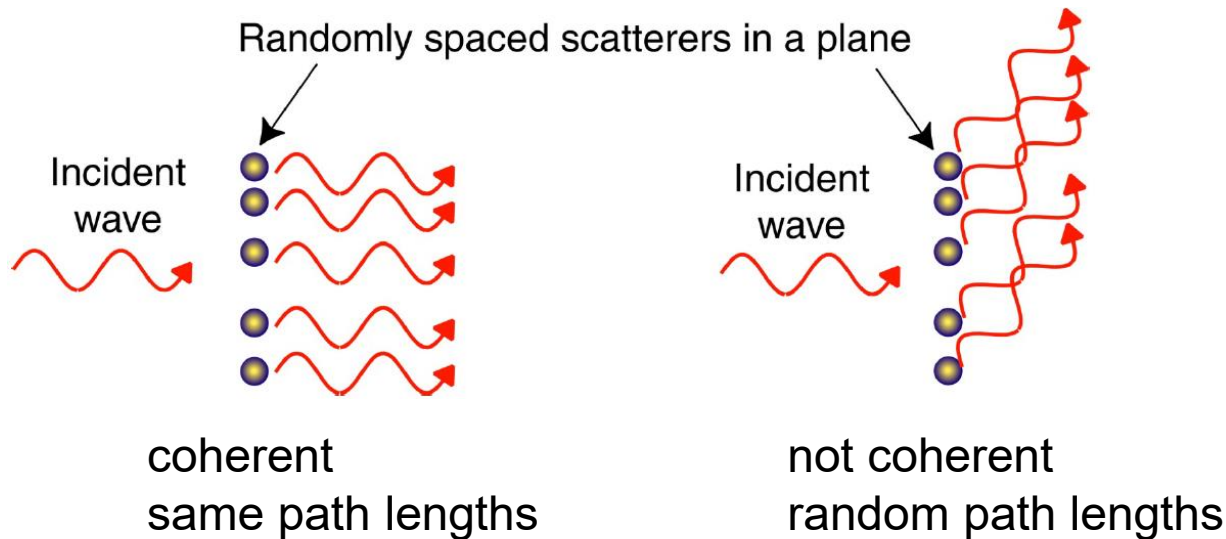
- Intensity decreases with increasing rainbow order, because
- only decreasing part of the original ray contributes to it
 - $n \sin \beta_{\max}$ is gradually approaching 1, i.e. $2\phi_{\max}$ happens for almost tangent rays, and drop has low cross-section for them

Combination with other phenomena



Light scattering

From the individual atom's point of view, the scattering always takes place, each atom scatters part of the light, in all directions including forward (Rayleigh: cross section $\sim \lambda^{-4}$).



But what matters is in which way do the waves scattered by individual atoms interfere

Light scattering

Homogeneous material:

Wave scattered by individual atoms forward and backward interfere constructively, the light intensity does not change. However, the scattering atoms do not oscillate in phase with the EM field, therefore $n > 1$ for transparent materials.

Wave scattered by individual atoms in other directions interfere destructively (there is always another atom corresponding to a path difference $\lambda/2$), i.e. scattering to sides is in a good approx. zero (increasingly exactly with increasing atomic density)

Light scattering

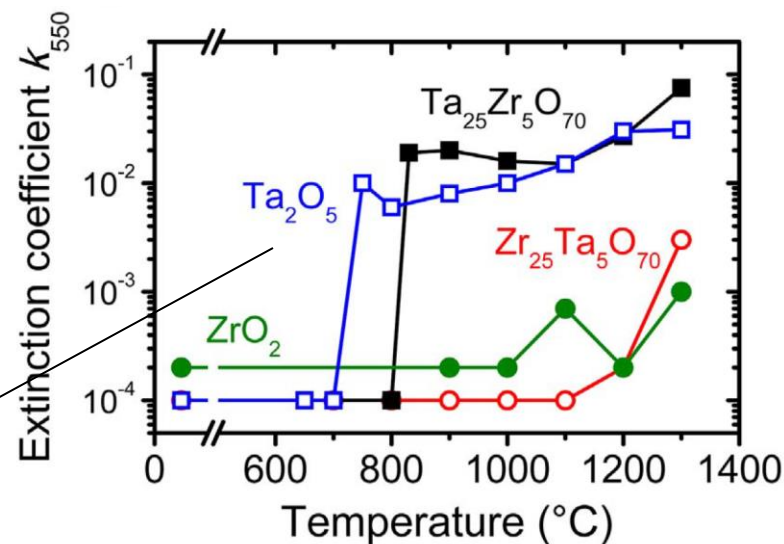
Heterogeneous material:

In other directions than forward and backward the waves do not interfere fully destructively, and the scattering in usual / macroscopic sense takes place

Scattering in solids (see below for the air) is important at the presence of crystals which are comparable to the wavelength

Annealing led to crystal formation

- Ta_2O_5 ($\approx 1\mu\text{m} \Rightarrow$ drop in the transmittance)
- ZrO_2 (order of mag. smaller $\Rightarrow$ effectively homogeneous medium)



Thermal stability of structure, microstructure and enhanced properties of Zr–Ta–O films with a low and high Ta content

Š. Zuzjaková, P. Zeman, S. Haviar, R. Čerstvý, J. Houška, J. Rezek, J. Vlček
Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Univerzitní 8, 306 14 Plzeň, Czech Republic

Light scattering

Slides on spectrophotometry silently assume
Transmittance + Reflectance + Absorption = 1

In reality

Transmittance + Reflectance + Absorption + Scattering = 1

or from the point of view of individual atoms

Scattering forward + Scattering backward + Absorption +
Scattering to sides = 1

Why is sky blue and clouds white

Owing to the aforementioned Rayleigh relationship (cross section for scattering $\sim \lambda^{-4}$) the blue light scatters most

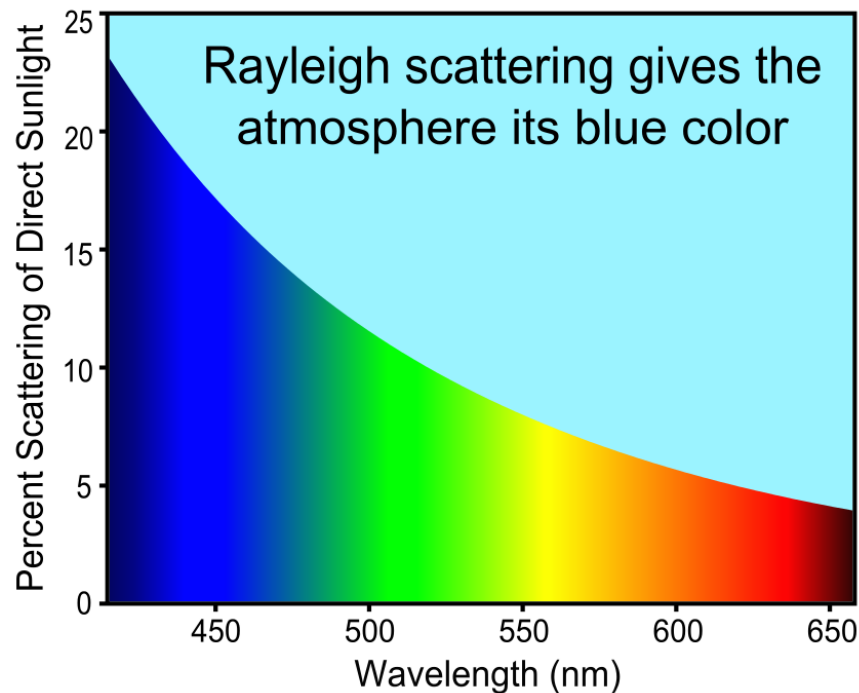
The more red color remains in the weakly scattered light from the direction close to the Sun, especially for horizon Sun when the light has to travel longer distance through the atmosphere



Why is sky blue and clouds white

Owing to the aforementioned Rayleigh relationship (cross section for scattering $\sim \lambda^{-4}$) the blue light scatters most

But what does light scatter on, where are the inhomogeneities comparable to λ ? Molecules are too small. Dust has limited content, and only close to surface (sky is blue also from plane)



Why is sky blue and clouds white

Owing to the aforementioned Rayleigh relationship (cross section for scattering $\sim \lambda^{-4}$) the blue light scatters most

But what does light scatter on, where are the inhomogeneities comparable to λ ? Molecules are too small. Dust has limited content, and only close to surface (sky from plane is also blue)

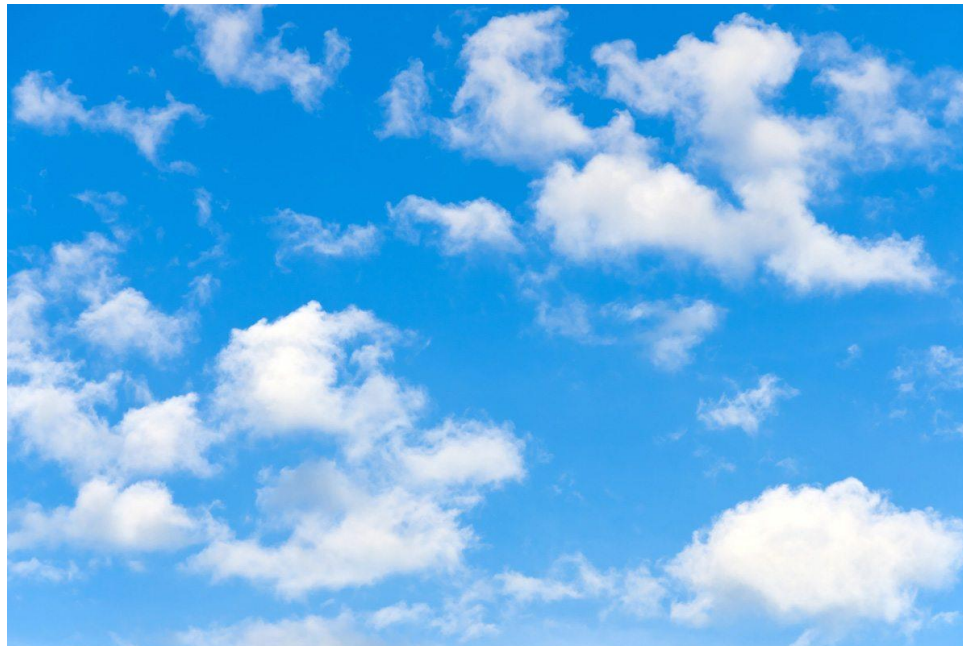
The scattering is a consequence of density fluctuations (this is the difference of gas and solid, that's why scattering in air and not in glass), happens on random local density maxima/minima.

It is a matter of viewpoint if this is scattering on individual molecules followed by interference, or scattering on whole local density maxima and minima, the result is the same.

Why is sky blue and clouds white

Clouds contain drops orders of magnitude larger than λ ,
 $\Rightarrow$ scatter (refract) all wavelengths similarly $\Rightarrow$ are white

The storm clouds contain even more water and almost no light can go through them, which is why they look grey/black.
When looking on their top from a plane ($\Rightarrow$ reflectance, not transmittance) they are white like all other clouds.



Navigation

The scattered light is partially polarized, in a direction tangent to a circle around the Sun (light originally polarized in a plane 'xy' and scattered in the direction y is polarized in the direction x), the same hold if we take it as reflected (note the different Fresnel equations for the reflection of p- a s-polarized light)

Birefringence allows us to find the direction of polarization of light coming from various sky points, and the intersect of the corresponding normals is the direction to the hidden Sun

Already Vikings (*Sólarsteinn* - probably the aforementioned Iceland spar=calcite)

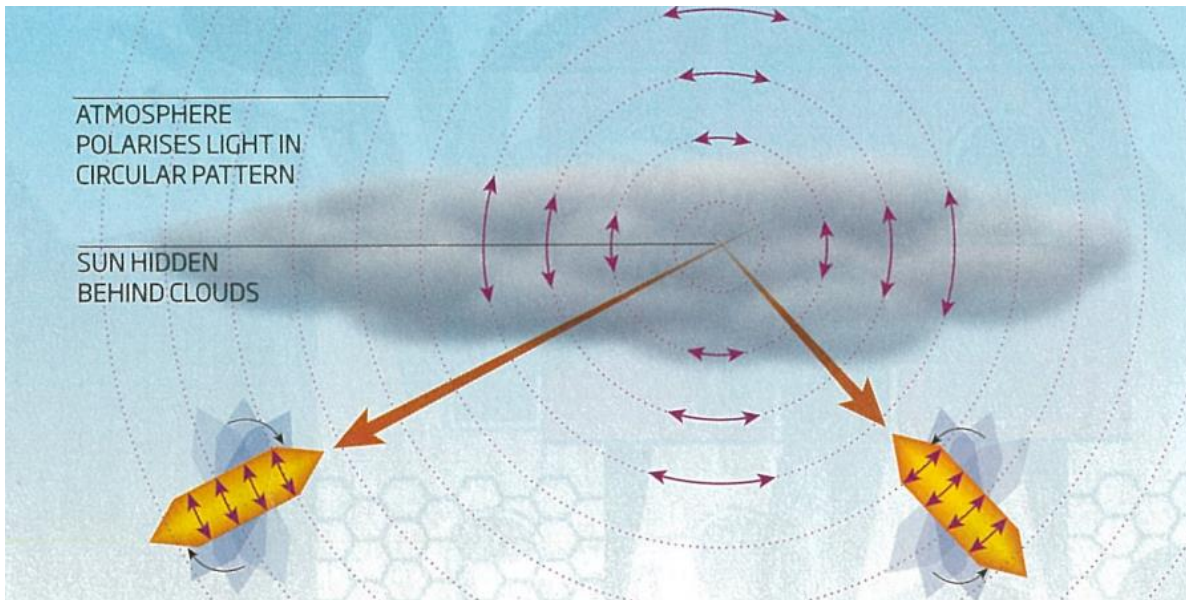
"Hustě sněžilo, jak Sigurd (Sigurdor, Siegfried) předpověděl. Král povolal Raudúlfurovy syny, Sigurda a Dagura. Král je vyzval, aby se podívali ven, na celé obloze nebylo možno vidět jasné nebe. Pak se král zeptal Sigurda. Odpověděl jasně. Poté se král chopil slunečního kamene a držel ho směrem vzhůru. Viděl, kam směřoval paprsek světla z kamene, a byl to přesně tentýž směr, který určil Sigurd."

Lost in translation



Navigation

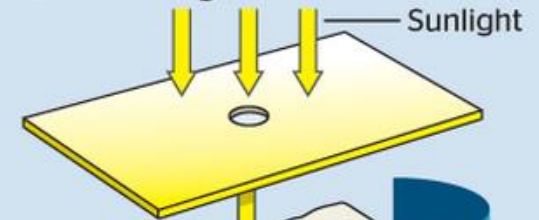
Birefringence allows us to find the direction of polarization of light coming from various sky points, and the intersect of the corresponding normals is the direction to the hidden Sun



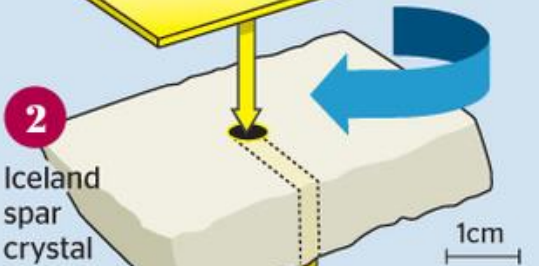
Navigating through clouds

On a cloudless day, the crystal is calibrated to work out at what angle relative to the Sun it will produce two equally bright beams of light

1 Pinhole channels sunlight into a single beam



2 Iceland spar crystal splits light into two beams



3 The crystal is rotated until the two projected beams are equal in brightness to give a direction reading for the position of the Sun behind the clouds

11) Photoinduced properties

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

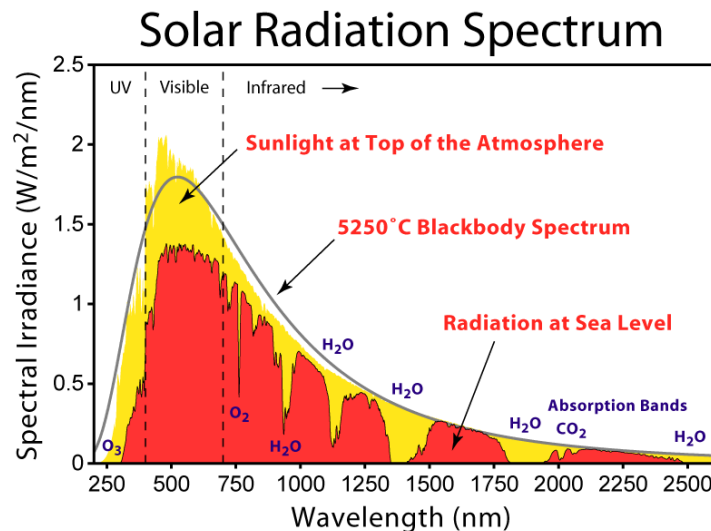
- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Utilization of light (usually sunlight)

When a material absorbs photon, it converts its energy to potential energy (creates a pair electron+hole)

Proper band gap width is needed: narrower than photon energy (no excitation otherwise - electron does not get absorbed), but non-zero (excitation or hole do not make sense for metals)

The point is to utilize the aforementioned potential energy (in a more useful way than for radiation of new phonon)

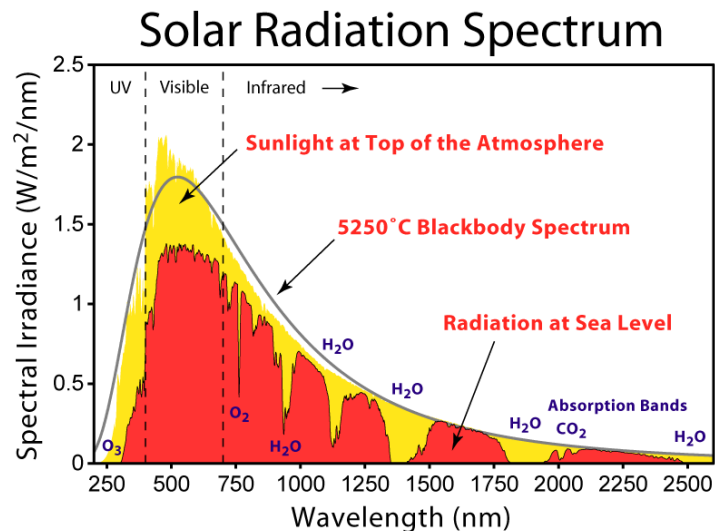


Utilization of light (usually sunlight)

The point is to utilize the aforementioned potential energy (in a more useful way than for radiation of new phonon)

Four options are discussed below:

- i) oxidation (decomposition) of organics
- ii) water splitting
- iii) hydrophobicity and hydrophilicity
- iv) solar cells



Oxidation and reduction reactions

(reminder of the terms)

Oxidation reaction (oxidation of the matter of interest):
different meaning in different contexts

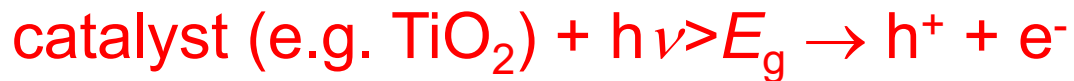
- gain of O
- loss of H
- loss of electron

Reduction reaction (reduction of the matter of interest):
different meaning in different contexts

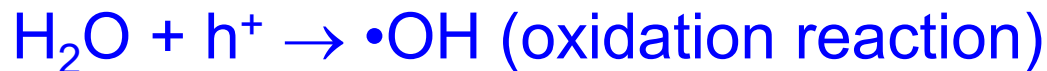
- loss of O
- gain of H
- gain of electron

Ox. of organics (self-cleaning effect)

1) incident photon (with energy higher than the band gap, E_g) creates pair electron+hole



2a) hole reacts with water to highly reactive radical OH



2b) electron reacts with oxygen to highly reactive radical O_2^-

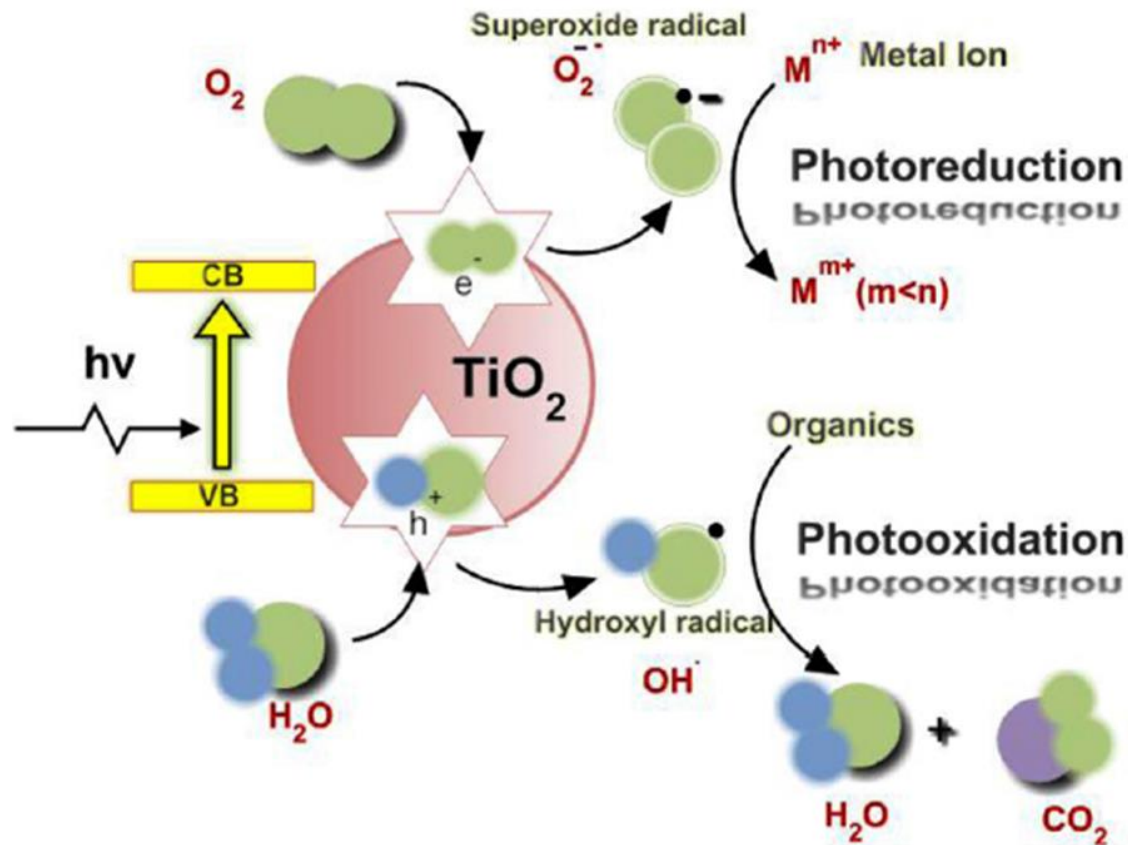


3) biologist/chemist: these highly reactive radicals then react with organic molecules and decompose them (details are not a topic for solid state physics - what we want are materials which guarantee that points 1 a 2 take place)

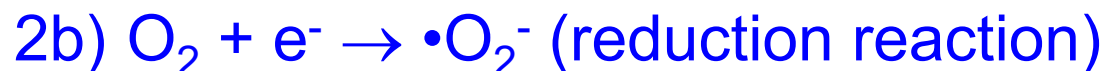
physicist: there is a potential energy in the form of radicals in the system, eventually it will get invested into something ... in this case into breaking of bonds in the organic dirt

Ox. of organics (self-cleaning effect)

3) these highly reactive radicals then react with organic molecules and decompose them



Ox. of organics (self-cleaning effect)



Energy levels where the reactions take place must be inside the band gap (otherwise there is no energetical motivation).

ad 2a) potential level of donor (H_2O) must be above the valence band (due to point 1, there is a hole ready and willing to move up)

ad 2b) potential level of acceptor (O_2) must be above the conduction band (due to point 1, there is an electron ready and willing to move down)

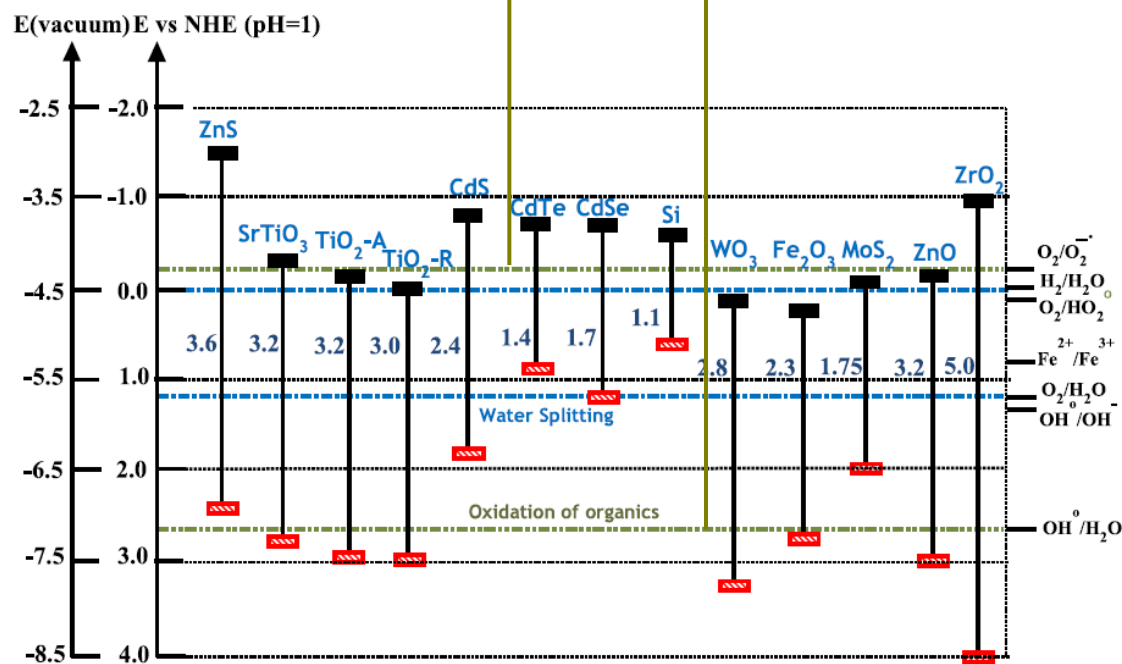
Ox. of organics (self-cleaning effect)

1) catalyst (e.g. TiO_2) + $h\nu > E_g \rightarrow h^+ + e^-$

2a) $\text{H}_2\text{O} + h^+ \rightarrow \bullet\text{OH}$ (oxidation reaction)

2b) $\text{O}_2 + e^- \rightarrow \bullet\text{O}_2^-$ (reduction reaction)

Energy levels where the reactions take place must be inside the band gap (otherwise there is no energetical motivation).



[R. Vinu et al.,
J. Indian Inst. Sci.
90, 193 (2010)]

Water splitting (production of H₂ fuel)

1) incident photon (with energy higher than the band gap, E_g) creates pair electron+hole



2a) hole reacts with water to oxygen and hydrogen ions



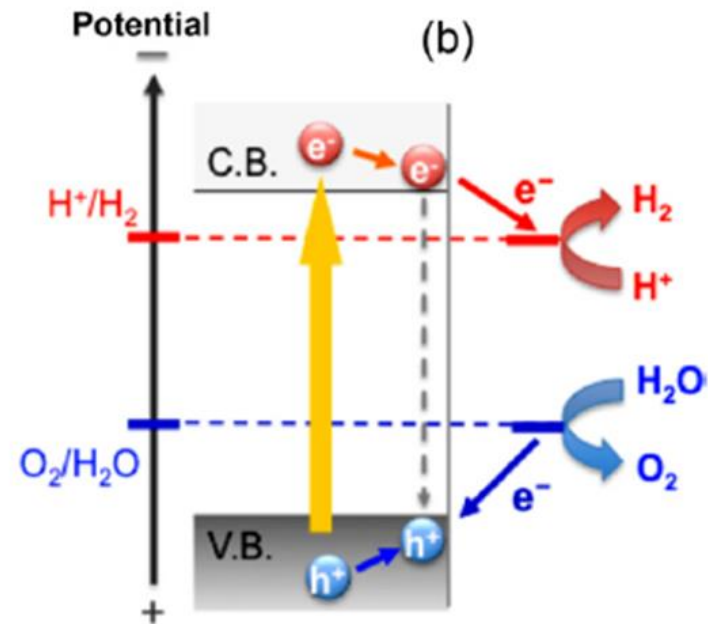
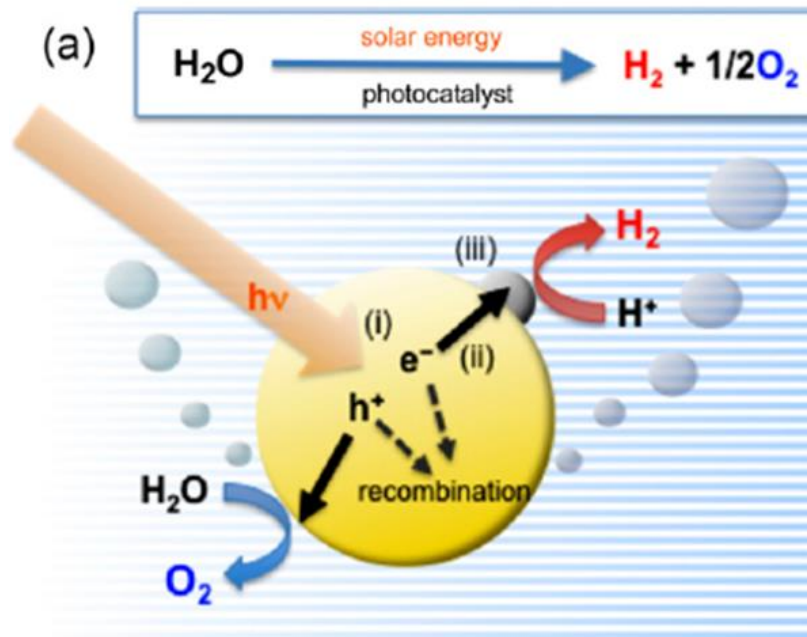
2b) electron complements hydrogen ions to hydrogen



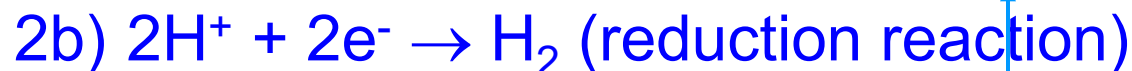
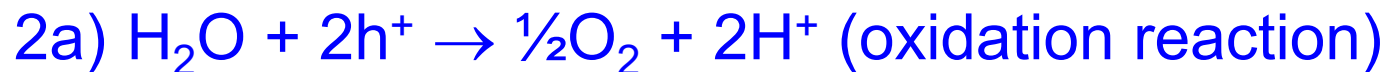
3) so we get, for free (non-consumed catalyst + water + Sun), hydrogen fuel

Water splitting (production of H₂ fuel)

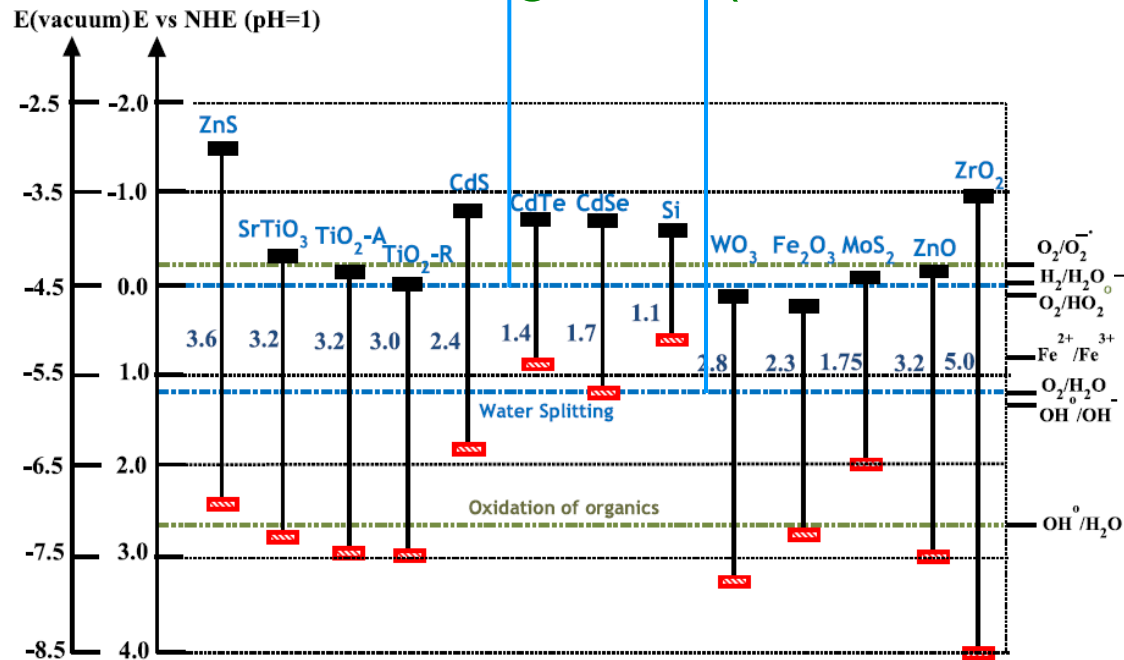
3) so we get, for free (non-consumed catalyst + water + Sun), hydrogen fuel



Water splitting (production of H₂ fuel)



Energy levels where the reactions take place must be inside the band gap (otherwise there is no energetical motivation), like in the case of oxidation or organics (but the levels are different).



denoted
sometimes H₂/H₂O,
sometimes H⁺/H₂

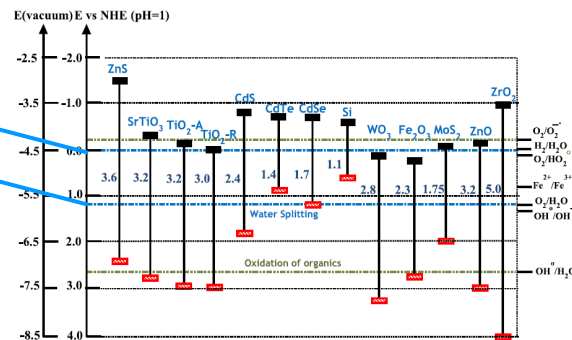
Water splitting (production of H₂ fuel)

Levels in the figure are
1.23 eV from each other

Cross-check against
the energy balance:

- formation energy of H₂O from H₂ + O₂ is 2.46 eV (237 kJ/mol)
- that of the aforementioned reactions which is endothermic (H₂O + 2h⁺ → ½O₂ + 2H⁺) includes 2 holes, so each has to contribute 2.46 / 2 = **1.23 eV** ⇒ agrees with the above value

In praxis we want band gap of at least several tenths eV wider (additional energy to overcome reaction barriers ⇒ reactions are faster)



Water splitting (production of H₂ fuel)

In addition to

- 1) proper band gap width and
- 2) energy levels inside the gap (see above)

there are also other conditions:

- 3) electrons and hole should not recombine with each other before they react with water, and
- 4) H₂ and O₂ - created next to each other - should not recombine to water before they leave to the atmosphere (where hydrogen is collected).

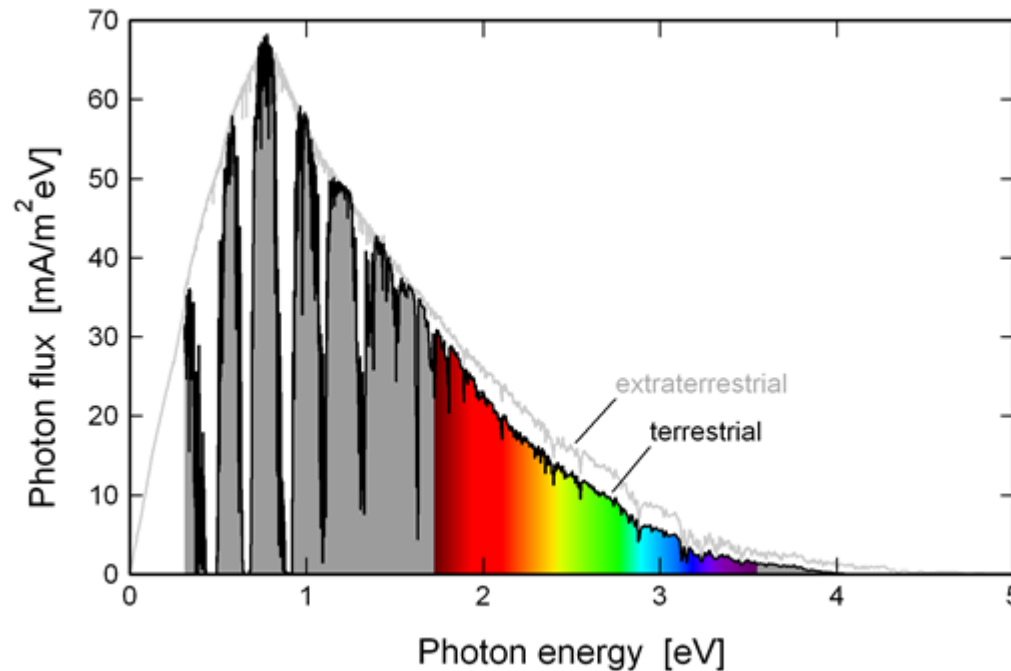
Solution (hopefully at least partial ...): metallic nanoclusters at the surface of semiconductive catalytic material. Electrons move to them and produce H₂ there, holes stay in the semiconductor and produce O₂ far from H₂.

Effective utilization of Sun spectrum

Wider band gap (E_g) increases the probability that the aforementioned energy levels will be inside the gap

Narrower E_g increases the usable part of the Sun spectrum
($\Leftrightarrow$ part of photons which can excite electrons to cond. band)

These trends go against each other, making the topic interesting

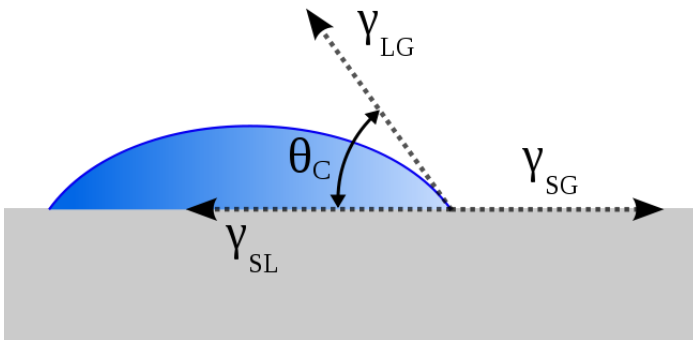


Hydrophobicity a hydrophilicity

Reminder: contact angle $\theta_C > 90^\circ \Rightarrow$ hydrophobic
 $\theta_C < 90^\circ \Rightarrow$ hydrophilic

Contact angle of a water droplet is given by the ratio

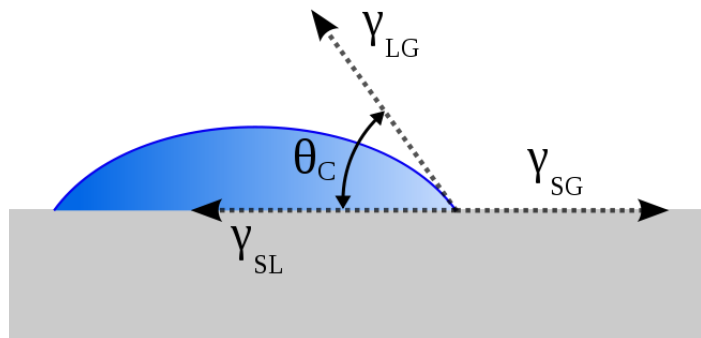
- material's surface energy (γ_{SG}),
- water surface energy (γ_{LG}) and
- energy of the boundary material-water (γ_{SL})



$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta_C$$

(Young equation)

Hydrophobicity a hydrophilicity



$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta_C$$

(Young equation)

How to affect the energies: e.g. by electronegativity of the elements used. For metal oxides and nitrides:

- metal has lower electroneg. $\Rightarrow$ does not form coordination bonds to water O so much $\Rightarrow$ surface is more hydrophobic
- nitride instead of oxide $\Rightarrow$ electrons are less localized on nitrogen (lower electroneg., only one lonepair) $\Rightarrow$ weaker hydrogen bonds to water H $\Rightarrow$ surface is more hydrophobic

Journal
of the American Ceramic Society

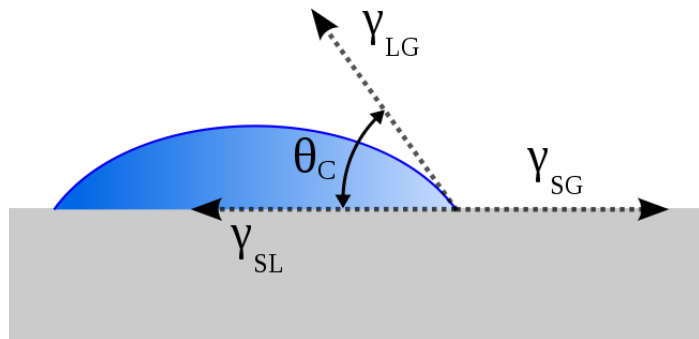


Rapid Communication

Hydrophobicity of Thin Films of Compounds of Low-Electronegativity Metals

Sergei Zenkin, Šimon Kos, Jindřich Musil

Hydrophobicity a hydrophilicity



$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta_C$$

(Young equation)

So much for ideally flat surface. Rough surface:
introduce r = real surface area / apparent square area



For contact angles on flat (θ_C) and slightly rough (θ_C^*) surface
it holds $\cos \theta_C^* = r \cdot \cos \theta_C$ (Wenzel equation)

$r > 1 \Rightarrow$ increases $|\cos \theta_C^*| \Rightarrow$ moves θ_C away from $90^\circ \Rightarrow$
roughness makes - **hydrophobic surface more hydrophobic**
- **hydrophilic surface more hydrophilic**

Photoinduced hydrophilicity

1) incident photon (again $h\nu > E_g$) creates pair electron+hole catalyst (e.g. TiO_2) + $h\nu > E_g \rightarrow h^+ + e^-$

2a) electron reduces Ti^{4+} to Ti^{3+}

$\text{Ti}^{4+} + e^- \rightarrow \text{Ti}^{3+} \Rightarrow$ there are too many O atoms around

2b) holes use the excess O ions to produce free O_2

$4h + 2\text{O}^{2-} \rightarrow \text{O}_2 \Rightarrow$ O vacancies appear in the material

3) groups OH bond to free places (aforementioned vacancies)

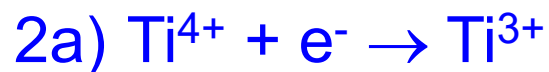


change of the network of hydrogen and coordination covalent bonds (previously from water O and H to surface Ti and O, now from water O to surface H)

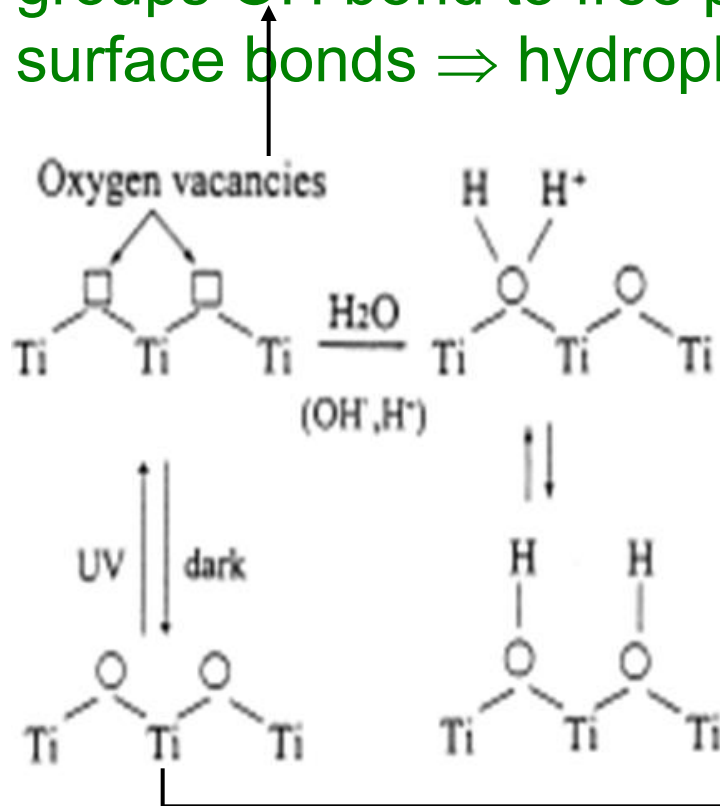


change of the surface energy in the formula for contact angle
 $\Rightarrow$ hydrophilicity instead of hydrophobicity

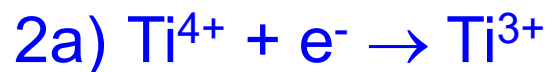
Photoinduced hydrophilicity



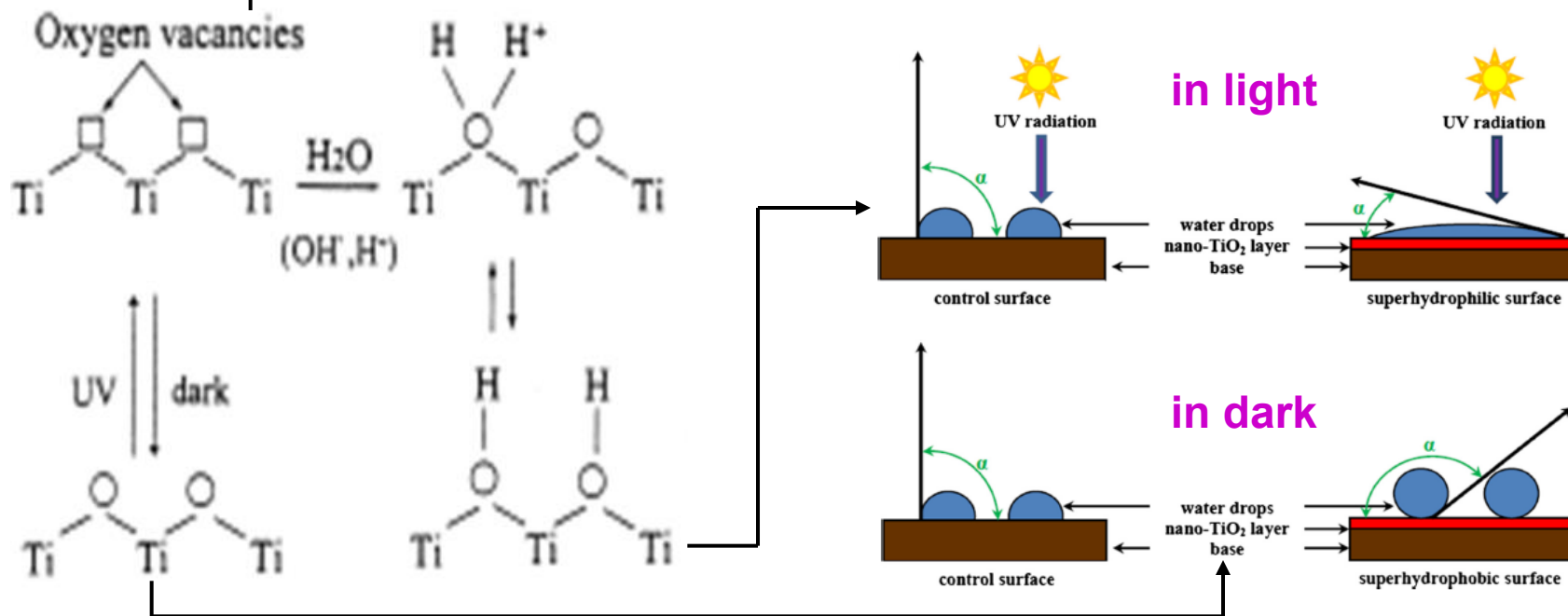
3) groups OH bond to free places $\Rightarrow$ change of the network of surface bonds $\Rightarrow$ hydrophilicity instead of hydrophobicity



Photoinduced hydrophilicity



3) groups OH bond to free places $\Rightarrow$ change of the network of surface bonds $\Rightarrow$ hydrophilicity instead of hydrophobicity



[figure from J. Bogdan et al.,
Nanoscale Res. Lett. 10, 57 (2015)]

Photovoltaic effect (solar cells)

Principle in general

- 1) incident photon (with energy higher than the band gap, E_g) creates pair electron+hole: $\text{Si} + h\nu > E_g \rightarrow h^+ + e^-$
- 2) electrons and holes randomly diffuse through the solar cell, the cell contains a membrane which allows passage of electrons only in one and holes only in the opposite direction



opposite charges cumulate on opposite ends of the solar cell, giving rise to a voltage

- 3) equilibrium is restored by connecting ends of the cell through a load which utilizes the electrical power, charge carriers return through the load to their original location

Principle more specifically: the "membrane" is PN junction

Photovoltaic effect (solar cells)

PN junction (reminder)

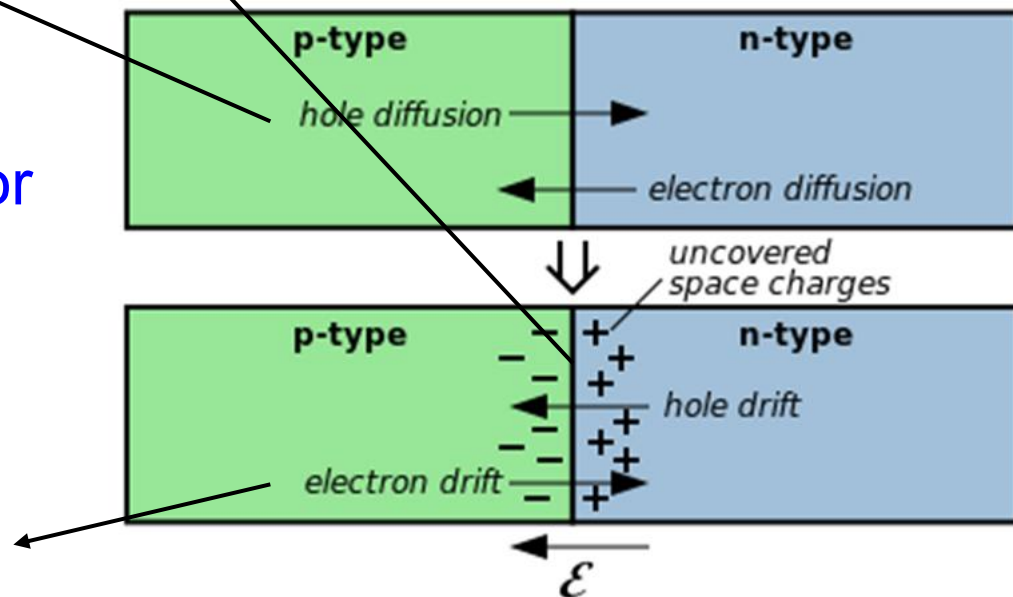
at a junction of p- and n-doped semiconductor, diffusion of majority charge carriers leads to their recombination



only immobile ions (of the same sign which have majority charge carriers in the other semiconductor) remain there



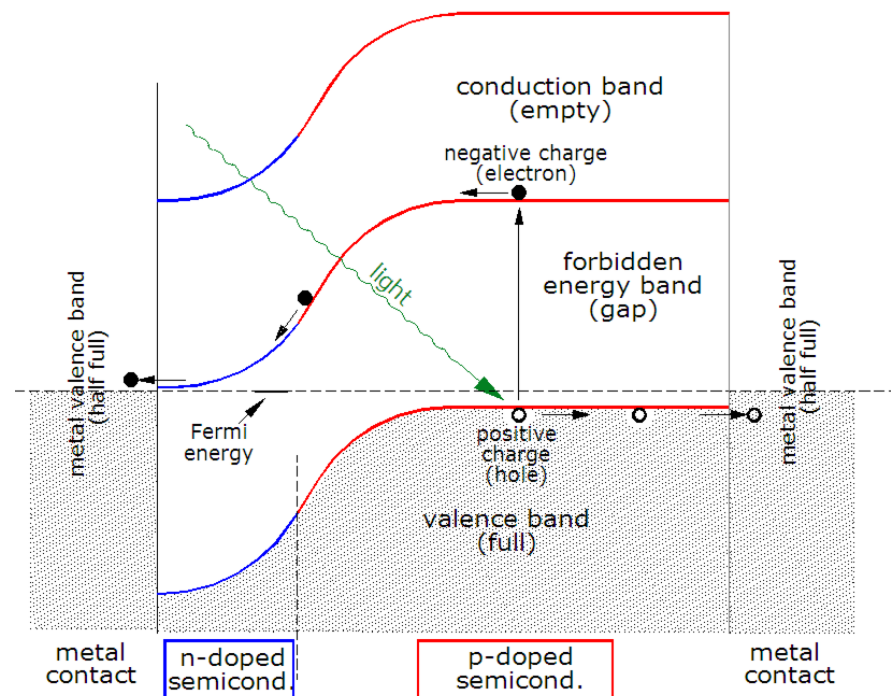
majority charge carriers from the other semiconductor are repulsed by these ions, i.e. the junction is impassable for them
(PN junction is passable for minority carriers)



Photovoltaic effect (solar cells)

The same in graphical form. Electrons and holes must (i) diffuse to the depleted region (without free charge carriers) around PN junction, and (ii) make it through it, which is energ. preferable for minority carriers - they do not have to rely on diffusion anymore

See also the remark about **importance of minority carriers** in chapter 7: solar cell functionality is given by their concentration (due to illumination) & diffuse length

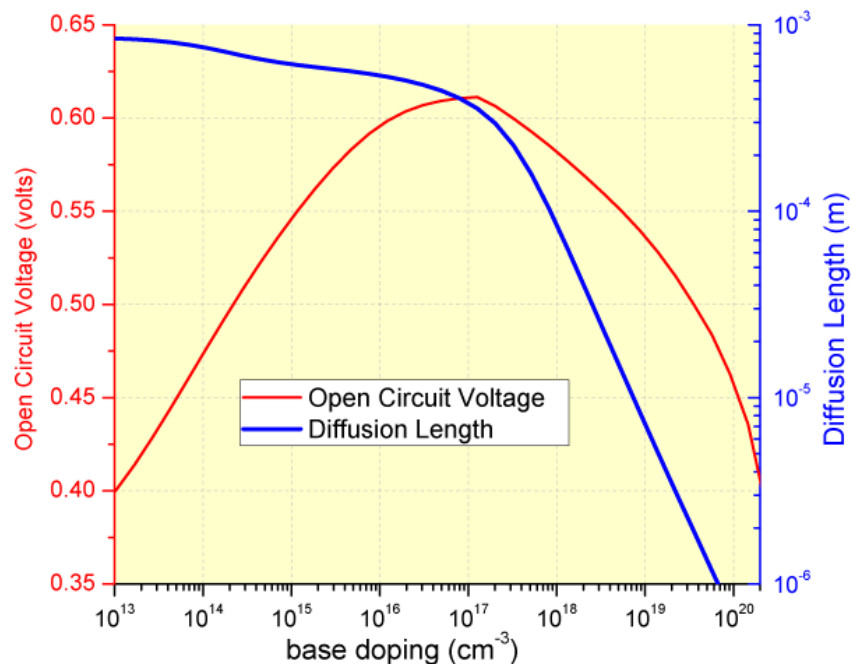


Photovoltaic effect (solar cells)

The same in graphical form. Electrons and holes must (i) diffuse to the depleted region (without free charge carriers) around PN junction, and (ii) make it through it, which is energ. preferable for minority carriers - they do not have to rely on diffusion anymore

See also the remark about **importance of minority carriers** in chapter 7: solar cell functionality is given by their concentration (due to illumination) & diffuse length

Higher doping level is good for the difference between p- and n- doped Si (source of voltage), but bad for diffusion length



[figure from www.pveducation.org]

Photovoltaic effect (solar cells)

Shockley-Queisser limit

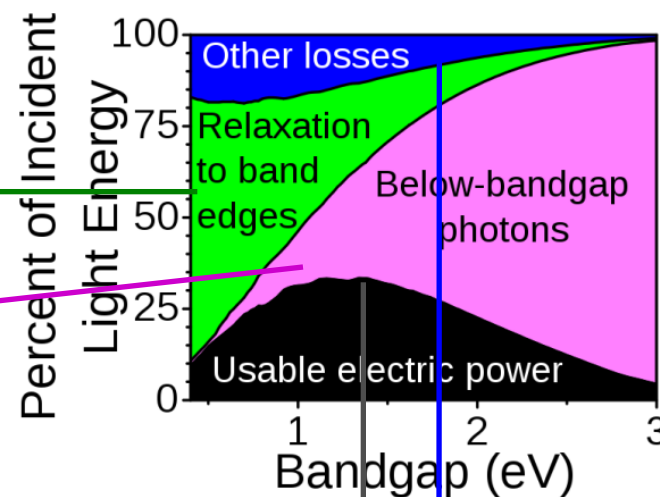
In the real Sun spectrum, there are not only photons with the ideal energy corresponding to the band gap width E_g

Some photons have unnecessarily high energy - we can utilize only that part corresponding to E_g

Some photons have energy lower than E_g - these cannot be used at all

Other losses are due to e.g. recombination (photons created by it; clearly cannot be avoided because at non-zero temperature, solar cell must radiate)

The consequence is **Shockley-Queisser limit** for the efficiency of solar cell with single PN junction: 33.7% (for $E_g = 1.34$ eV)



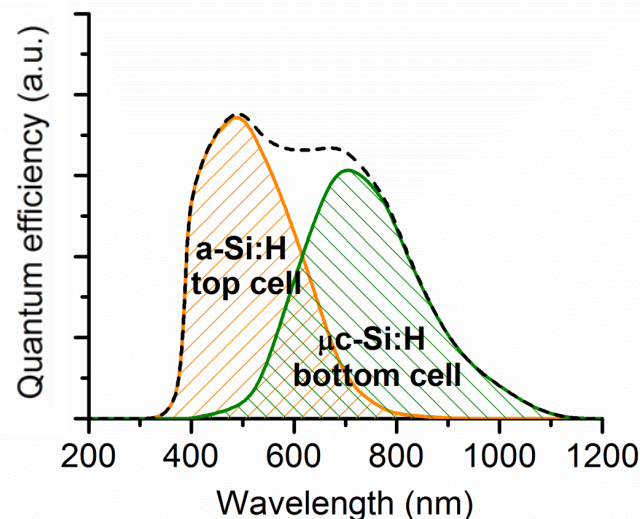
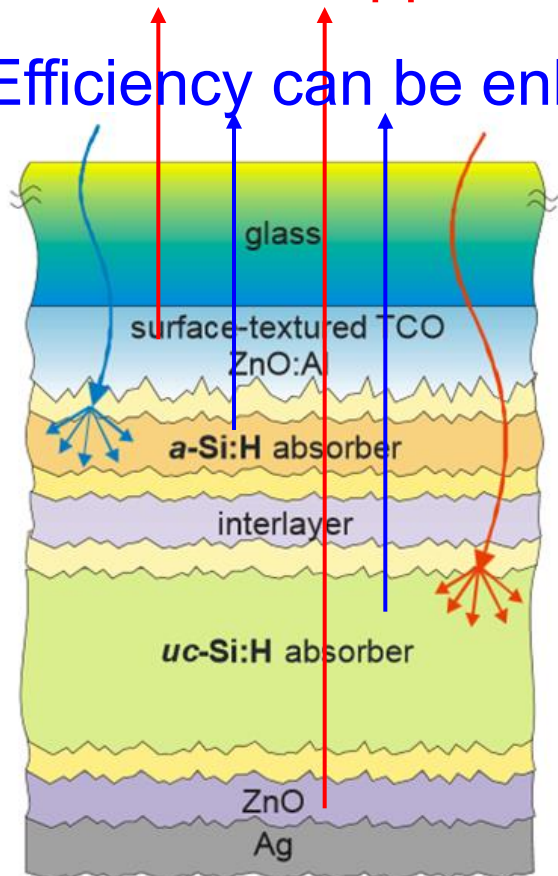
Photovoltaic effect (solar cells)

construction

Transparent conductive oxides - see above - as electrodes
(at least the upper one)

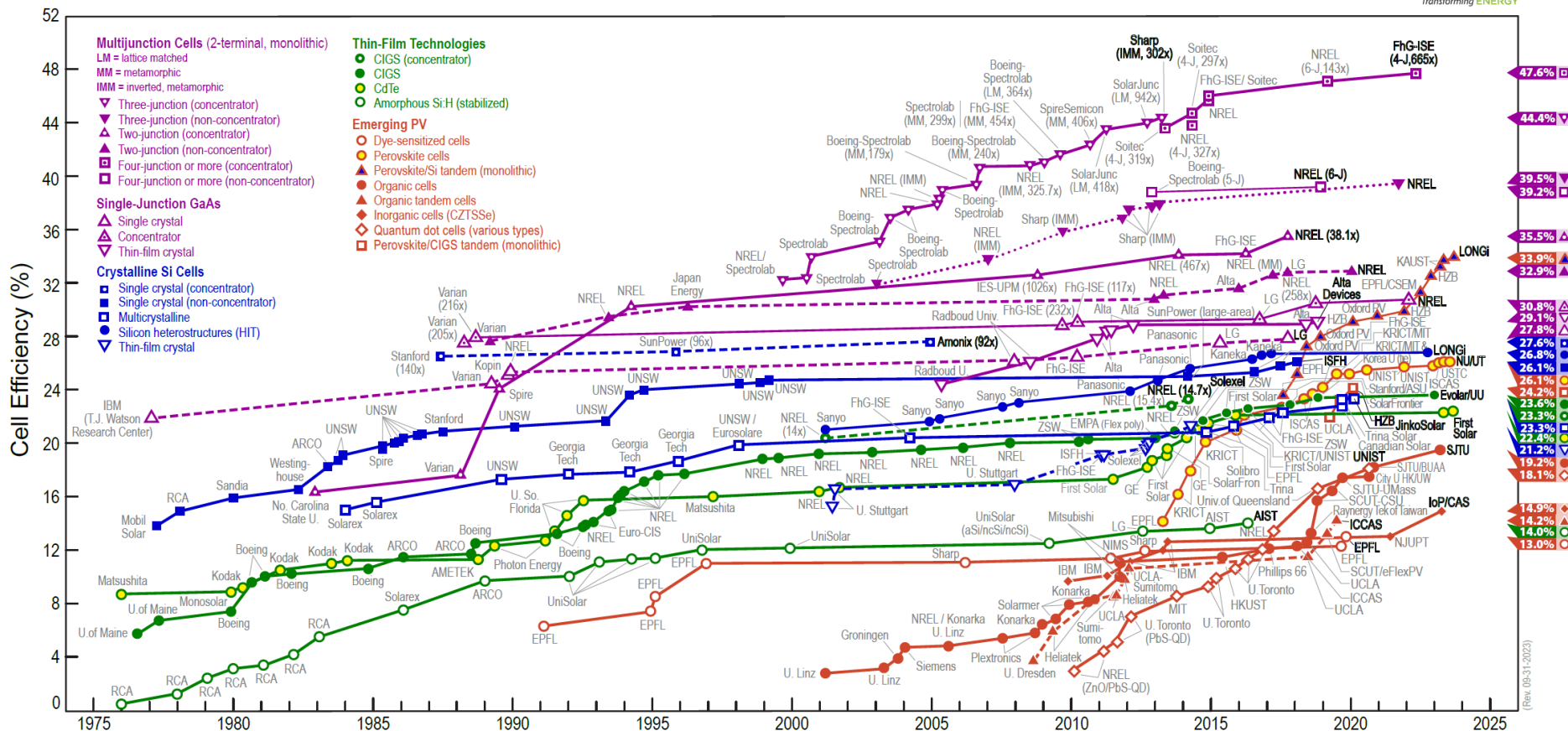
Efficiency can be enhanced by multilayers of different semicond.

(Shockley-Queisser limit is 33.7% for one PN junction, 42% for two PN junctions, 49% for three PN junctions, ...)



Photovoltaic effect (solar cells)

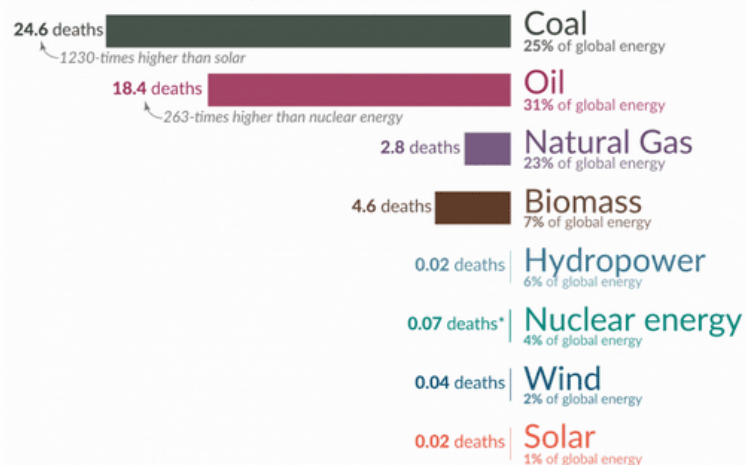
Best Research-Cell Efficiencies



Speaking about energy sources

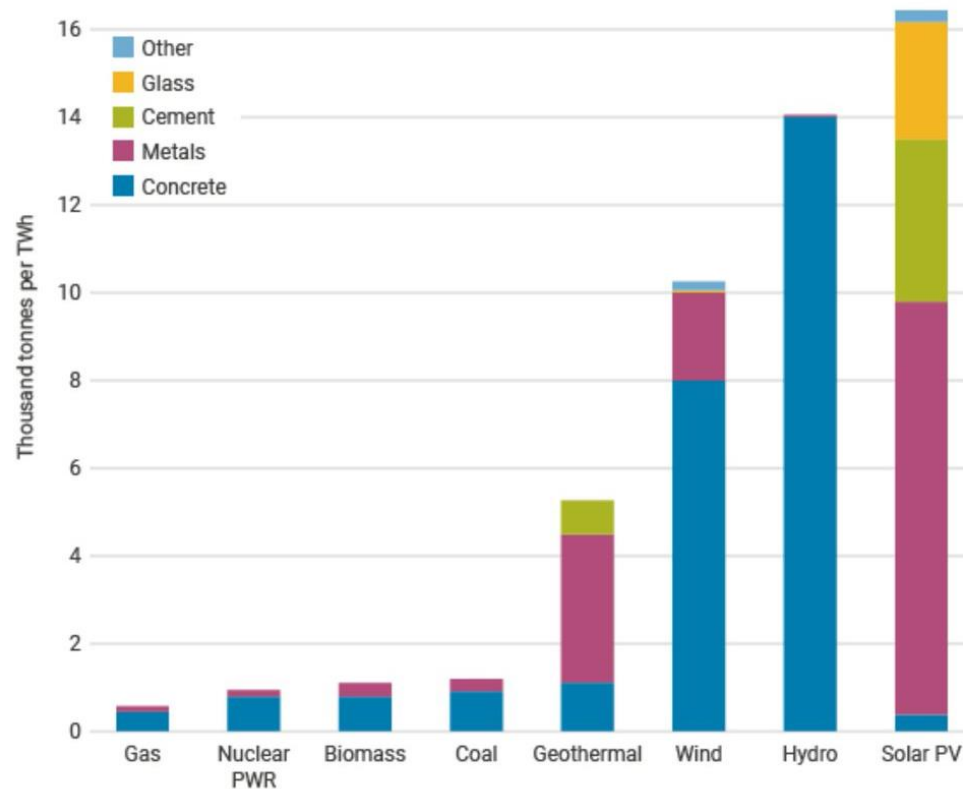
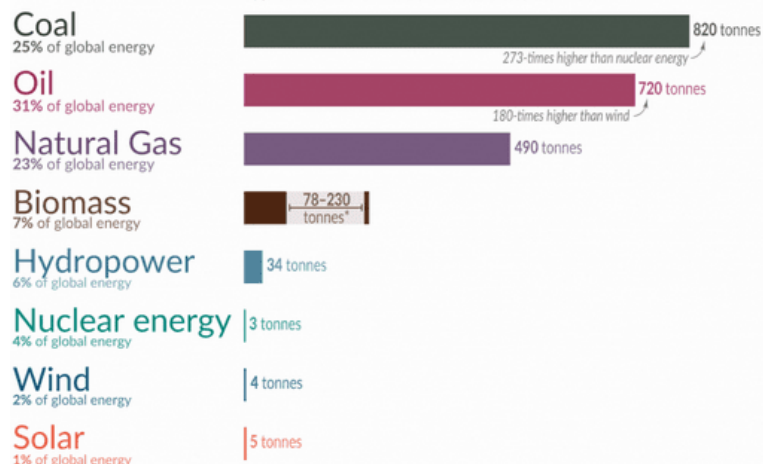
Death rate from accidents and air pollution

Measured as deaths per terawatt-hour of energy production.
1 terawatt-hour is the annual energy consumption of 27,000 people in the EU.



Greenhouse gas emissions

Measured in emissions of CO₂-equivalents per gigawatt-hour of electricity over the lifecycle of the power plant.
1 gigawatt-hour is the annual electricity consumption of 160 people in the EU.



[see ourworldindata.org for references]

[US Department of Energy]

12) Other functional properties

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Relatively heterogeneous chapter

- i) Thermochromic and electrochromic effect
- ii) Thermoelectric effects
- iii) Galvanic cells
- iv) Carbon structures, especially nanotubes
- v) Thermal diffusivity and effusivity
- vi) Colorimetry

Thermochromic effect

Many materials have temperature-dependent atomic structure

Optical properties may be independent of that (e.g. high E_g in both cases)

It may qualitatively affect optical properties
(thermochromic mat.)

Either change "only" between two opaque colors,

... or a qualitative change between transparent and non-transparent state (for some λ)

The transition can take place at some uninteresting temperature

... or at a temperature which makes the effect useful
(e.g. desired room temperature)

Thermochromic effect - VO_2

Low temperature (monoclinic structure):

band gap

transparent

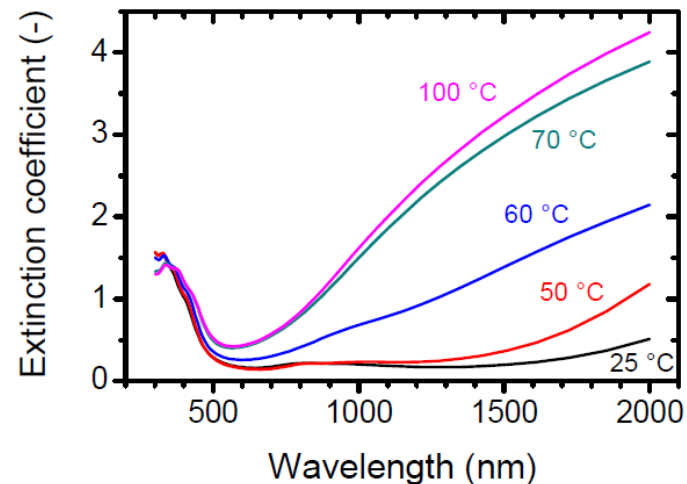
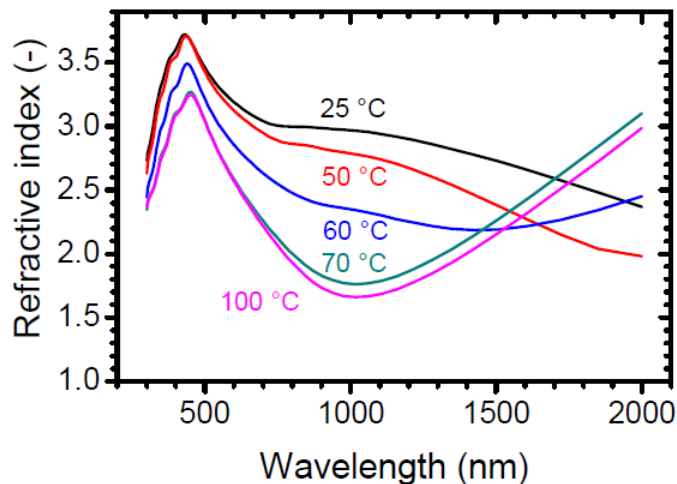
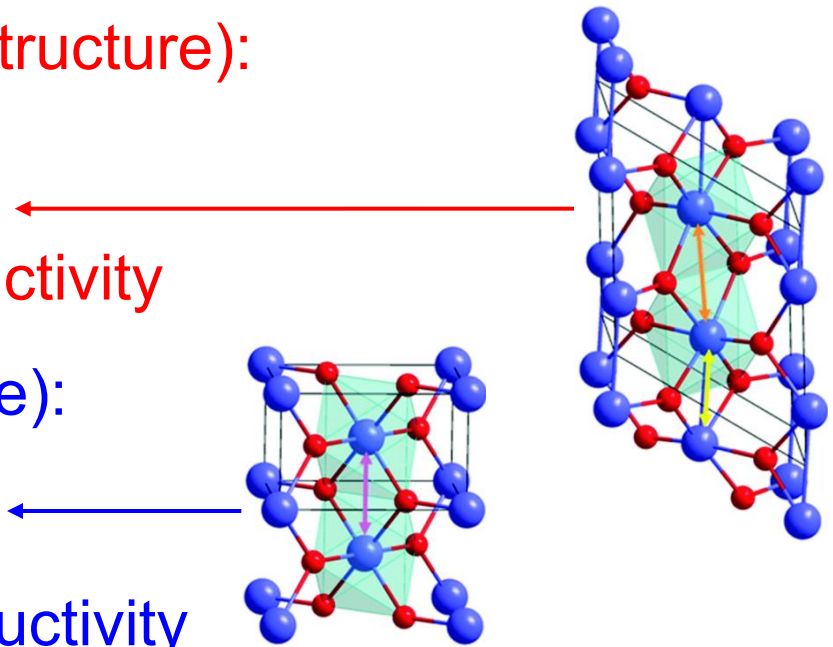
low electrical and thermal conductivity

High temperature (rutile structure):

closing on band gap

more opaque in IR

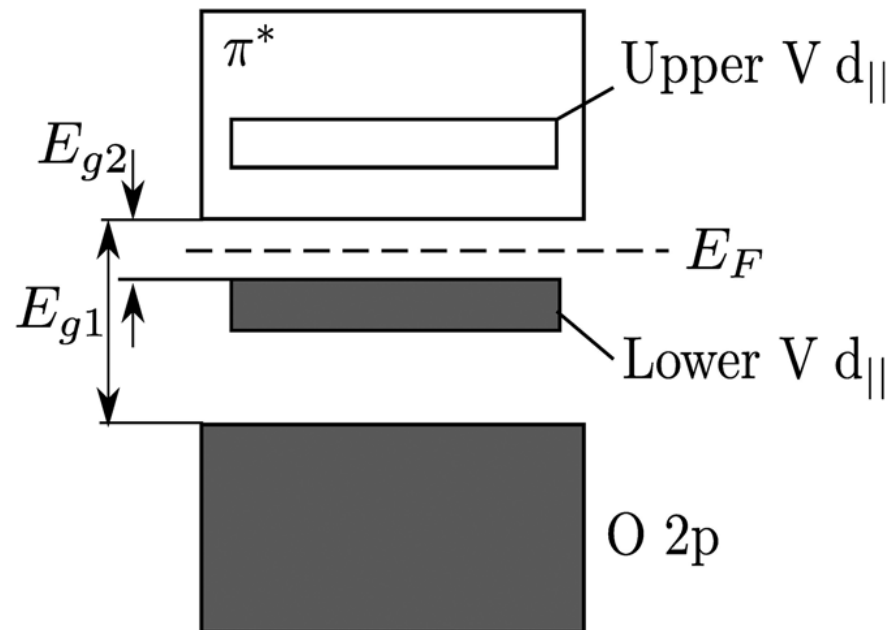
high electrical and thermal conductivity



Thermochromic effect - VO_2

Low temperature:

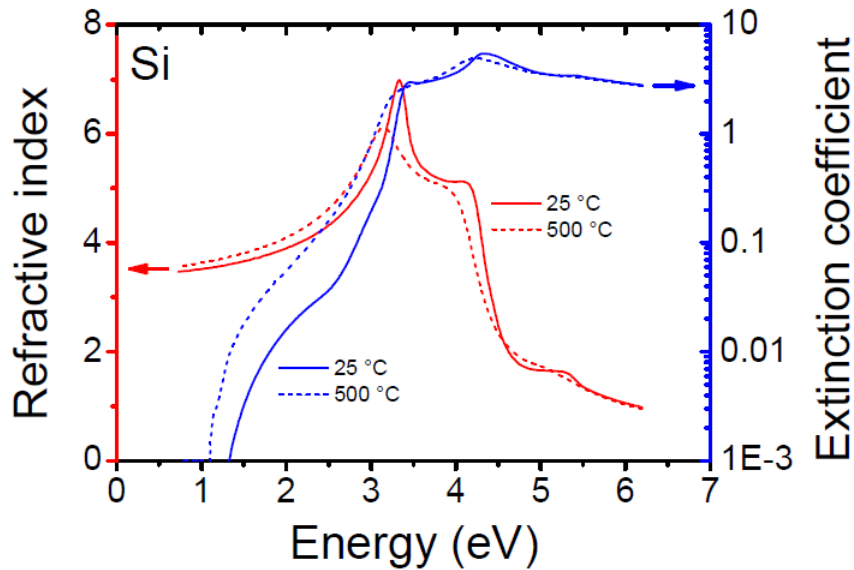
- band gap $E_{g2} \approx 0.6 \text{ eV}$
- transparent
- low conductivity



High temperature:

- closing of E_{g2} (the band Vd_{||} is not split anymore) $\Rightarrow$ decreasing transmittance in IR, high conductivity (but not so high to prevent transmittance in the visible on its own)
- still open band $E_{g1} \approx 2 \text{ eV}$, crucial for preserved transmittance in the visible in parallel to the modulation in IR

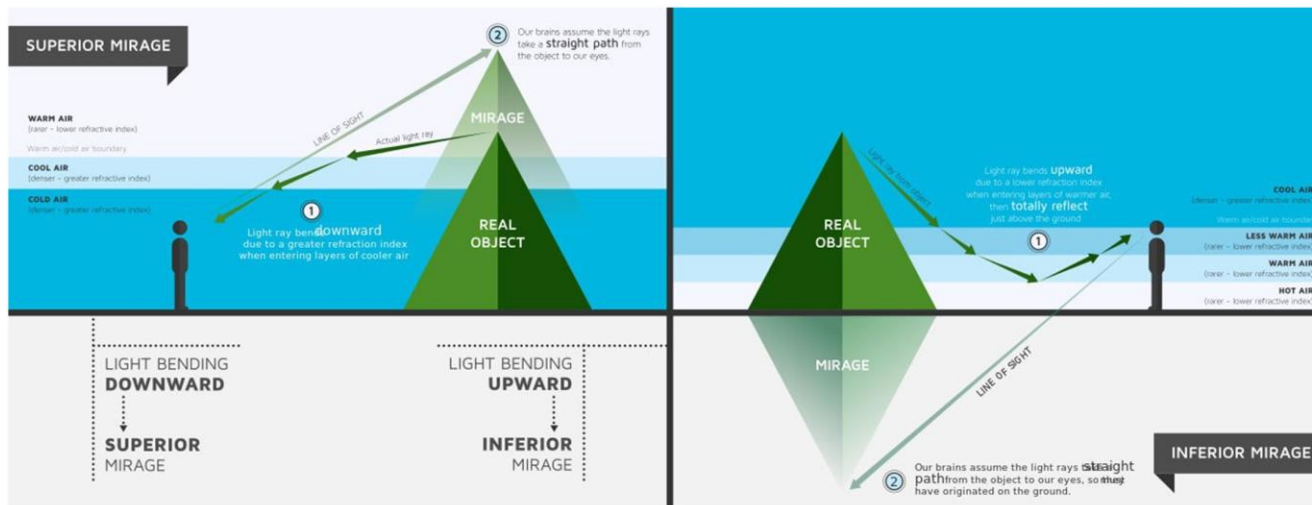
Mirage



In parallel to the "true" thermochromic effect (structure changes), optical properties depend on T due to density changes (even for the same structure).

First example: Si

Second example: air (warmer air has lower density, therefore lower n)
 $\Rightarrow$ mirage

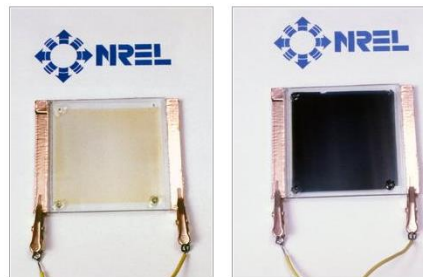


Electrochromic effect

Change of optical properties ($\Leftrightarrow$ el. structure) after

- addition of an electron (cathodic coloration)
oxides W (WO_3 ; most used), Mo, Ta, Nb, V, ...
- removal of an electron (anodic coloration)
oxides Cr, Mn, Fe, Co, Ni, again V, ...

In order to preserve neutrality, the electron must be followed by ion (H^+ , Li^+) waiting until then at an opposite electrode (design of the device - e.g. electrochromic windows - has to include it). **So this is not only about changing atomic coordinates (like in the case of thermochromic effect), but about changing the set of present atoms in itself.**



Electrochromic effect

Change of optical properties ($\Leftrightarrow$ el. structure) after

- addition of an electron (cathodic coloration)
oxides W (WO_3 ; most used), Mo, Ta, Nb, V, ...
- removal of an electron (anodic coloration)
oxides Cr, Mn, Fe, Co, Ni, again V, ...

In order to preserve neutrality, the electron must be followed by ion (H^+ , Li^+) waiting until then at an opposite electrode.

More exact mechanism have been proposed. What do thermochromic oxides have in common are six-coordinated metal atoms (building blocks are MO_6 octahedrons).

Works also for amorphous materials.

Contrary to thermoch. effect, this one needs external voltage. But the energy is delivered only once, coloration is permanent.

Thermoelectric effect

Seebeck coefficient S

Opposite ends of a material are at different temperatures



Diffusion of warmer charge carriers is faster, so in a stationary state the charge carriers cumulate at the cold end and we get the voltage

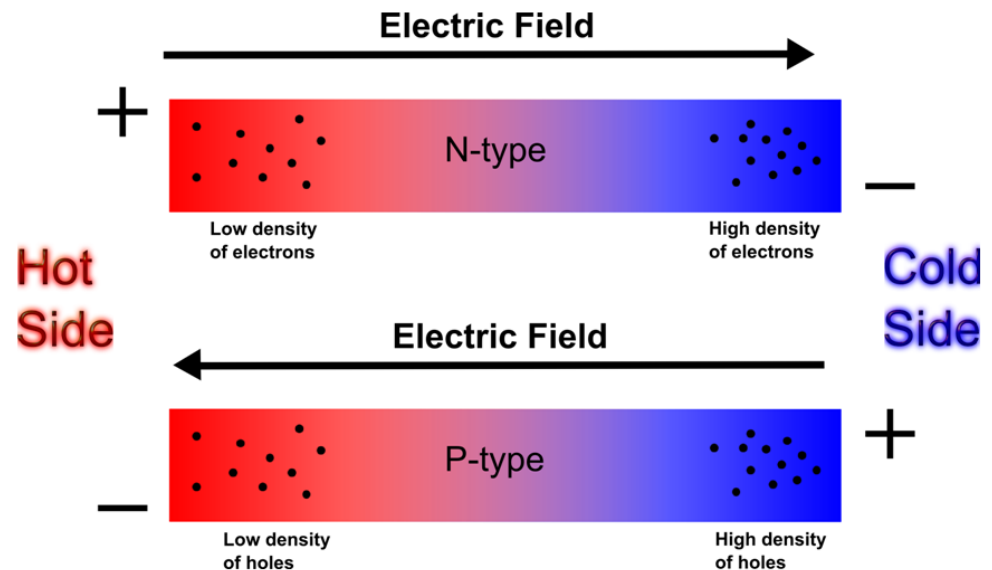
$$U = -S\Delta T$$

Positive charge carriers

$$\Leftrightarrow S > 0$$

Negative charge carriers

$$\Leftrightarrow S < 0$$



Thermoelectric effect

Seebeck effect (more practical setup)

Now, ends of **two** materials with different Seebeck coefficients have different temperatures.



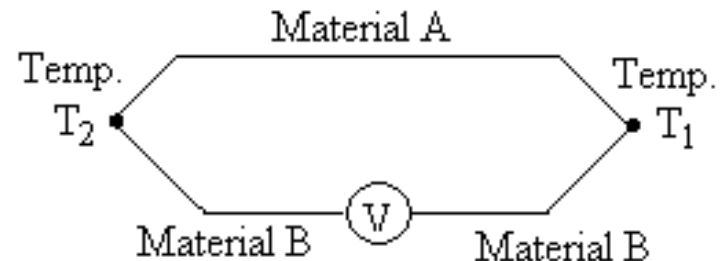
Thanks to that, we can anywhere (not only between the warmest and coldest point like in the previous side) interrupt the loop and get the voltage

$$U = \Delta S \Delta T,$$

or

$$U = \int \Delta S(T) dT$$

if S depends on temperature



Thermoelectric effect

Seebeck effect (more practical setup)

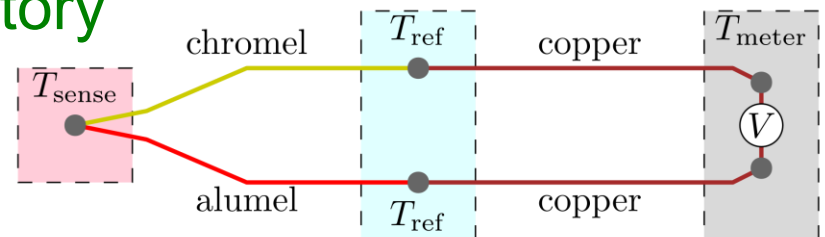
Now, ends of **two** materials with different Seebeck coefficients have different temperatures.



Thanks to that, we can anywhere (not only between the warmest and coldest point like in the previous side) interrupt the loop and get the voltage

$$U = \Delta S \Delta T$$

Not only source of energy, but also possibility to measure the temperature difference which gave rise to the voltage - see the thermocouples in any our laboratory



Jules Verne

Twenty Thous. Leagues Under the Sea

Lost in translation

KAPITOLA XII . VŠECHNO ELEKTRINOU

„Pane profesore,“ řekl kapitán Nemo, ukazuje na přístroje visící na stěnách jeho kabiny, „to jsou přístroje, které potřebuji k řízení *Nautilu*. Tady je mám stejně jako v salóně stále na očích. Ukazují mi polohu a přesný směr v oceánu. Některé už znáte, jako třeba teploměr, který udává vnitřní teplotu *Nautilu*; tlakoměr zaznamenává tlak vzduchu a předpovídá změny počasí; vlhkoměr mi udává stav vlhkosti vzduchu; bouřkový tlakoměr rozkladem své směsi oznamuje příchod bouře; busola řídí mou plavbu; sextantem měřím výšku slunce a určuji tak zeměpisnou šířku; chronometrem vypočítávám zeměpisnou délku; a konečně denní i noční dalekohledy mi slouží k pozorování všech částí obzoru, když se *Nautilus* vynoří na hladinu.“

„To jsou běžné mořeplavecké přístroje,“ odpověděl jsem. „Vím, k čemu se jich užívá. Ale jsou i jiné, které zřejmě slouží zvláštním potřebám *Nautilu*. Není tento číselník s pohyblivou ručičkou manometr?“

„Ano, je to opravdu manometr. Je spojen s okolní vodou a udává mi její tlak. Zaznamenává mi také hloubku, v níž má loď zrovna je.“

„A co tyto zvláštní sondy?“

„To jsou teploměrné sondy, kterými měřím teplotu v různých hloubkách.“

„A co další přístroje, jejichž užití neznám?“

„Tady vám budu muset, pane profesore, něco vysvětlit,“ řekl kapitán Nemo. „Račte mě vyslechnout.“

Na chvíli se odmlčel a pak pokračoval:

„Existuje mocná, poslušná, rychlá a snadno dostupná energie, které lze ke všemu použít a která vládne i na mé lodi. Vykonává zde všechnu práci. Svítí mi, hřeje mě, je duší mých strojů. A tato energie je elektrina.“

„Elektrina!“ zvolal jsem udiveně.

„Ano, pane profesore.“

„Vy však docílujete přímo úžasné rychlosti, což se se slou elektriny nesrovnává. Její pohybová síla je dosud velmi omezená a může vyvinout jen nepatrný účín.“

„Pane profesore,“ odpověděl kapitán Nemo, „moje elektrina není onou

obecně známou elektrinou. Jistě mi prominete, že víc už vám prozradit nemohu.“

„Nenaléhám, pane kapitáne, a spokojím se jen s nesmírným údivem nad jejím účinkem. Dovolte mi jedinou otázku, na kterou mi neodpovídejte, bude-li vtravá. Články, kterých užíváte k výrobě té zázračné energie, musí se rychle opotřebovat.*) Jak doplňujete třeba zinek, když nemáte žádné spojení se zemí?“

„Na tuhle otázku vám odpovím,“ prohlásil kapitán Nemo. „Napřed vám řeknu, že na dně moře jsou ložiska zinku, železa, stříbra a zlata a že jich jednou bude docela jistě využito. Ale z těchto pozemských kovů jsem si nevzal nic. Chtěl jsem, aby mi prostředky k výrobě mé elektriny dodalo jen moře.“

„Moře?“

„Ano, pane profesore. A těch prostředků mám dost. Mohl bych třeba spojit dráty ponořené do různých hloubek a získal bych elektrinu prostým rozdílem teplot v drátech. Dal jsem však přednost způsobu mnohem praktičtějšímu.“

„Jakému?“

„Jistě znáte složení mořské vody. V tisíci gramech má devět set šedesát gramů vody a asi šestadvacet gramů chloridu sodného neboli kuchyňské soli. Dále obsahuje v malém množství chlorid hořečnatý, síran hořečnatý, chlorid draselný, bromid hořečnatý, síran vápenatý a uhličitán vápenatý. Víte tedy, že chloridu sodného je v ní značné množství. A právě sodíkem, který získávám z mořské vody, plním své články.“

„Sodíkem?“

„Ano, pane profesore. Sodík se rtuť tvoří amalgám a tím nahrazuji v Bunsonových článcích zinek. Rtuť se nikdy nepotřebuje. Ubývá jen sodíku a ten mi dodává moře. Řeknu vám ještě, že sodíkové články nutno pokládat za nejvýkonnější a že jejich elektromotorická síla je dvakrát tak velká jako síla článků zinkových.“

„Výhody sodíku ve vašich podmínkách dobře chápu, pane kapitáne. Moře ho má dost. Dobrá. Nutno jej však získávat z vody, prostě vyrábět. Jak to děláte? K výrobě byste mohl jistě použít svých článků; ale nemýlím-li se, pak by spotřeba sodíku v elektrickém zařízení byla větší než jeho výroba. Tak by se stalo, že byste ho spotřeboval víc, než jste si ho vyrobil!“

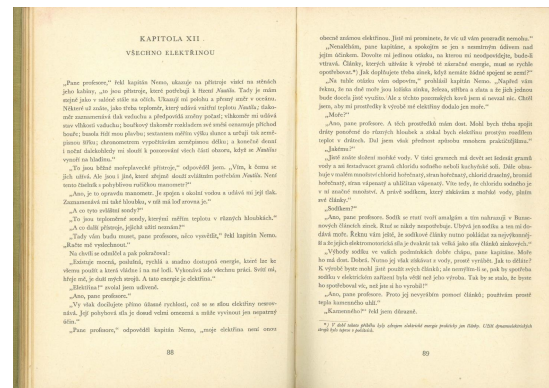
„Ano, pane profesore. Proto jej nevyrábím pomocí článků; používám prostě tepla kamenného uhlí.“

„Kamenného?“ řekl jsem důrazně.

*) V době tohoto příběhu byly zdrojem elektrické energie prakticky jen články. Užití dynamoelektrických strojů bylo teprve v počátcích.

Jules Verne Twenty Thous. Leagues Under the Sea

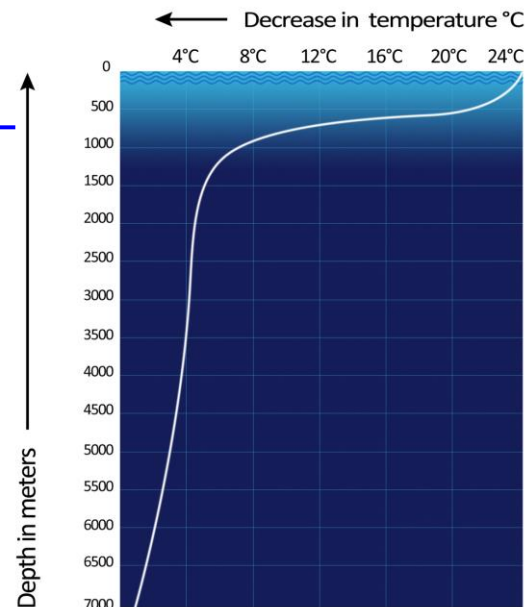
As a small boy, I did not understand the book (1870)
Now I know that author means thermochromic effect (Seebeck, 1821).



Qualitatively, it may work (especially in tropic sea - higher ΔT)

Detailed checking (acceleration in the shell during the trip to Moon, karst formations in granite [and parallel occurrence of creatures of all continents, from seals to porcupine] on the Mysterious Island, description of the production and properties of steel and cast iron in the Steel city or before the trip to Moon, ...)

of Verne is not good idea.



Jules Verne

Lost in translation

Twenty Thous. Leagues Under the Sea

Speaking about this: as captain Nemo did not want to rely on thermoelectric effect, how did he obtain electrical power?

„Ano, pane profesore. A těch prostředků mám dost. Mohl bych třeba spojit dráty ponořené do různých hloubek a získal bych elektřinu prostým rozdílem teplot v drátech. Dal jsem však přednost způsobu mnohem praktičtějšímu.“
„Jakému?“

...

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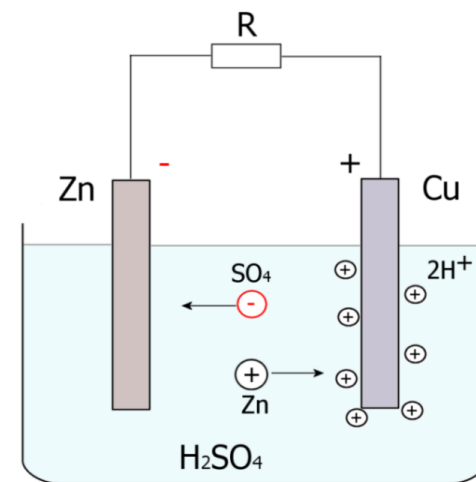
I see: Bunsen cell with Na instead of Zn

Galvanic cells

first the simpler **Volta cell** (1799, 1.1 eV)

Zn (anode) + Cu (cathode) in H_2SO_4 (electrolyte)

Zn easier oxidizes ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$) $\Rightarrow$
ions Zn^{2+} leave anode for the electrolyte
(reaction $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$) $\Rightarrow$
negative charge stays on the Zn electrode.
Cu (noble metal) dissolves in the electrolyte
less, the charge on Cu electrode is less
negative $\Rightarrow$ potential difference.



Original version (Galvani): brass hook
instead of Zn, iron rail (or iron knife)
instead of Cu, frog legs as an
electrolyte and voltmeter at once



Galvanic cells

Volta cell (1799, 1.1 eV)

Zn (anode) + Cu cathode) in H_2SO_4 (electrolyte)



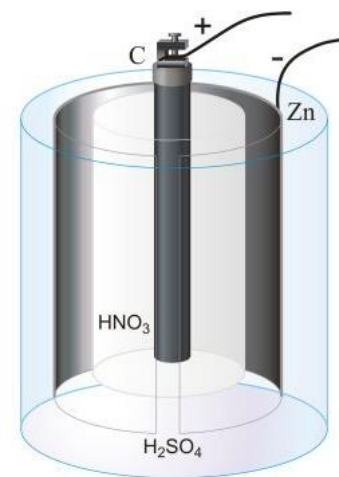
Bunsen cell (1841, 1.9 eV)

Zn (anode) in H_2SO_4 (electrolyte) + C (cathode)
in HNO_3 (oxidant, also called depolarizer),
separated by a membrane



or also H_2CrO_4 or $\text{H}_2\text{Cr}_2\text{O}_7$ (both leads to ions $\text{Cr}_2\text{O}_7^{2-}$)

instead of HNO_3 : not so much because of slightly higher voltage, but to avoid gas (H_2 , NO_2) formation during reaction



Galvanic cells

Zinc-carbon cell (1.5 eV, dry - electrolyte as a paste)

Zn (anode) in NH_4Cl (electrolyte) + C (cathode) in MnO_2 (oxidant)



Zinc-chloride cell (1.5 eV, "heavy duty")

Zn (anode) in ZnCl_2 (electrolyte) + C (cathode) v MnO_2 (oxidant)



yet drier: H_2O is on the left-hand side, i.e. is consumed

most frequent version of **Lithium cell** (3.3 V)

Li (anode) in LiClO_4 (electrolyte) + C (cathode) v MnO_2 (oxidant)

(here, MnO_2 is often not called oxidant or depolarizer but directly cathode, while C/metal is called current collector)



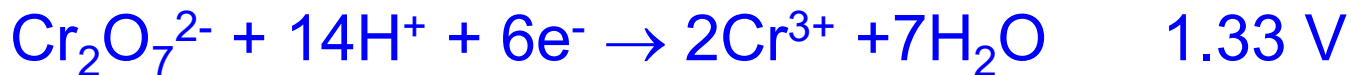
Jules Verne

Twenty Thous. Leagues Under the Sea

Bunsen cell (version with $\text{H}_2\text{Cr}_2\text{O}_7$):



Verne-Nemo cell:



Indeed twice as high, Verne is right about this
(but the experiment - throwing of sodium into sulfuric acid -
has to be made far from me)

Thermoelectric effect

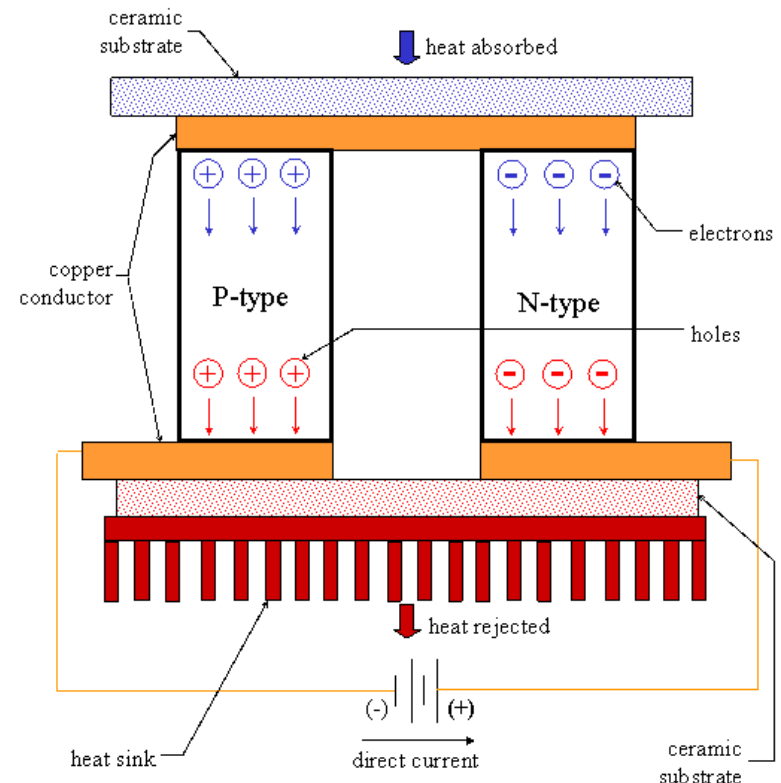
Peltier effect

Opposite of Seebeck (where a difference of temperatures leads to voltage): the same circuit as 3-4 slides above, but switch input and output - **voltage is a source of temperature difference**

$$dQ/dt = (\Pi_A - \Pi_B) \cdot I \text{ (details below)}$$

For the voltage polarity in the figure, charge carriers in both materials move down and carry heat down

Used e.g. for cooling of CCD chips (e.g. in detectors of our Raman spectroscope)



Thermoelectric effect

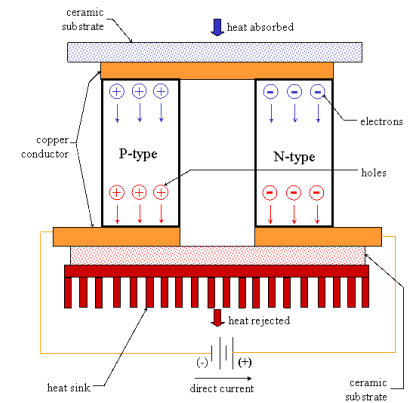
Peltier effect and the electronic structure

When leaving metal for 'n' semiconductor (**top** part of fig.), electrons have to jump up from the Fermi level to the conduction band, **cool** their surroundings of the energy used

When leaving 'n' semicond. (**bottom** part of fig.), electrons fall back to the Fermi level, **heat** surroundings by the excess energy

When leaving metal for 'p' semiconductor (**bottom** part of fig.), electrons from Fermi level annihilate with holes in valence band below the Fermi level, **heat** surroundings by the excess energy

When leaving 'p' semiconductor (**top** part of fig., where holes are created) electrons have to jump up from valence band to the Fermi level (leaving hole), **cool** surroundings of the energy used



Thermoelectric effect

Thomson effect

Absorption or release of heat by a conductor which conducts current, if there is a temperature gradient along the conductor

This is not the power $I.U = I.R^2$, but "extra" heat (even at $R = 0$)

Mathematician: "2nd order correction" resulting from (possible) temperature-dependence of Seebeck ($\Leftrightarrow$ Peltier) coefficient

Physicist: continuous version of Peltier effect described above: if the temperature-dependent Seebeck ($\Leftrightarrow$ Peltier) coefficient changes along a conductor (because of T gradient), each point is a "junction of two different materials" where - depending on I direction - heat is absorbed or released (Peltier effect)

$dQ/dt = K.I.\nabla T.dx$ (details below)

Thermoelectric effect - formulas

Contact voltage

- voltage V_C creates barrier for diffusion of charge carriers (conc. n_A, n_B), making their flux (without external voltage) zero:
 $n_A \cdot e^{-eV_C/k_B T} = n_B$, so $V_C = (k_B T/e) \cdot \ln(n_A/n_B)$

Peltier effect:

- released or absorbed heat at the junction is equal to the product of current and accelerating/decelerating voltage:
 $dQ/dt = V_C \cdot I$ (energy conservation law)
- sign depends on a convention; minus can be found as well (similarly for Thomson effect, i.e. continuous version of Peltier), in any case it changes with the direction of current
- using the definition 3 slides above $dQ/dt = (\Pi_A - \Pi_B) \cdot I$
we get $\Pi = (k_B T/e) \cdot \ln(n)$

Thermoelectric effect - formulas

Contact voltage

$$V_C = (k_B T/e) \cdot \ln(n_A/n_B)$$

Peltier effect

$$dQ/dt = \Delta\Pi \cdot I \text{ where } \Delta\Pi = V_C$$

Seebeck effect

- along a loop of two materials we measure a difference of both contact voltages: $\Delta V_C = (k_B/e) \cdot \ln(n_A/n_B) \cdot \Delta T$
- using the definition 13 slides above $U = \Delta S \Delta T$ we get $\Delta S = (k_B/e) \cdot \ln(n_A/n_B)$
- thus the relationship with Peltier coefficient $S = \Pi/T$, $\Delta S = \Delta\Pi/T$

Thermoelectric effect - formulas

Contact voltage

$$V_C = (k_B T/e) \cdot \ln(n_A/n_B)$$

Peltier effect

$$dQ/dt = \Delta\Pi \cdot I \text{ where } \Delta\Pi = V_C$$

Seebeck effect

$$U = \Delta S \Delta T \text{ where } \Delta S = (k_B/e) \cdot \ln(n_A/n_B) = \Delta\Pi/T$$

Thomson effect

- continuous version of Peltier effect, where $dQ/dt = V_C \cdot I = \Delta S \cdot T \cdot I$
- therefore $dQ/dt = (dS/dx) \cdot T \cdot I \cdot dx = (dS/dT) \cdot (dT/dx) \cdot T \cdot I \cdot dx = (dS/dT) \cdot \nabla T \cdot T \cdot I \cdot dx$
- using the definition 3 slides above $dQ/dt = K \cdot I \cdot \nabla T \cdot dx$
we get **$K = T \cdot (dS/dT)$**

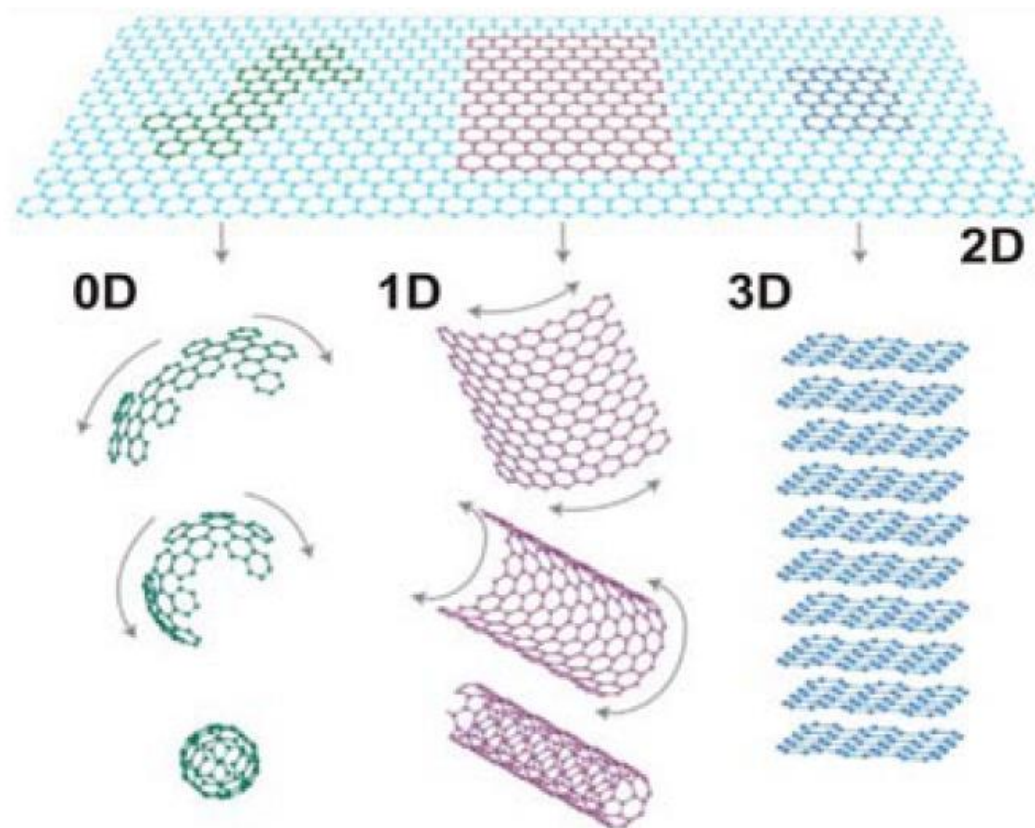
Carbon (nano)structures

3D graphite

2D graphene (from purely geometrical point of view - not in reality - precursor of the other 3, see the figure)

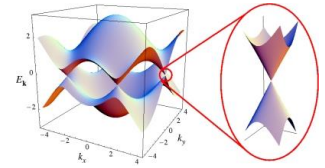
1D nanotubes

0D fullerenes



Carbon (nano)structures

3D graphite: see chapter 2. Metallic, because val. and cond. band touch in a single point



2D graphene: popular, but not more interesting than graphite from the present point of view. Extremal properties are given

- high electrical and thermal conductivity: the reason is purity, not new physics. (Single layer is easier to prepare without defects, and there is higher motivation for that - graphite in pencils includes impurities intentionally.)
- transparency: the reason is low thickness (absorbs 2.3% per monolayer, but there is only one), not new physics.

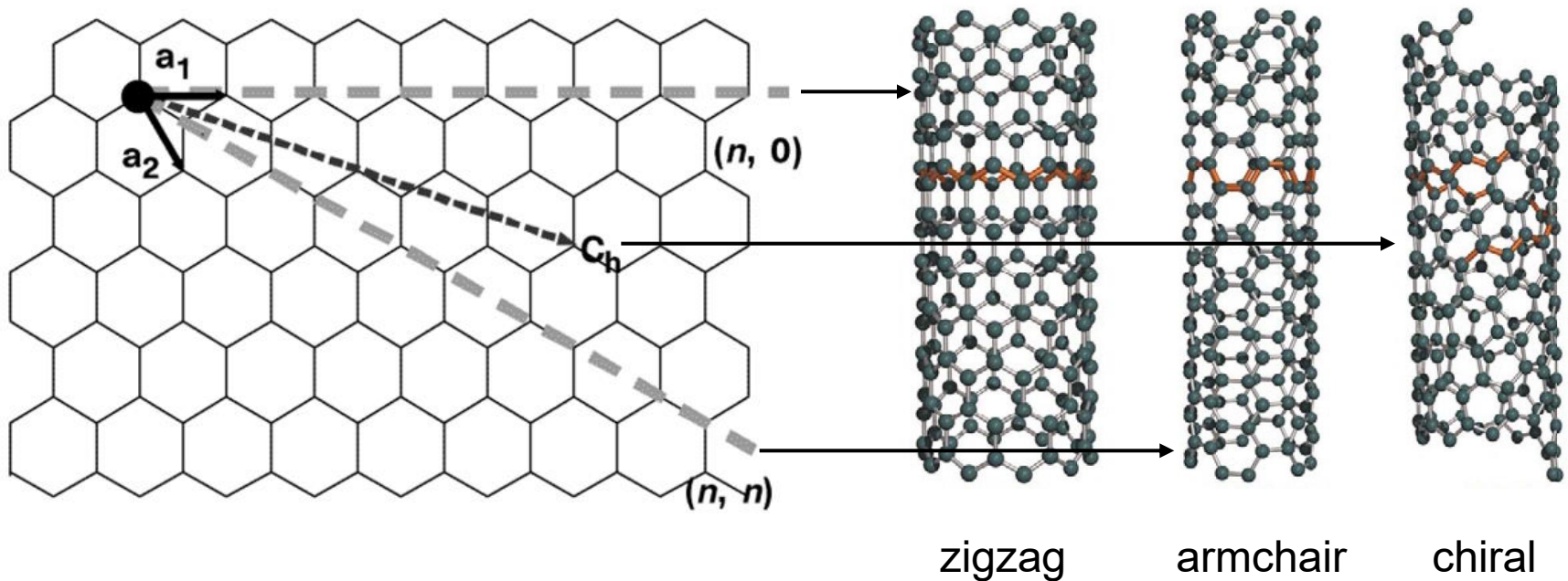
1D nanotubes: details below

0D fullerenes: organic chemistry, experiments with superconductivity

Carbon nanotubes

While terms graphite or graphene represent single material, there is **infinite number** of qualitatively different nanotubes.

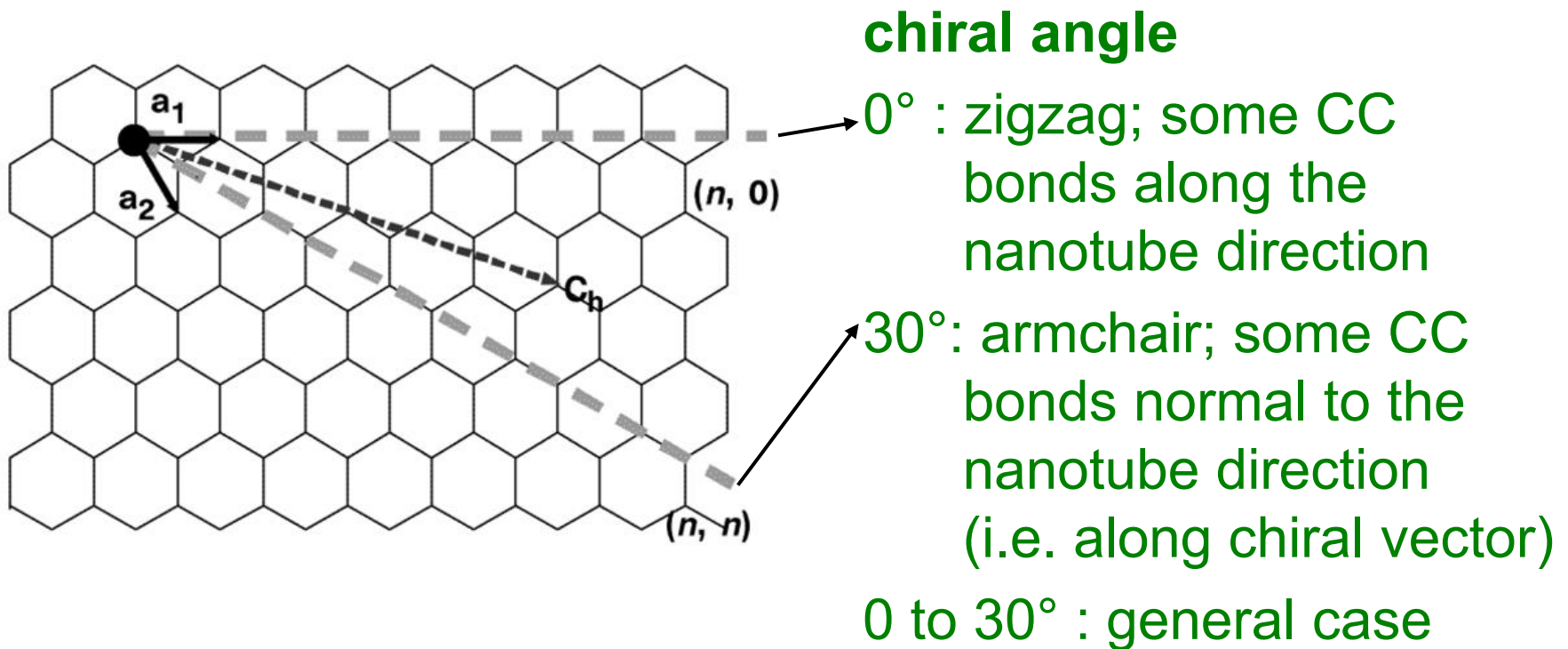
They are characterized by the direction of bending (followed by a perpendicular cut), the **chiral vector** (and **chiral angle**).



Carbon nanotubes

While terms graphite or graphene represent single material, there is **infinite number** of qualitatively different nanotubes.

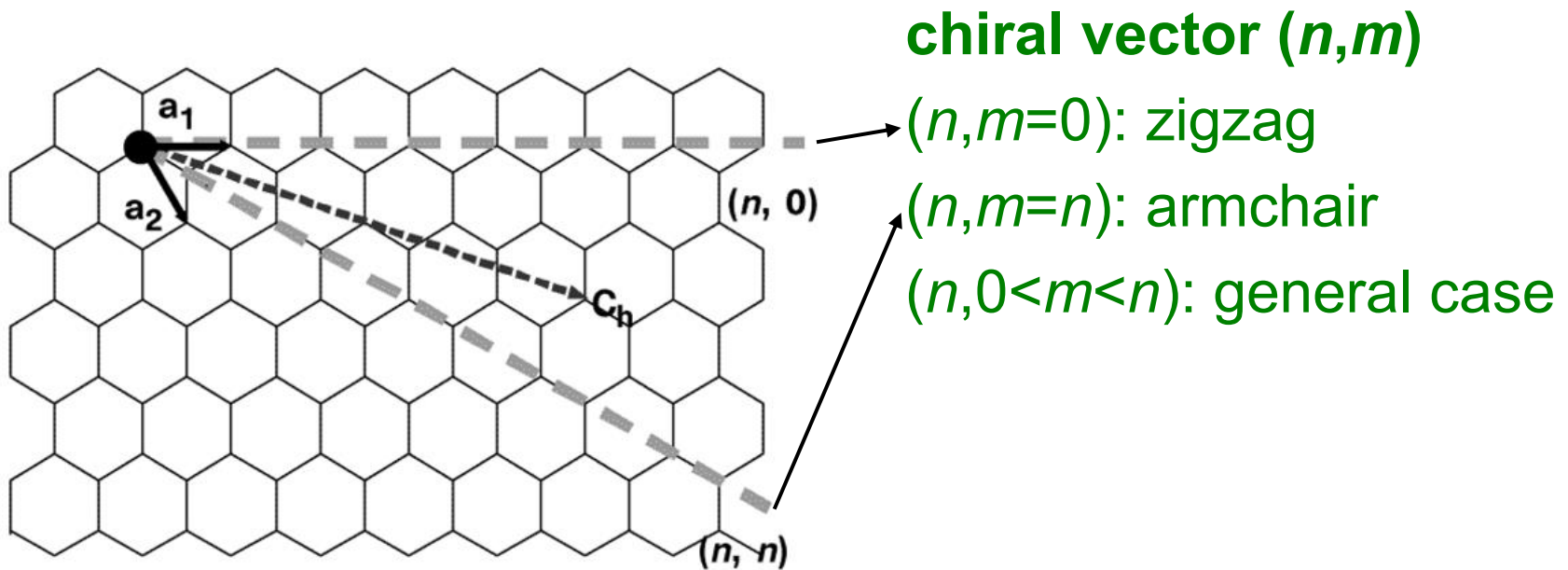
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Carbon nanotubes

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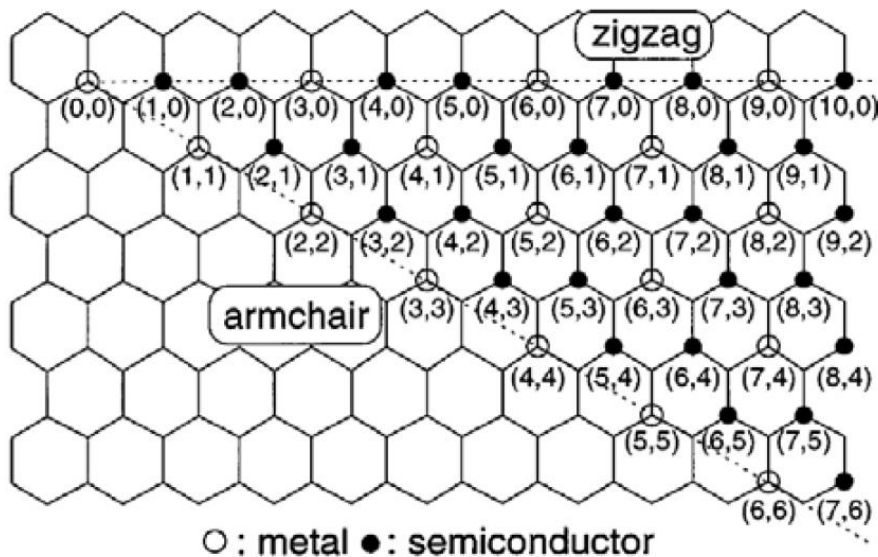
They are characterized by the direction of bending (followed by a perpendicular cut), the **chiral vector** (and **chiral angle**).



Carbon nanotubes

Reminder: graphite & graphene have metallic properties due to the touch of valence and conduction band in a single point

So it is not surprising, that small deformation of electronic structure (using graphene to make nanotube) can open a band gap, and metallic material becomes semiconductive



decided by chiral vector

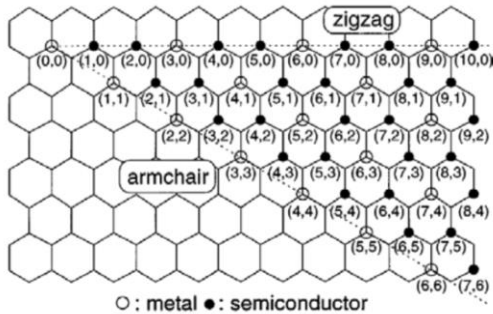
n-m divisible by 3 (e.g. all armchair: $n-m = 0$)

⇒ **metal**

n-m not divisible by 3

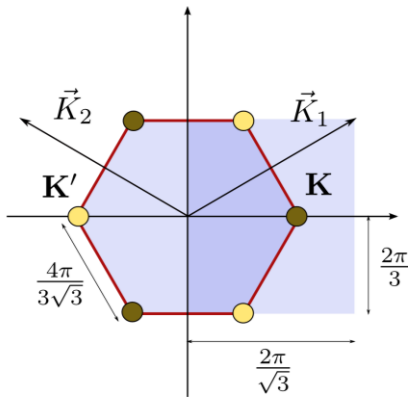
⇒ **semiconductor**

Carbon nanotubes



$n-m$ divisible by 3 $\Rightarrow$ **metal**
 $n-m$ not divisible by 3 $\Rightarrow$ **semiconductor**
Why in this way?

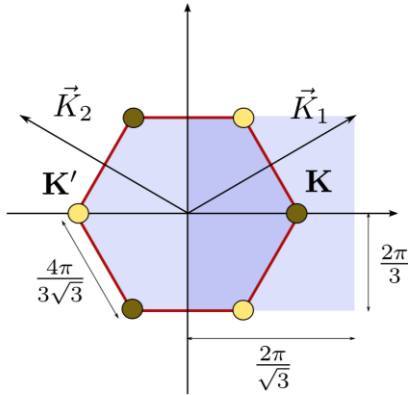
Chiral vector $\mathbf{C} = n\mathbf{R}_1 + m\mathbf{R}_2$ brings new symmetry, which the wavefunction has to respect (while in graphene plane it can differ of phase, i.e. factor $e^{i\mathbf{k}\cdot\mathbf{C}}$ - see Bloch theorem). Thus, out of graphene electronic states, only those with wave vector $\mathbf{k}$ which fulfils $\mathbf{k}\cdot\mathbf{C} = 2\pi N$ (integer N) are allowed



In the first Brillouin zone of graphene, valence and conduction band touch in corners of the hexagon, i.e. points $\pm(\mathbf{K}_1 - \mathbf{K}_2)/3$, $\pm(\mathbf{K}_1 + 2\mathbf{K}_2)/3$ and $\pm(2\mathbf{K}_1 + \mathbf{K}_2)/3$

Carbon nanotubes

Chiral vector $\mathbf{C} = n\mathbf{R}_1 + m\mathbf{R}_2$ brings new symmetry, which the wavefunction has to respect $\Rightarrow \mathbf{k} \cdot \mathbf{C} = 2\pi N$ (integer N)



In the first Brillouin zone of graphene, valence and conduction bands touch in corners of the hexagon, i.e. points $\pm(\mathbf{K}_1 - \mathbf{K}_2)/3$, $\pm(\mathbf{K}_1 + 2\mathbf{K}_2)/3$ and $\pm(2\mathbf{K}_1 + \mathbf{K}_2)/3$

After substituting to $\mathbf{k} \cdot \mathbf{C} = \mathbf{k} \cdot (n\mathbf{R}_1 + m\mathbf{R}_2) = 2\pi N$ (remembering $\mathbf{K}_i \cdot \mathbf{R}_j = 2\pi\delta_{ij}$):

$\mathbf{k} = \pm(\mathbf{K}_1 - \mathbf{K}_2)/3$ is allowed for $\pm(2\pi n - 2\pi m)/3 = 2\pi N$

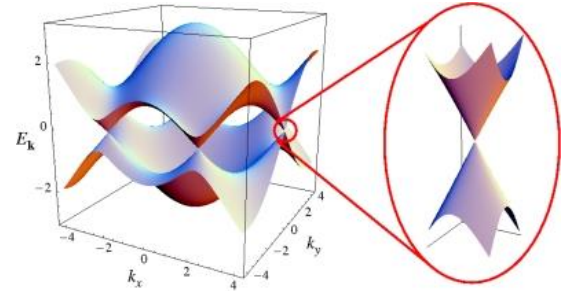
$\mathbf{k} = \pm(\mathbf{K}_1 + 2\mathbf{K}_2)/3$ is allowed for $\pm(2\pi n + 4\pi m)/3 = 2\pi N$

$\mathbf{k} = \pm(2\mathbf{K}_1 + \mathbf{K}_2)/3$ is allowed for $\pm(4\pi n + 2\pi m)/3 = 2\pi N$

All equations yield the same condition $(n - m) = 3N$

Effective mass in graphene plane

Above we derived $1/m^* = 1/\hbar^2 \cdot d^2E(k)/dk^2$
But what if the dependence $E(k)$ around E_F is **linear**? m^* is then infinite (while the exp. value is, on the contrary, almost 0).



Let's try to derive m^* a bit differently than in chapter 7:

- m^* does not replace m in the eq. of motion, but in relation for p
- for simplicity, assume that bands do not touch in K ($k \neq 0$) but in Γ ($k=0$) (i.e. transformation $k' = k-K$)

$$p = m^* v_g$$

$$p = \hbar k$$

$$v_g = d\omega(k)/dk = 1/\hbar \cdot dE(k)/dk$$

(new assumption)

(also used previously)

(also used previously)

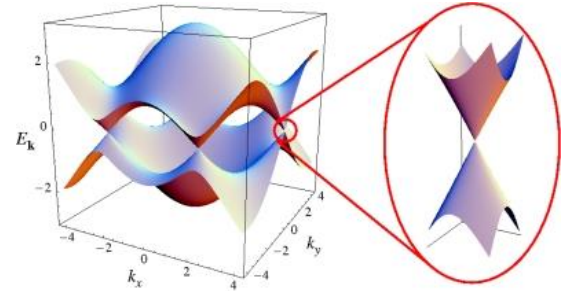
↓ (substitute for v_g in $m^* v_g = \hbar k$)

$$1/m^* = 1/(\hbar^2 k) \cdot dE(k)/dk$$

for free electron ($E = \hbar^2 \cdot k^2/2m$) also here $m^* = m$

Effective mass in graphene plane

Above we derived $1/m^* = 1/\hbar^2 \cdot d^2E(k)/dk^2$
But what if the dependence $E(k)$ around E_F is **linear**? m^* is then infinite (while the exp. value is, on the contrary, almost 0).



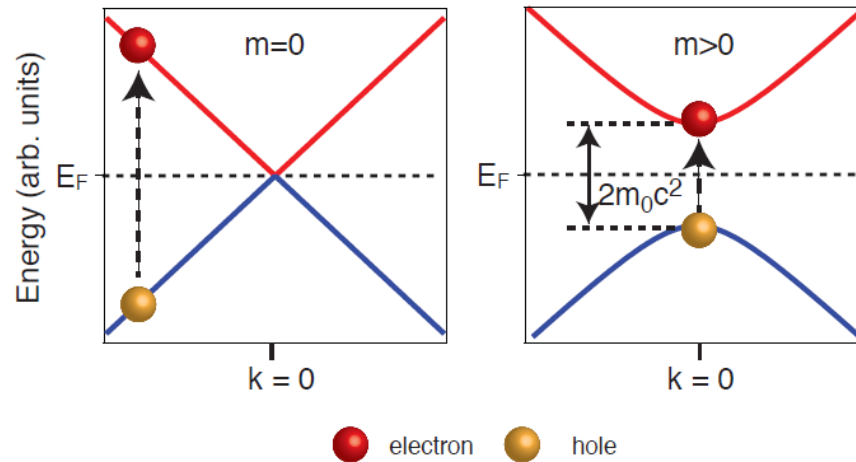
Alternative formula $1/m^* = 1/(\hbar^2 k) \cdot dE(k)/dk$ was derived
- good thing (agrees with exp. for graphene) is $m^* \rightarrow 0$ for $k \rightarrow 0$
- bad thing is division by zero for $k=0$

Understanding the division by zero, i.e. zero m^* : massless particles are known to move by the speed of light $\Rightarrow$ consider equations known from special relativity. The real velocity of "massless" electrons has the role of "speed of light".

- in general: $E^2 = (pc)^2 + (m_0c^2)^2$
- $m_0 = 0$: $E = pc = \hbar kc = \hbar kv_g$: observed linear dependence

Effective mass in graphene plane

Understanding the division by zero, i.e. zero m^* :



- in general: $E^2 = (pc)^2 + (m_0c^2)^2$
(electron and hole are in this interpretation antiparticles)
- $m_0 = 0$: $E = pc = \hbar kc = \hbar kv_g$: observed linear dependence
(owing to the possibility of pseudorelativistic description, people really talk about relativistic electrons and holes, or Dirac fermions)

Effective mass in graphene plane

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(owing to the possibility of pseudorelativistic description, people really talk about relativistic electrons and holes, or Dirac fermions)

The aforementioned almost-zero effective mass is consistent with the high achieved mobility in a pure graphene layer

- graphene: up to 200 000 cm²/V.s
- TCO: often around 40 cm²/V.s

(see e.g. the figure Steinhauser et al. in chapter 7):

Thermal diffusivity and effusivity

Quantities which need no introduction:

- thermal conductivity, λ (or k or κ)
- heat capacity per unit of mass, c
- heat capacity per unit of volume, $c_{\text{vol}} = \rho c$

What is their relationship with

- thermal diffusivity, α
- thermal effusivity, e ?

Thermal diffusivity and effusivity

Quantities which need no introduction:

- thermal conductivity, λ (or k or κ)
- heat capacity per unit of mass, c
- heat capacity per unit of volume, $c_{\text{vol}} = \rho c$

Thermal diffusivity

$$\alpha = \lambda / \rho c = \lambda / c_{\text{vol}}$$

means the rate of equilibration of temperature differences

Example: rate of cooling after local melting (after an energetic particle impact)

Thermal diffusivity and effusivity

Thermal diffusivity

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means the rate of equilibration of temperature differences

Example: rate of cooling after local melting (after an energetic particle impact)

PHYSICAL REVIEW B

VOLUME 56, NUMBER 5

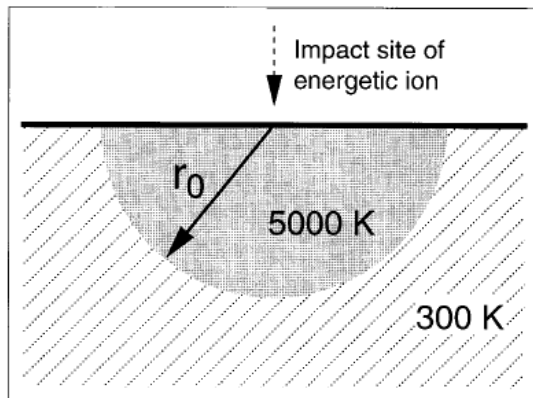
1 AUGUST 1997-1

Evidence for subpicosecond thermal spikes in the formation of tetrahedral amorphous carbon

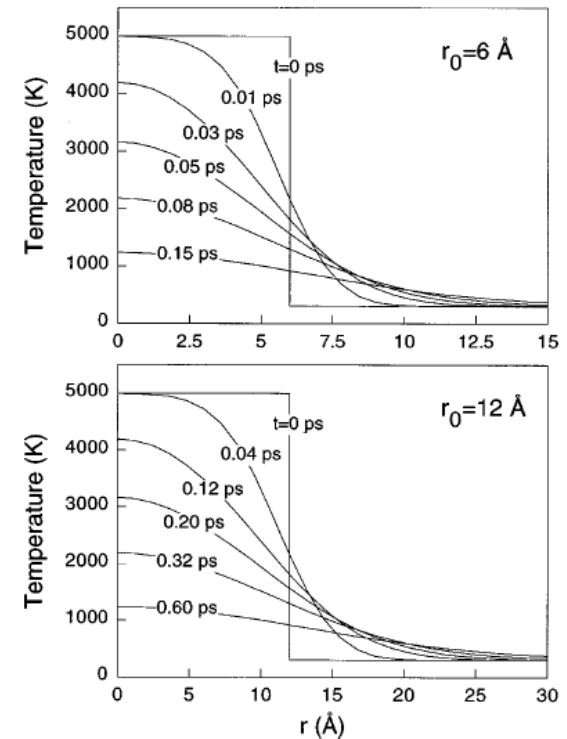
N. A. Marks

Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234, Australia

(Received 12 February 1997)



$$t_{\text{quench}} \propto \frac{c\rho}{\kappa} r_0^2.$$



Thermal diffusivity and effusivity

Quantities which need no introduction:

- thermal conductivity, λ (or k or κ)
- heat capacity per unit of mass, c
- heat capacity per unit of volume, $c_{\text{vol}} = \rho c$

Thermal effusivity

$$e = \sqrt{\lambda \rho c} = \sqrt{\lambda c_{\text{vol}}}$$

means material's resistance against temperature changes

Example 1: temperature on a boundary of two materials is approximately given by the ratio of their thermal effusivities.

Example 2: if a material is exposed to oscillating ambient temperature, amplitude of oscillations of its own (surface) temperature is given by its thermal effusivity

Thermal diffusivity and effusivity

Quantities which need no introduction:

- thermal conductivity, λ (or k or κ)
- heat capacity per unit of mass, c
- heat capacity per unit of volume, $c_{\text{vol}} = \rho c$

Thermal effusivity

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means material's resistance against temperature changes

Thermal diffusivity and effusivity characterize the **thermal inertia** (in the broad sense which denotes whole field).

Sometimes the term **thermal inertia** (in the narrow sense which denotes a quantity) is used for thermal effusivity.

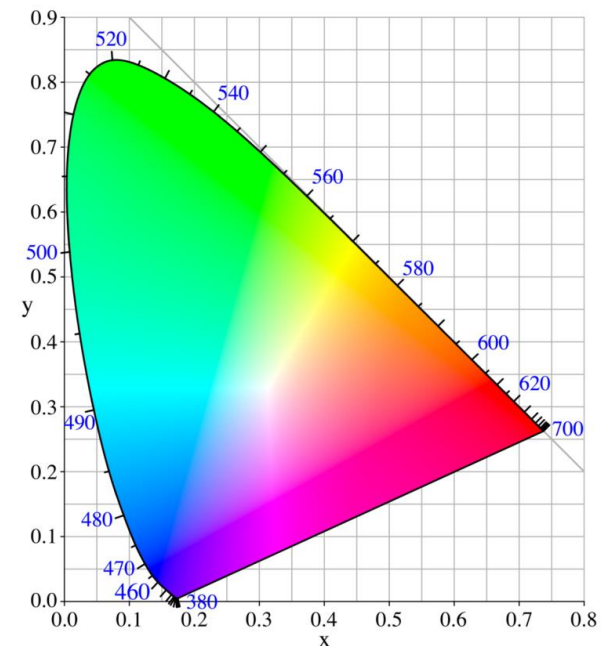
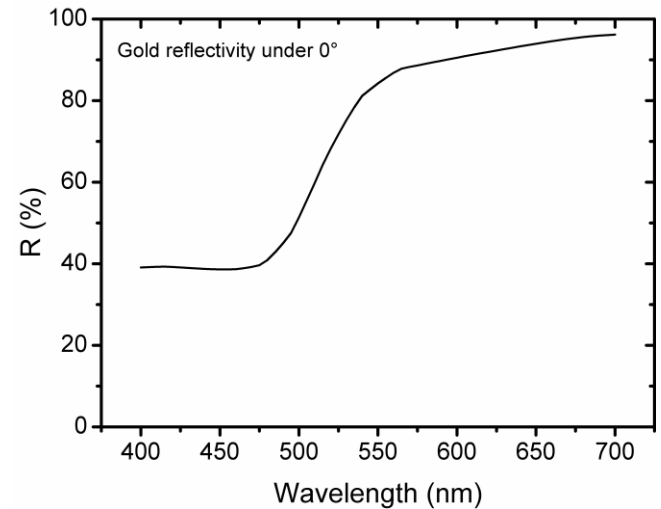
Colorimetry

Motivation:

we have (for given angle of rays)
dependence of reflectance (R)
or transmittance (T) on λ
- either experimental
- or predicted using n and k

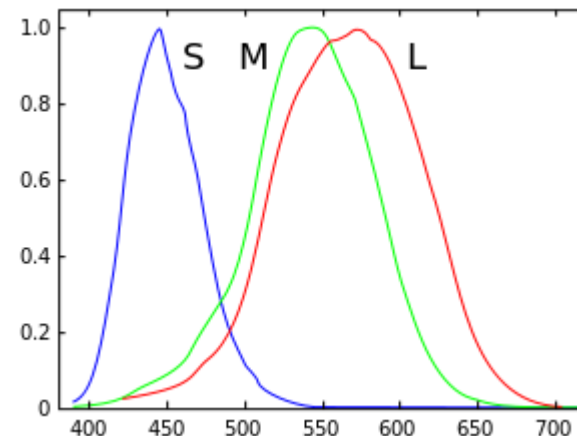
We want to convert this information
to visual impression (several
numbers like RGB, CMYK, ...)

Organization behind the norms below:
Commission internationale de l'éclairage
(abbreviation **CIE** used below)



Color space (CIE 1931)

In eye there are 3 kinds of corresponding cone cells (Short, Middle, Long wavelength; see figure for spectral sensitivity). The color space is therefore **three-dimensional**.



It is possible to separate

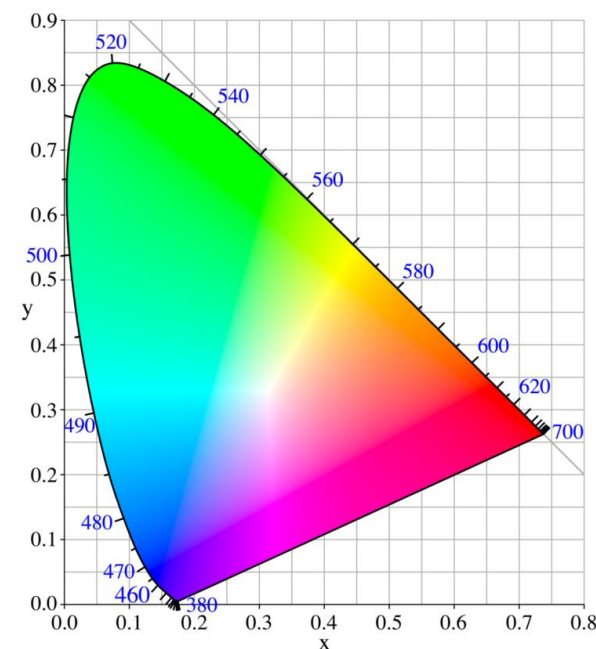
- **chromaticity:**

two dimensions in the figure ('x' and 'y' is defined below)

- **brightness:**

the third (vertical) dimension

E.g. white, grey and black have same chromaticity, but different brightness



Color space (CIE 1931)

Figure shows (for max. brightness) all visible colors

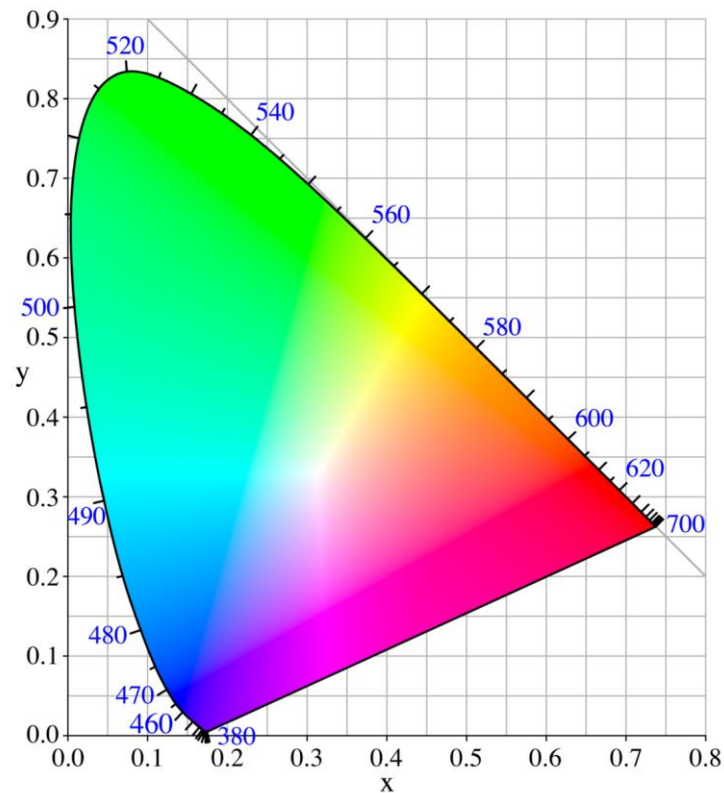
Colors at the bow are spectral (wavelength 380 - 700 nm)

Colors on horseshoe base (line of purples) are non-spectral

Colors on the edge (bow + base) are saturated

Mixtures of two colors are along lines connecting them

Complementary colors are on opposite ends of lines going through white



Color space (CIE 1931)

Brightness-independent: **chromaticity**, also **chromacity**

Brightness-related:

brightness: rather subjective impression than physical quantity

luminance, also **luminosity** (here - not always - synonyms):
quantifies brightness, Y in the norm XYZ below

relative luminance: Y/Y_n where Y_n is the maximum (of given display, etc.), i.e. from 0 to 1 (the corresponding factor can be found already in formulas for X,Y,Z)

lightness: another way how to quantify brightness, L & L^*
in the norms Lab & $L^*a^*b^*$ below, from 0 to 100

Dominant component of the color:

hue: which saturated color (i.e. point on the edge of the figure above - end of line starting in white) corresponds to it

Color space (CIE 1931)



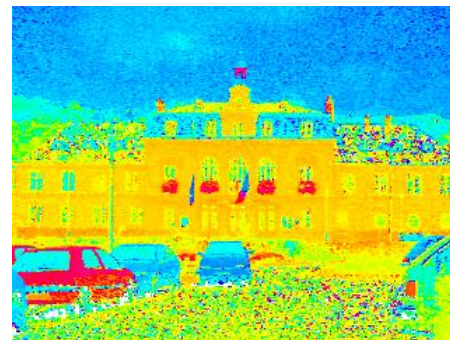
starting figure:
3D color space



chromacity for
max. brightness: 2D



saturated colors
after subtracting
white/grey: 2D



hue, i.e. saturated
with maximum
brightness: 1D



brightness: 1D



response of 'S'
cells (blue car
is brighter)



response of 'M'
cells (yellow wall
is brighter)



response of 'L'
cells (car on the right
has brighter light)

Color space

(mathematical descriptions)

There are 3 kinds of cone cells in eye $\Rightarrow$ color space is 3D.

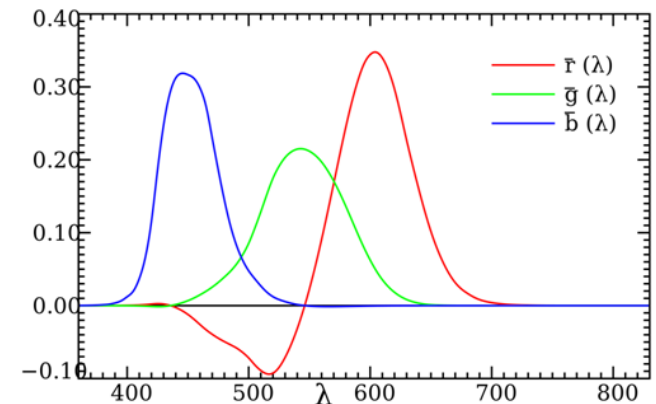
Mathematician: so any color can be obtained as a linear combination of any 3 "linearly independent" base colors.

For CIE RGB: red 700 nm, green 546.1 nm, blue 435.8 nm

Physicist: but there are no such base colors leading to non-negative coefficients in all these linear combinations

For spectral colors λ , coefficients in the linear combinations are called **color matching functions** and denoted $\bar{r}$, $\bar{g}$, $\bar{b}$ (for CIE RGB see figure).

For non-spectral colors $I(\lambda)$, coefficients are labelled by the same letters R, G, B as colors themselves. By integration $R = \int I(\lambda) \bar{r}(\lambda) d\lambda$ (similarly for G and B).



Color space

(mathematical descriptions)

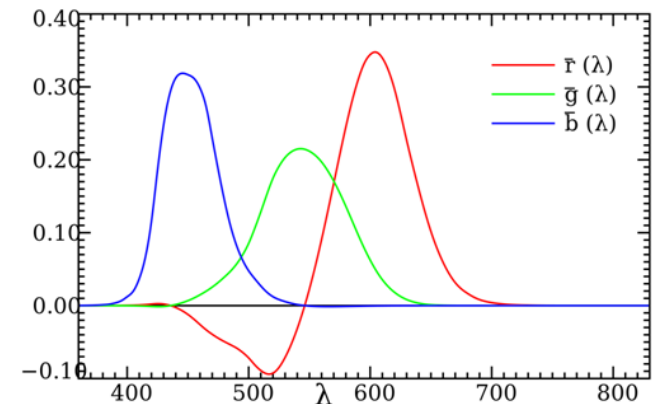
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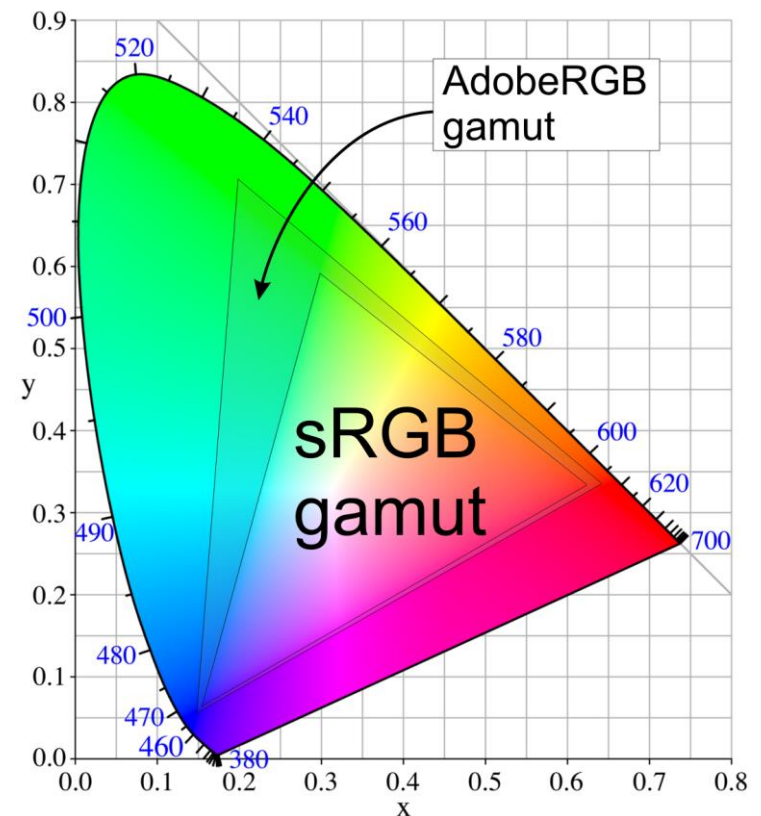
Because we want/have to avoid negative coefficients in experimental color mixing, we can in fact utilize only the triangle defined by the chosen base colors (**gamut**)



Color space

(mathematical descriptions)

Because we want/have to avoid negative coefficients in experimental color mixing, we can in fact utilize only the triangle defined by the chosen base colors (**gamut**)



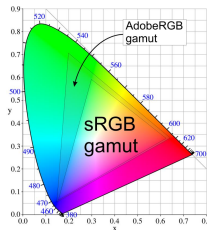
Color space

(mathematical descriptions)

So which color spaces (triads of coordinate axes) do exist?

1) device-dependent (best known, but not scientific) - depends on device producer, capture only part of colors (limited gamut)

- **RGB** (color model) with many versions (color spaces): sRGB (standard: Microsoft, HP), Adobe RGB, Apple RGB, ProPhoto RGB, etc. Used in devices working with **emitted light** (computer screens).
- **CMY** (and CMYK - the fourth black color is not necessary from physics point of view, but in real devices it is simpler and cheaper to add it than to produce it by mixing C+M+Y). Used in devices working with **reflected light** (printers) - reason for complementary colors.
- and others



Color space

(mathematical descriptions)

2) device-independent, capture all colors

(at the cost of the fact that the mixed colors are not real)

- **CIE 1931 XYZ** (starting point for all later):
instead of real (even monochromatic) colors and
(sometimes negative) coefficients R , G , B we have
fictitious "colors" and (non-negative) coefficients X , Y , Z .

Color space

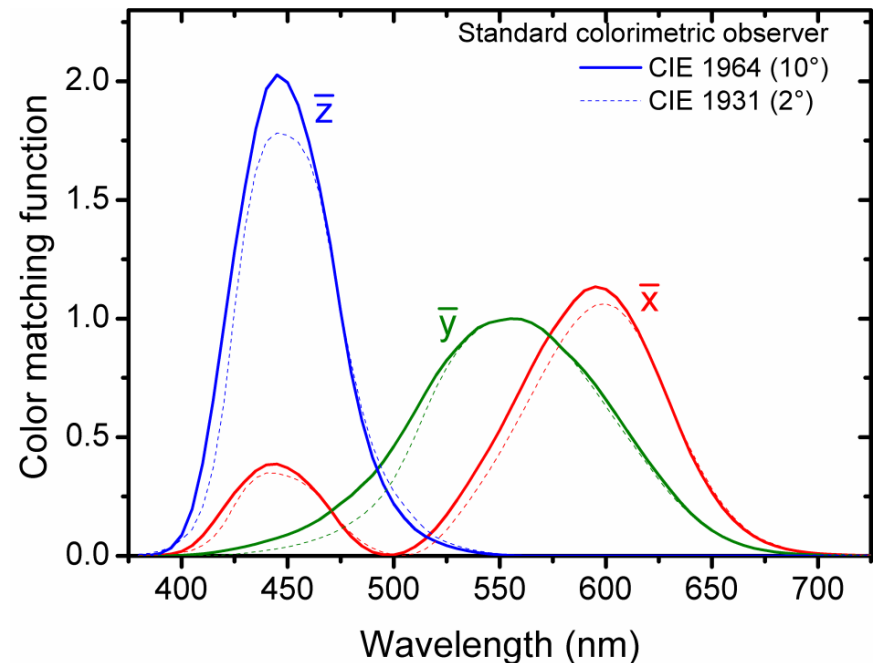
(mathematical descriptions)

2) device-independent, capture all colors

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- **CIE 1931 XYZ** (starting point for all later):
for light $I(\lambda)$ it holds $X = \int I(\lambda) \bar{x}(\lambda) d\lambda$ (similarly for Y and Z)
where $\bar{x}$, $\bar{y}$, $\bar{z}$ are newly introduced, contrary to $\bar{r}$, $\bar{g}$, $\bar{b}$ **non-negative, color matching functions.**

They are arbitrary anyway, so they were chosen in that way that **Y is brightness** ($\bar{y}$ is sensitivity of eye).



Color space

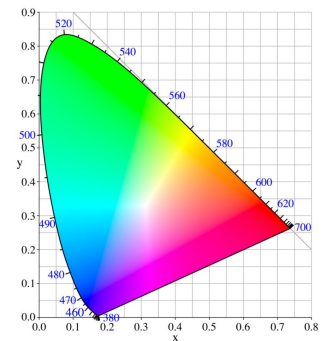
(mathematical descriptions)

2) device-independent, capture all colors

(at the cost of the fact that the mixed colors are not real)

- **CIE 1931 XYZ** (starting point for all later):
for light $I(\lambda)$ it holds $X = \int I(\lambda) \bar{x}(\lambda) d\lambda$ (similarly for Y and Z)
- **CIE xyY**: normalization $x = X / (X+Y+Z)$, $y = Y / (X+Y+Z)$
(coordinates 'x' and 'y' from the figure above), brightness
can be expressed using the original Y

The triangle [1,0], [0,1] and [0,0] indeed includes all visible colors, at the cost of the aforementioned fact that its corners do not correspond to real visible colors..



Color space

(mathematical descriptions)

2) device-independent, capture all colors

(at the cost of the fact that the mixed colors are not real)

- **CIE 1931 XYZ** (starting point for all later):
for light $I(\lambda)$ it holds $X = \int I(\lambda) \bar{x}(\lambda) d\lambda$ (similarly for Y and Z)
- **CIE xyY**: normalization $x = X / (X+Y+Z)$, $y = Y / (X+Y+Z)$
(coordinates 'x' and 'y' from the figure above), brightness can be expressed using the original Y
- **Lab** (Hunter Lab) & **L*a*b*** (CIE Lab): transformation of XYZ
L (0 to 100) expresses brightness ($\Rightarrow$ function of Y)
'a' and 'b' (convention -128 to 128) express chromacity
advantage compared to XYZ is **perceptual uniformity**, i.e.
difference of $(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2 =$ difference for observer
- and others

Transformation RGB → XYZ

$$\begin{bmatrix} R \\ G \\ B \end{bmatrix} = \begin{bmatrix} 0.418,47 & -0.158,66 & -0.082,835 \\ -0.091,169 & 0.252,43 & 0.015,708 \\ 0.000,920,90 & -0.002,549,8 & 0.178,60 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \frac{1}{0.176,97} \begin{bmatrix} 0.490,00 & 0.310,00 & 0.200,00 \\ 0.176,97 & 0.812,40 & 0.010,630 \\ 0.000,0 & 0.010,000 & 0.990,00 \end{bmatrix} \begin{bmatrix} R \\ G \\ B \end{bmatrix}$$

Example for CIE RGB, other versions of RGB lead to other matrices. Scaling factor can vary (1, 1/255, etc.), provided for R,G,B 0 to 1 and the white point $1/0.17697 = 5.6508 \text{ cd/m}^2$

Contribution of R,G,B to brightness: $0.17697 : 0.81240 : 0.01063$
(least square fit of $\bar{r}$, $\bar{g}$, $\bar{b}$ to spectral sensitivity $\bar{y}$)

Transformation $XYZ \rightarrow L^*a^*b^*$

$$f(X/X_n) = (X/X_n) / 3(6/29)^2 + 4/29 \quad \text{for } X/X_n = 0 \text{ to } (6/29)^3$$
$$(X/X_n)^{1/3} \quad \text{for } X/X_n = (6/29)^3 \text{ to } 1$$

similarly for $f(Y/Y_n)$, $f(Z/Z_n)$

$$L^* = 116f(Y/Y_n) - 16$$

strongly nonlinear: for middle grey - lightness 50 (%) - we need only relative luminance of 18.4 %

$$a^* = 500 [f(X/X_n) - f(Y/Y_n)]$$

$$b^* = 200 [f(Y/Y_n) - f(Z/Z_n)]$$

factors 500 and 200 well guarantee the aforementioned perceptual uniformity

Colorimetry

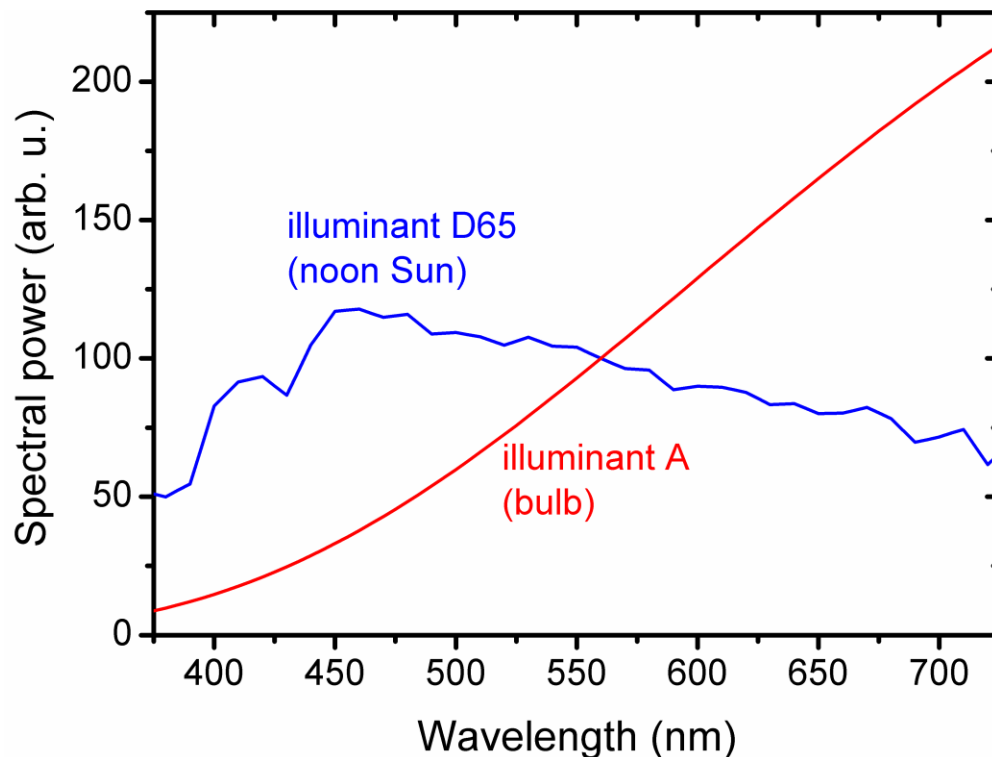
role of illuminant (CIE standard illuminants)

bulbs: illuminant A (incandescent 2856 K), B, C

Sun: illuminant D65 (noon Sun ~6500 K)

illuminant D50 (horizon Sun ~5000 K), D55, D75

others: illuminant F1-F12 (fluorescent lamps)

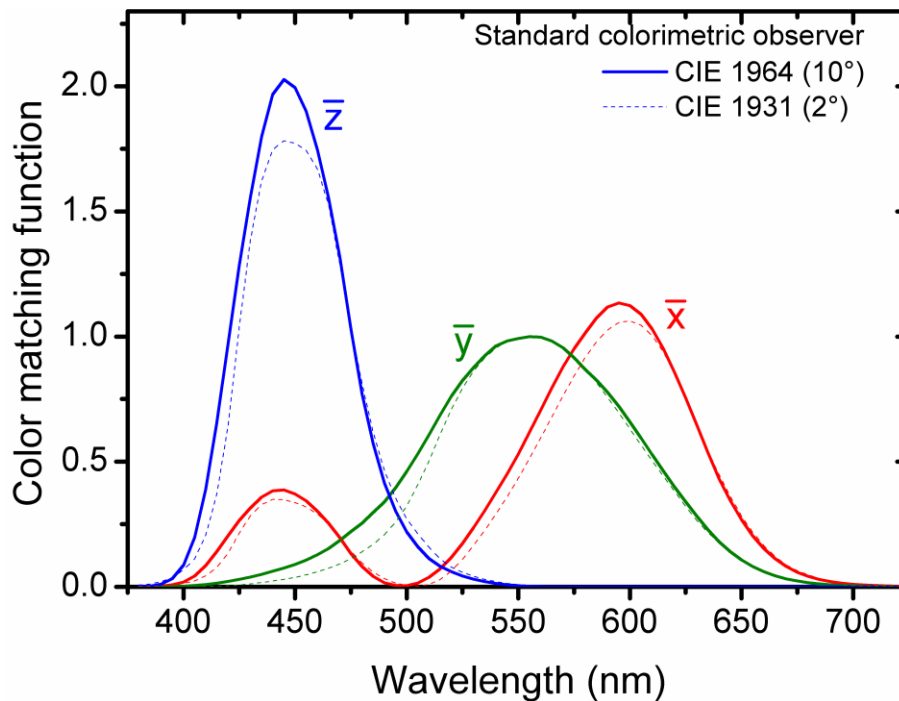


Colorimetry

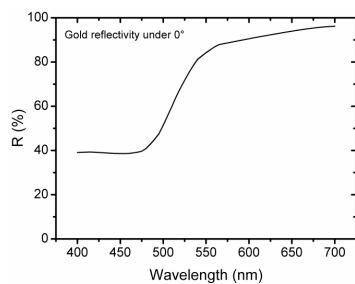
role of observer (CIE standard observers)

Density of cone cells is different in different points of retina (highest: yellow spot × lowest: blind spot)

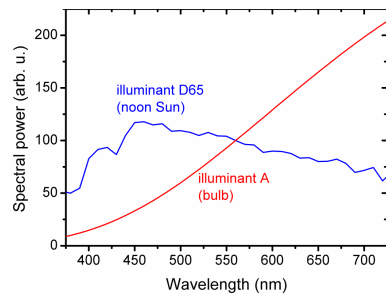
Fitted color matching functions therefore depend on the observation angle (which the test persons were asked to focus on): standards for 2° (older, probably still prevailing) and 10°.



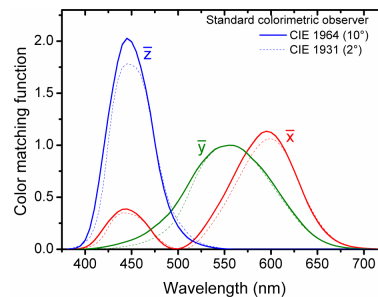
Colorimetry - summary



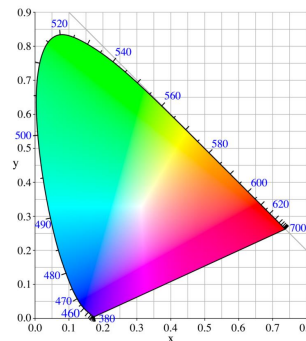
×



×



=



R or T

×

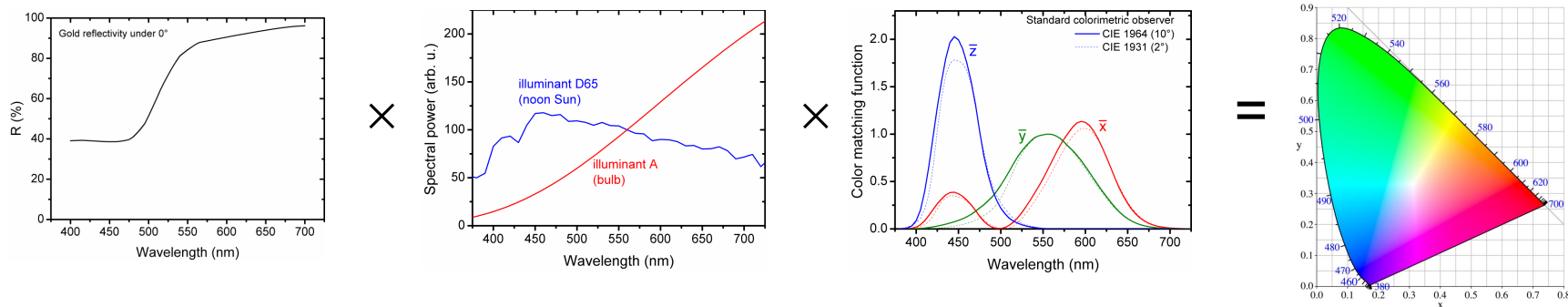
illuminant

×

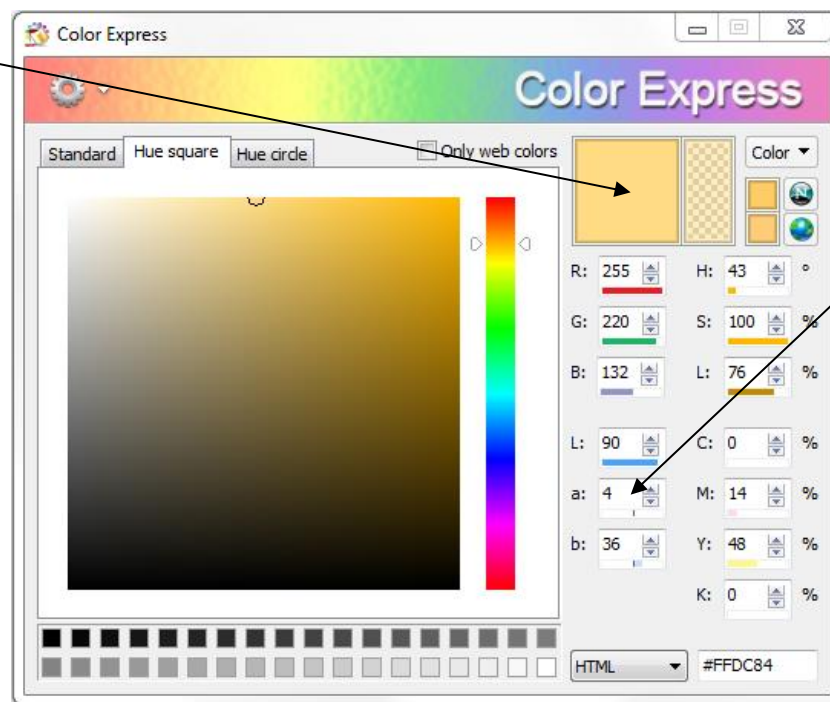
observer

= XYZ, Lab, ...

Colorimetry - example 1

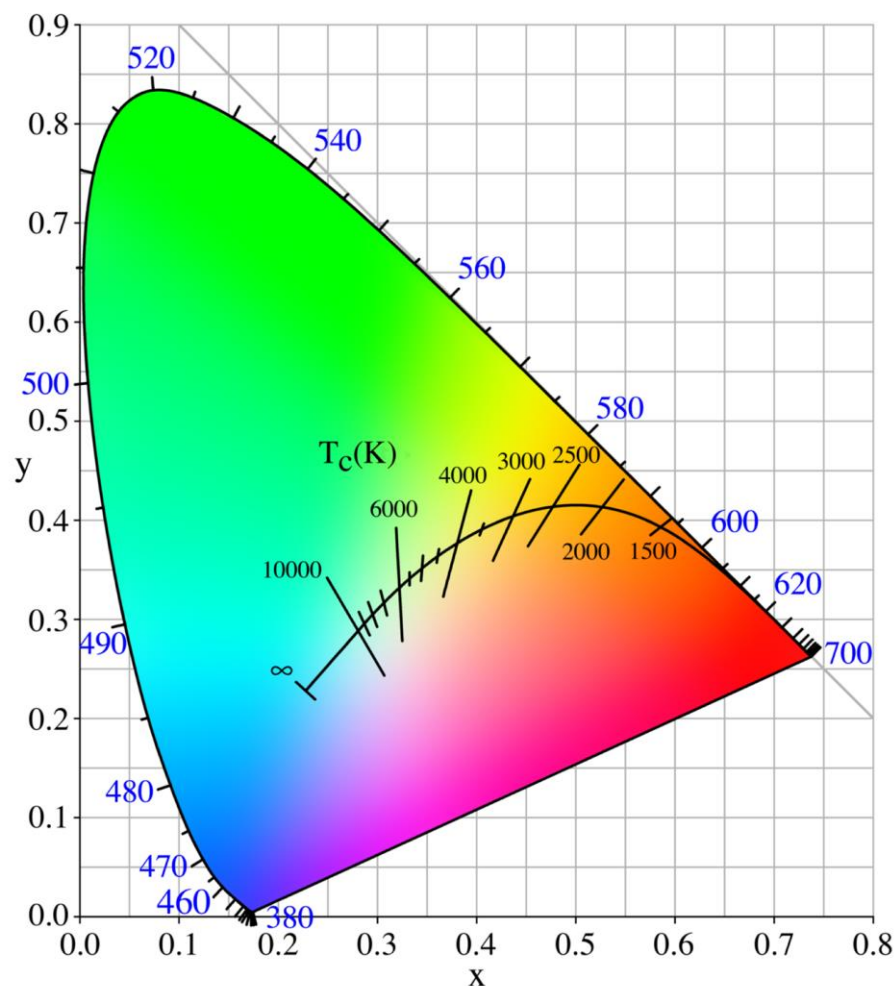
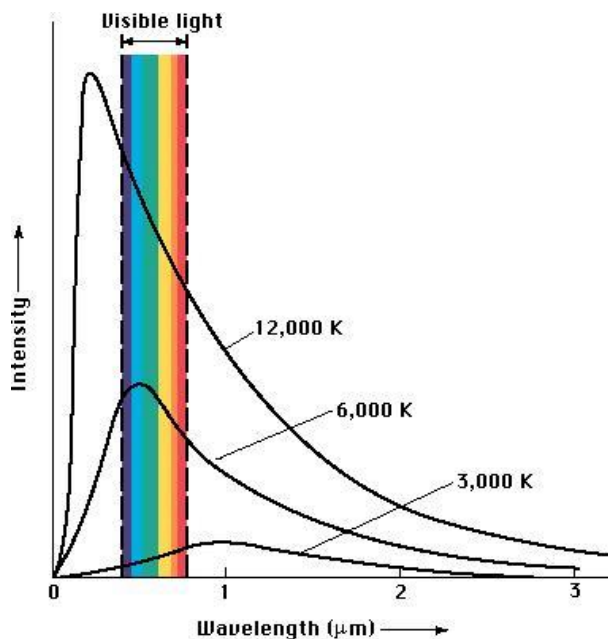


R of gold $\times$ illuminant D65 $\times$ 1931 CIE observer = L*a*b* 90 4 36



Colorimetry - example 2

Colors obtained by substituting $I(\lambda)$ in the equations above by spectrum of black body of various temperatures
(**Planckian Locus**)

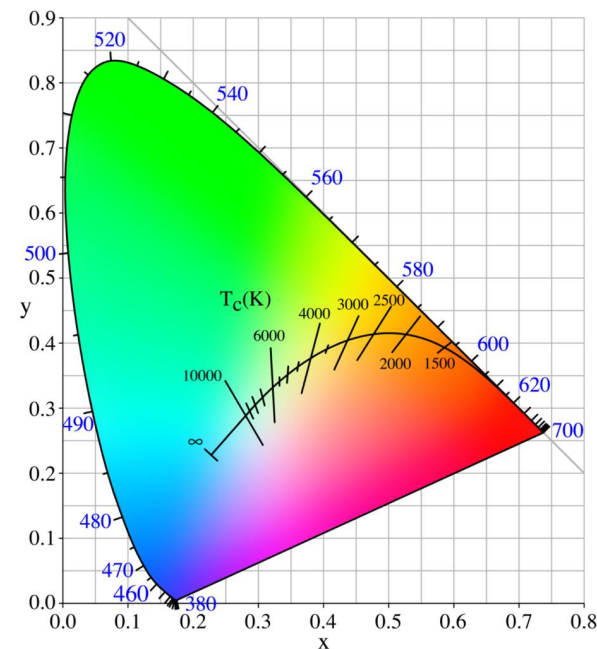


Colorimetry - example 2

Colors obtained by substituting $I(\lambda)$ in the equations above by spectrum of black body of various temperatures

Green color also corresponds to some T ($\lambda.T = 0.002897$ mK $\Rightarrow$ e.g. 5267 K for the spectral maximum at 550 nm). So why the curve goes around the green area? Why, in agreement with the curve, do exist red/yellow/blue stars but no green stars?

Color	Example	Surface Temp Celsius
	Spica (Virgo)	28,000 - 11,000
	Vega (Lyra)	11,000 - 7,500
	Sun	6,000 - 5,000
	Arcturus (Bootes)	5,000 - 3,600
	Antares (Scorpius)	3,600 - 2,000

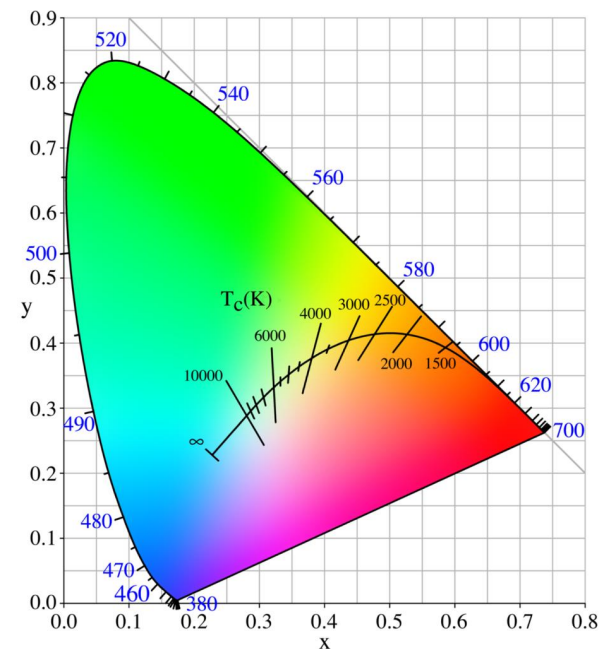


Colorimetry - example 2

Colors obtained by substituting $I(\lambda)$ in the equations above by spectrum of black body of various temperatures

Green color also corresponds to some T ($\lambda.T = 0.002897$ mK $\Rightarrow$ e.g. 5267 K for the spectral maximum at 550 nm). So why the curve goes around the green area? Why, in agreement with the curve, do exist red/yellow/blue stars but no green stars?

Because green is in the middle of visible, i.e. many green photons also mean many photons of other wavelengths which collectively lead to whiter color



There is not only trichromatism

The fact that there are 3 kinds of cells in eye (**trichromacy**) and that the human color space is therefore 3D is not automatic, it has nothing to do with the 3-dimensionality of the real space

Monochromatic: water and night mammals (which cannot utilize color vision) - whale, dolphin, raccoon, some night monkeys

Dichromatic: most mammals - dog, cat, horse, many New World monkeys

Trichromatic: human (previous slides), Old World monkeys including primates, marsupials, many fish

Tetrachromatic: many birds and insects, some ornamental fish, polar reindeer (Sun low over the horizon $\Rightarrow$ increasing benefit from the sensitivity on UV light which refracts more)

Pentachromatic: exceptional birds (pigeon) and insects (some butterflies)

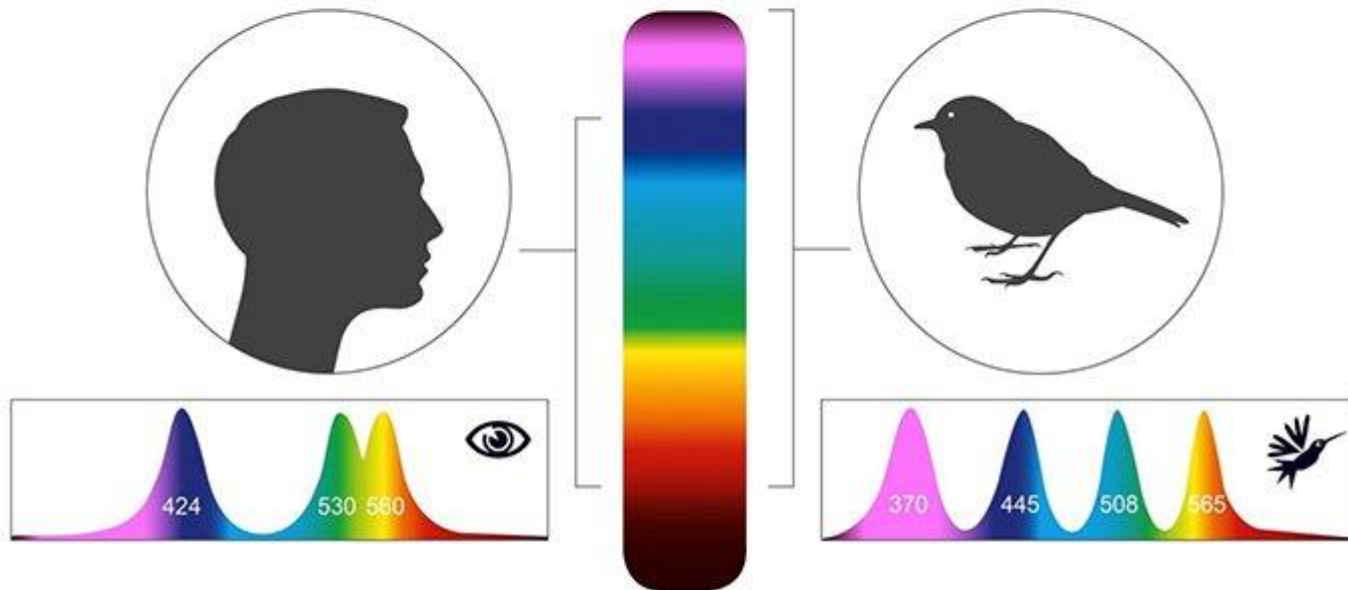
European Starling



Human Vision



Bird Vision



There is not only trichromatism

Human genetic deviation can not only be the source of mono- or dichromatism ($\Rightarrow$ color blindness), but also of tetrachromatism

SCIENCE

THIS WOMAN SEES 100 TIMES MORE COLORS THAN THE AVERAGE PERSON

A UNIQUE GENETIC MUTATION AND A WELL-WIRED BRAIN MEAN THAT CONCETTA ANTICO IS LIKE NO OTHER ARTIST ON EARTH.

By Alexandra Ossola October 13, 2014



ConcettaAntico.com

To tetrachromatic artist Concetta Antico, the world is, "like a mosaic of color."

When Concetta Antico looks at a leaf, she sees much more than just green. "Around the edge, I'll see orange or red or purple in the shadow; you might see dark green but I'll see violet, turquoise, blue," she said. "It's like a mosaic of color."

Antico doesn't just perceive these colors because she's an artist who paints in the impressionist style. She's also a **tetrachromat**, which means that she has more receptors in her eyes to absorb color. The difference lies in Antico's cones, structures in the eyes that are calibrated to absorb particular wavelengths of light and transmit them to the brain. The average person has three cones, which enables him to see about one million colors. But Antico has four cones, so her eyes are capable of picking up dimensions and nuances of color—an estimated 100 million of them—that the average person cannot. "It's shocking to me how little color people are seeing," she said.

"You might see dark green but I'll see violet, turquoise, blue. It's like a mosaic of color."

There is not only trichromatism

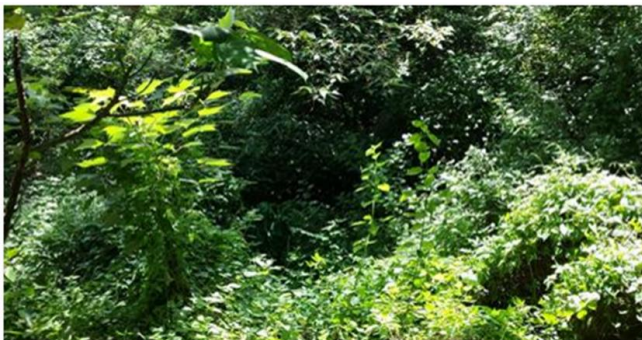
Even dichromatism can be an advantage: greater sensitivity to contrast $\Rightarrow$ revealing a camouflage against trichrom. observers

Color-Blind Observers for National Defense

June 2, 2010 Professions

Here is an interesting little story about colorblind people working for the army. This story was published in the Time magazine on the 5th of August in 1940—so quite a while ago.

One man in 20 is color-blind in greater or lesser degree and for that reason ineligible for training as an Army Air Corps pilot or observer. Last week the Air Corps's School of Flight Medicine reported an interesting incident. In a plane at Fort Sill, Okla. early this summer, an Air Corps observer was able to spot only ten of 40 camouflaged artillery fieldpieces on the ground. An observer of the Field Artillery in a plane spotted all 40 and accurately plotted their positions on his map. The explanation: the artilleryman, selected under less rigorous examination than the Air Corps man, was colorblind. Camouflage, designed to deceive the normal eye, fooled him not a whit.



Snipers are no match for the colour blind.

One of the most underrated advantages of being colour blind is the ability to much more easily spot contrasts. Popularly throughout time colour blind individuals have been trained as snipers in the...

CUTTHECOLOUR.WORDPRESS.COM



Home » March » In Combat, Stick With the Color-Blind

FROM THE MARCH 2006 ISSUE

In Combat, Stick With the Color-Blind

By Elise Kleeman | Friday, March 03, 2006

RELATED TAGS: SENSES, SEX & GENDER



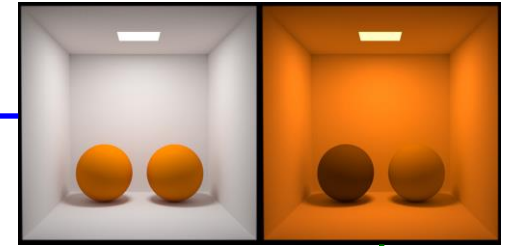
Red-green color-blind people may miss out on the subtle tones of a forest or a bouquet of roses, but they do get compensation. Biologists at Cambridge University and the University of Newcastle upon Tyne in England find that color-blind men are extraordinary connoisseurs of khaki.

Metamerism

Each color (numbers $L^*a^*b^*$, RGB, etc.) corresponds to infinitely many radiation spectra

Thus, objects can have (for given illuminant) the same color, even though their spectral power distributions differ

Difference is revealed by another illuminant



Utilization of metamerism (in praxis often in a broad sense, including IR spectrum): one kind of security elements on banknotes, documents, etc.



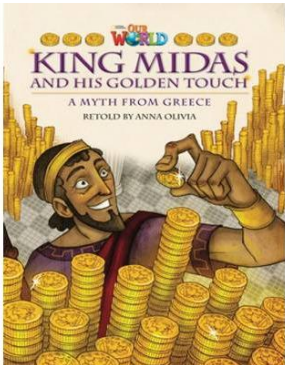
Metamerism

Each color (numbers $L^*a^*b^*$, RGB, etc.) corresponds to infinitely many radiation spectra

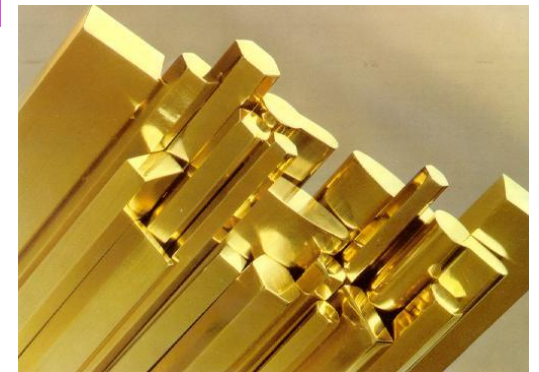
Thus, objects can have (for given illuminant) the same color, even though their spectral power distributions differ

Another example: **gold** × **brass** (Cu+Zn)

Note also the ancient legend about Phrygian king Midas ("everything he touched became gold"): while the countries around, like Greece, mined only Cu and Sn $\Rightarrow$ "orange" bronze, Phrygia mined also Zn $\Rightarrow$ "yellow" brass



gold



brass

13) Thermodynamics and s. solutions

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Frequent minimization of free enthalpy

Basic thermodynamics of gases

$$G = H - TS = U + PV - TS$$

$$dG = Vdp - SdT$$

G minimized at a given pressure and temperature

Frequent minimization of free enthalpy

Basic thermodynamics of gases

$$dG = Vdp - SdT$$

Thermodynamics of condensed matter

$$dG = Vdp$$

Negligible for condensed phase

Frequent minimization of free enthalpy

Basic thermodynamics of gases

$$dG = Vdp - SdT$$

Thermodynamics of condensed matter

$$dG = Vdp - SdT$$

Negligible for condensed phase

Configuration entropy 6-12 slides below

Frequent minimization of free enthalpy

Basic thermodynamics of gases

$$dG = Vdp - SdT$$

Thermodynamics of condensed matter

$$dG = Vdp - SdT + \mu dN$$

Negligible for condensed phase

Configuration entropy 6-12 slides below

Comparison for correct N 2-3 slides below

Frequent minimization of free enthalpy

Basic thermodynamics of gases

$$dG = Vdp - SdT$$

Thermodynamics of condensed matter

$$dG = Vdp - SdT + \mu dN - VMdB_0$$

Negligible for condensed phase

Configuration entropy 6-12 slides below

Comparison for correct N 2-3 slides below

Inserting of materials into external magnetic field B_0 (see magnetism in chapter 14). It can be found also $+VB_0dM$, which holds when the minimization of G does not take place at fixed B_0 , and the total energy includes also energy of EM field.

Frequent minimization of free enthalpy

Basic thermodynamics of gases

$$dG = Vdp - SdT$$

Thermodynamics of condensed matter

$$dG = Vdp - SdT + \mu dN - VMdB_0 - VPdE_0$$

Negligible for condensed phase

Configuration entropy 6-12 slides below

Comparison for correct N 2-3 slides below

Inserting of materials into external magnetic field B_0 (see magnetism in chapter 14). It can be found also $+VB_0dM$, which holds when the minimization of G does not take place at fixed B_0 , and the total energy includes also energy of EM field.

Inserting of material into external electric field E_0 (dtto)

Frequent minimization of free enthalpy

Basic thermodynamics of gases

$$dG = Vdp - SdT$$

Thermodynamics of condensed matter

$$dG = Vdp - SdT + \mu dN - VMdB_0 - VPdE_0 + \gamma.dA$$

Negligible for condensed phase

Configuration entropy 6-12 slides below

Comparison for correct N 2-3 slides below

Inserting of materials into external magnetic field B_0 (see magnetism in chapter 14). It can be found also $+VB_0dM$, which holds when the minimization of G does not take place at fixed B_0 , and the total energy includes also energy of EM field.

Inserting of material into external electric field E_0 (dtto)

Surface energy (see hydrophobicity/hydrophilicity in chapter 11)

Formation energy - calculation

Often we want to compare not only energies or enthalpies or free enthalpies (the rules below hold for all these quantities) of homogeneous phases of the same composition, but also energy of solid solution with sum of energies of its components

Examples:

$$E_{\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}} - 1/2 \times E_{\text{TiN}} - 1/2 \times E_{\text{AlN}}$$

$$E_{\text{Ti}_{0.5}\text{Si}_{0.5}\text{N}} - 1/2 \times E_{\text{TiN}} - 1/6 \times E_{\text{Si}_3\text{N}_4} + 1/12 \times E_{\text{N}_2}$$

$$E_{\text{TiB}_{0.5}\text{N}_{0.5}} - 1/2 \times E_{\text{TiN}} - 1/4 \times E_{\text{TiB}_2} - 1/4 \times E_{\text{Ti}}$$

In each case, we must compare energies of such "competing" configurations which have **the same elemental composition** (e.g. in the second eq. it was necessary not to forget $1/12 \times E_{\text{N}_2}$)

Formation energy - utilization

Two simple - but surprisingly often ignored - rules

1) Compare energies per the same number of atoms

Example: who will more oxidize in O_2 , Zr or Ta

- comparing E_f per one O atom is **OK**
- comparing E_f per one mole of O atoms is **OK**
- comparing E_f per one mole of structural units ZrO_2 and Ta_2O_5 is most convenient (this is how E_f is often provided in experimental databases), but **wrong** - ratio of these E_f values differs $2.5\times$ from the above ratios

Physical conclusion should not depend on human convention. Whether the structural unit is ZrO_2 or e.g. Zr_2O_4 (with doubled E_f) is a human convention.

Formation energy - utilization

Two simple - but surprisingly often ignored - rules

2) Compare energies per the same number of atoms
present in both competing reactions

Example 1 : who will more oxidize in O_2 , Zr or Ta
(see also above)

⇒ compare E_f per one atom / mole O

Example 2 : will Zr in O_2+N_2 more oxidize (to ZrO_2) or more
nitride (to ZrN)

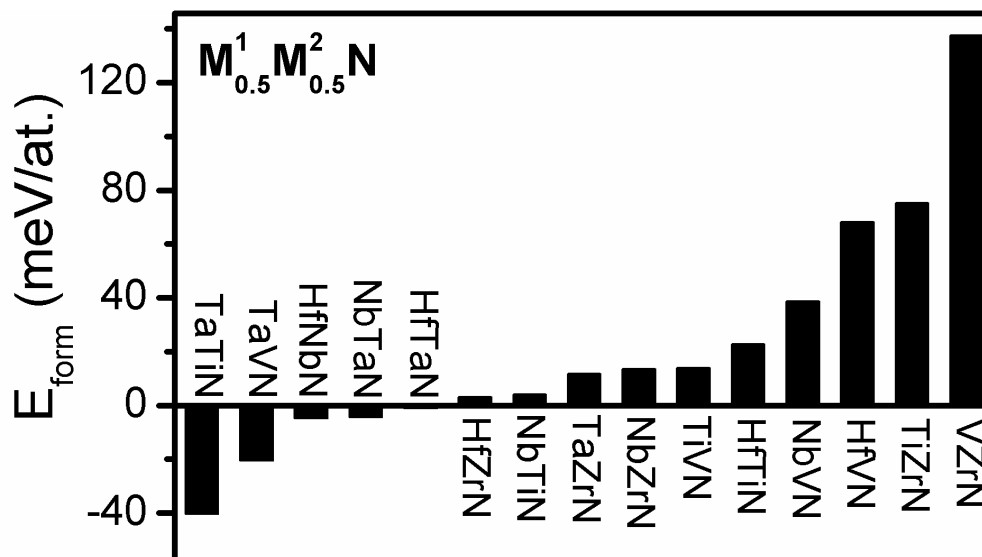
⇒ compare E_f per one atom / mole Zr

Ratio of E_f values per one gas atom (blind following of
Example 1) would again differ from the correct one (2×).

Formation energy - ab initio calc.

Formation energy can be effectively predicted (methodology indicated in chapter 8) for a wide range of materials

Example:



[V. Petrman and J. Houska,
J. Mater. Sci. 48, 7642 (2013)]

out of materials $M^1_{0.5}M^2_{0.5}N$ ($M^{1,2}$ z IVB-VB),

- $Ta_{0.5}Ti_{0.5}N$ is most stable

- $V_{0.5}Zr_{0.5}N$ is least stable

Example of necessary exactness

Calculated energy Ti_4BCN_2 **-892.3196 eV/at.**

Calculated energy TiN -930.5927 eV/at.

Calculated energy TiC -871.8798 eV/at.

Calculated energy TiB_2 -586.1533 eV/at.

Calculated energy Ti -1587.0457 eV/at.



$2 \times \text{TiN} + \text{TiC} + 0.5 \times \text{TiB}_2 + 0.5 \times \text{Ti}$ **-892.3604 eV/at.**

Difference in **fifth - sixth
significant digit** **0.0408 eV/at.**

Solid sol. Ti_4BCN_2 has higher energy than $\text{TiN} + \text{TiC} + \text{TiB}_2 + \text{Ti} \Rightarrow$
at zero temperature (non-zero T below) is metastable

Energy × enthalpy × free enthalpy

For solids at low temperatures, they are almost synonyms: ΔE (ΔU) $\approx \Delta H \approx \Delta G$ (or it is often silently assumed). Reminder for situations where we want to distinguish them (non-negligible difference between ΔH and $\Delta G = \Delta H - T\Delta S$ at high T):

Change of enthalpy ΔH says how much is the reaction (decomposition of solid solution, etc.) **exo / endothermic**

Change of free enthalpy (= Gibbs energy) ΔG says how much is the reaction **spontaneous** (which is if the main interest, but in many cases we know only the experimental value of ΔH)

Ab-initio calculations often for $T=0 \Rightarrow$ again $\Delta H = \Delta G$

What does the enthalpy depend on

(if we do not want to take it as purely empirical)

For simplicity equimolar binary material $A_{0.5}B_{0.5}$

A.R. Miedema (1970's)

$$\Delta H \sim -P(\Delta\Phi^*)^2 + Q(\Delta n_{WS}^{1/3})^2 \text{ where}$$

- Φ^* is *Miedema electronegativity*, strongly correlating with work function (even more than with Pauling electroneg.)

Note the minus sign: the elements want to mix if they are different in this way, if they exhibit a charge transfer (albeit less significant than e.g. during oxidation)

- n_{WS} is electron density at the edge of Wigner-Seitz cell
- $Q/P = 9.4$

Journal of the Less-Common Metals, 32 (1973) 117-136
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

117

THE ELECTRONEGATIVITY PARAMETER FOR TRANSITION METALS:
HEAT OF FORMATION AND CHARGE TRANSFER IN ALLOYS

A. R. MIEDEMA
Philips Research Laboratories, Eindhoven (The Netherlands)
(Received January 8, 1973)

What does the enthalpy depend on

(if we do not want to take it as purely empirical)

For simplicity equimolar binary material $A_{0.5}B_{0.5}$

A.R. Miedema (1970's)

$$\Delta H \sim -P(\Delta\Phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2$$

More recent and ambitious formulae:

e.g. considering also different atomic sizes

Today online interfaces (e.g. micid.top/modelbase/miedema)
and downloadable codes (např. micid.top/software/miedema)

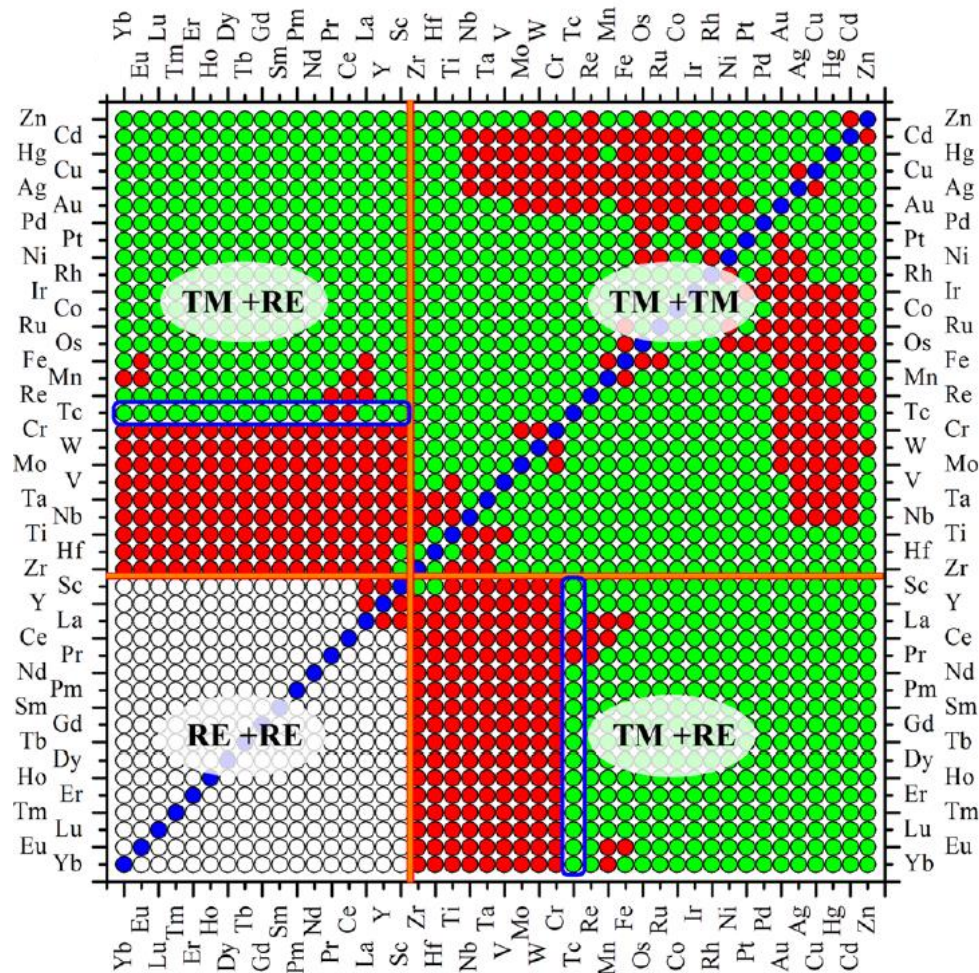
Fast estimation (but not explanation) of ΔH also via
calculation using universal force fields (building on chapter 4)

What does the enthalpy depend on

(if we do not want to take it as purely empirical)

Example of summary of
miscible and immiscible
metals

- important in itself
- 95% agreement with Miedema



[R.F. Zhang et al., Sci. Rep. 7, 9577 (2017)]

Configuration entropy

If we are interested in stability of solid solution at a specific temperature, it is desirable to distinguish

- ΔH (ab-initio results 2-3 slides above) and
- $\Delta G = \Delta H - T\Delta S$

Configurational entropy (Boltzmann formula)

- $\Delta S = k_B \ln W$ where W is number of configurations
- $\Delta S = -k_B \sum p_i \ln p_i$ where p_i are probabilities of configurations
if there are W states with equal probabilities
 $p_i = 1/W$, the second formula converts to the first one
- $\Delta S = -k_B \sum c_i \ln c_i$ where c_i are contents of components
- $\Delta S = -R \sum c_i \ln c_i$ if S is not per atom but per mole

Configuration entropy

Configurational entropy

- $\Delta S = k_B \ln W$ where W is number of configurations



photo from Wiener Zentralfriedhof
(log really means logarithm
with a base of 'e', not 10)

Configuration entropy

Configurational entropy

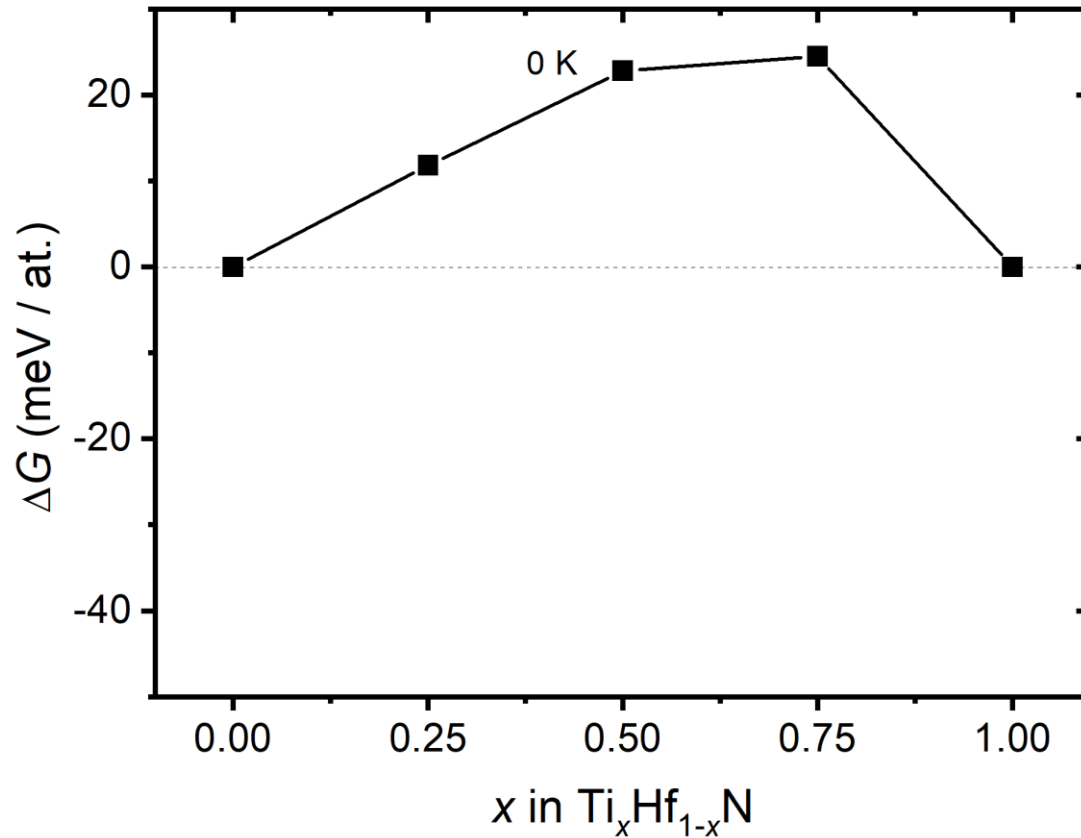
- $\Delta S = k_B \ln W$ where W is number of configurations



update after visiting
Vienna personally :-)

Configuration entropy

example for $\text{Ti}_x\text{Hf}_{1-x}\text{N}$

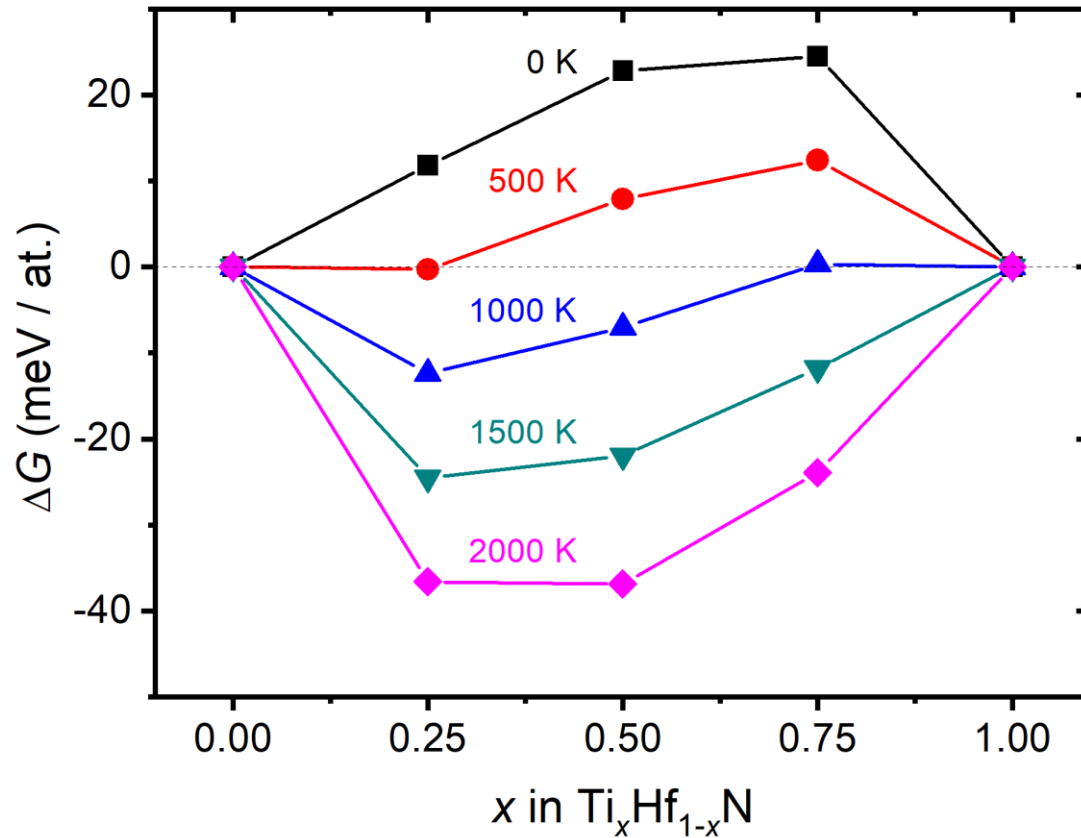


ΔH (ab-initio calculation $T = 0$ K)

at low temperatures, this solid solution is metastable

Configuration entropy

example for $\text{Ti}_x\text{Hf}_{1-x}\text{N}$

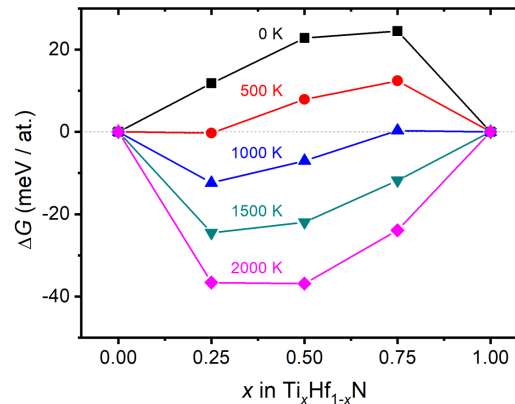


$$\Delta G = \Delta H + \frac{1}{2}k_B T \sum c_i \ln c_i = \Delta H + \frac{1}{2}k_B T [x \ln x + (1-x) \ln(1-x)]$$

thus, at high temperatures the solid solution can become stable

Configuration entropy

example for $\text{Ti}_x\text{Hf}_{1-x}\text{N}$



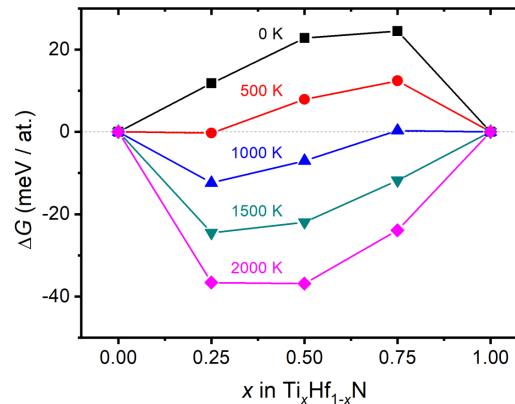
$$\Delta G = \Delta H + \frac{1}{2} k_B T \sum c_i \ln c_i = \Delta H + \frac{1}{2} k_B T [x \ln x + (1-x) \ln(1-x)]$$

Why the factor of $\frac{1}{2}$?

It was not in the original formula $\Delta S = -k_B \sum c_i \ln c_i$.

Configuration entropy

example for $\text{Ti}_x\text{Hf}_{1-x}\text{N}$



$$\Delta G = \Delta H + \frac{1}{2} k_B T \sum c_i \ln c_i = \Delta H + \frac{1}{2} k_B T [x \ln x + (1-x) \ln(1-x)]$$

Why the factor of $\frac{1}{2}$?

Because configurational entropy of the solid solution $\text{Ti}_x\text{Hf}_{1-x}\text{N}$ is related to only half of the material, specifically the metal sublattice $\text{Ti}_x\text{Hf}_{1-x}$. However, ΔG per atom (or mole) means per any atom (or per mole of structural units containing all atoms).

Binodal × spinodal decomposition

Consider a dependence on solid solution composition $G_{\text{form}}(x)$

1) G_{form} is convex in the whole range

⇒ solid solution is stable



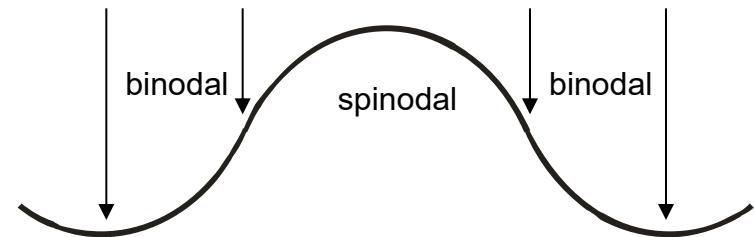
2) G_{form} is concave in the whole range

⇒ solid solution is metastable
(fast spinodal decomposition)



3) Complicated dependence ⇒

- in the concave part (between inflexion points) **spinodal dec.**
- in the rest of the part between local minima (more precisely: between the points of contact of ranges around local minima with their joint tangent) **slow binodal decomposition** (precipitation)



Binodal × spinodal decomposition

introduction of parameter Ω_{AB}

Gibbs energy for solid solution of mater. A and B at zero temp.:

$$G = (1-x_B)G_A + x_B G_B + \Omega_{AB}(1-x_B)x_B$$

At non-zero temperature (see the configurational entropy above)

$$G = (1-x_B)G_A + x_B G_B + \Omega_{AB}(1-x_B)x_B + k_B T[(1-x_B)\ln(1-x_B) + x_B \ln x_B]$$

(x_B refers to phase 'B', while k_B is Boltzmann constant)

What is, for simplicity, not considered in the equations

- possibility that only part of atoms take part in the mixing (discussed 2 slides above)
- dependence of G_A , G_B , Ω_{AB} on T
- energy of boundary between both phases (and its temperature dependence) in the case when solid solution does not form

Binodal × spinodal decomposition

for which comp. and T does spinodal decomp. take place?

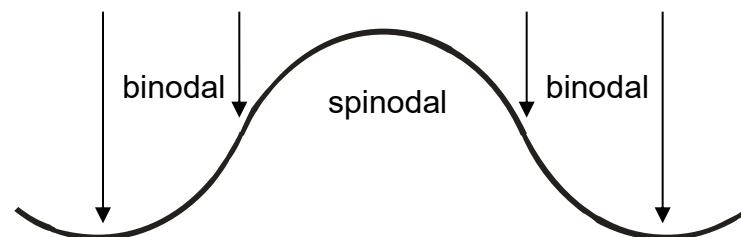
At non-zero temperature (neglected T -dep. of G_A , G_B , Ω_{AB}):

$$G = (1-x_B)G_A + x_B G_B + \Omega_{AB}(1-x_B)x_B + k_B T[(1-x_B)\ln(1-x_B) + x_B \ln x_B]$$

Ω_{AB} is constant positive:
at zero temperature



Ω_{AB} depends on composition:



When does spinodal decomp. take place (at least for some x_B)?

in general

$$: \partial^2 G / \partial x_B^2 < 0 \Rightarrow T < 2\Omega_{AB}(1-x_B)x_B/k_B$$

constant positive Ω_{AB}

$$: \partial^2 G / \partial x_B^2 < 0 \Rightarrow T < T_C = \Omega_{AB}/2k_B$$

Distribution of atoms in solid solution

(important for their theoretical description)

Option 1: various regular distributions
(some of them allow small size of
simulation cells, i.e. fast calculations)

Option 2: random distribution (requires large simulations cells),
in praxis, owing to the periodical boundaries, **pseudorandom**:
special quasirandom structure, **SQS**

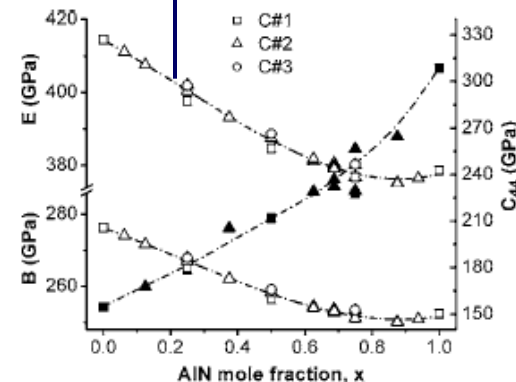
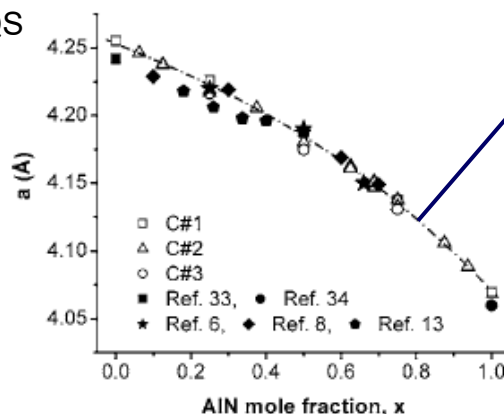
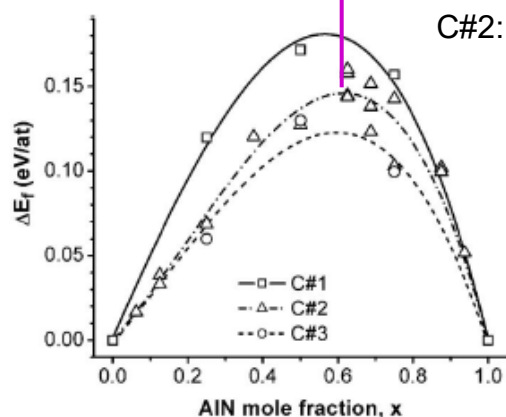
SQS leads to correlation functions (another viewpoint:
elemental composition of the set of nearest neighbours of
an atom, composition of the set of second nearest neighbours,
etc., as close to the truly random composition as possible

SQS leads to energy close to the middle of interval of possible
values, rather than to a minimum energy. That is, it leads to
kinetically rather than thermodynamically preferred structure.

Distribution of atoms in solid solution

SQS leads to energy close to the middle of interval of possible values, rather than to a minimum energy. That is, it leads to kinetically rather than thermodynamically preferred structure.

Trends of energies & lattice constants & mechanical properties (sometimes even the quantitative values) obtained using regular and pseudorandom distribution are often similar

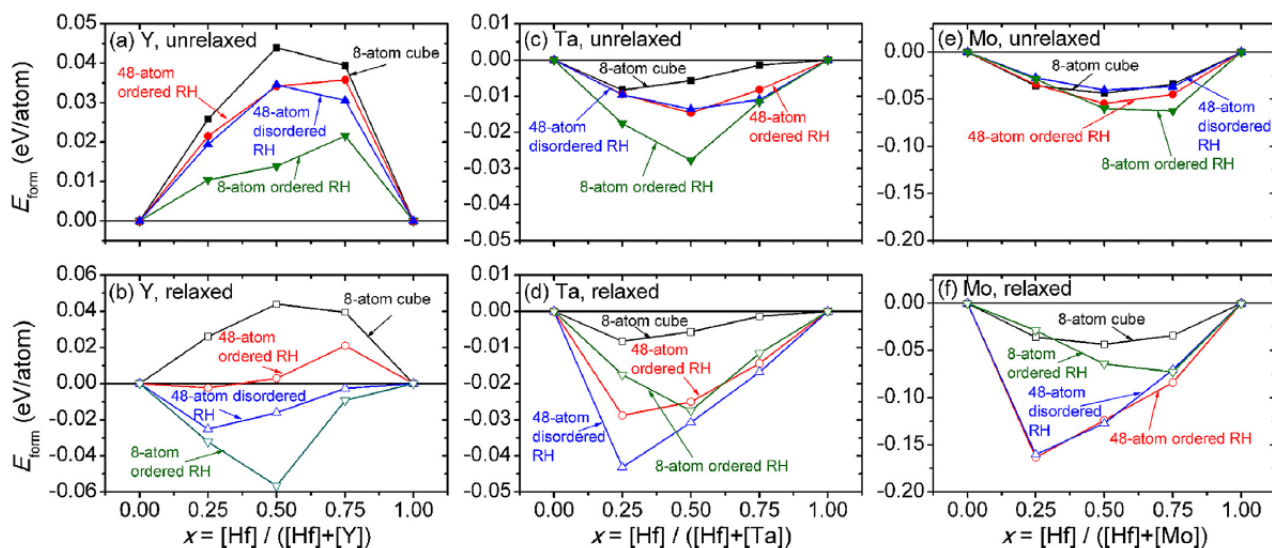


[P.H. Mayrhofer et al., J. Appl. Phys. 100, 094906 (2006)]

Distribution of atoms in solid solution

SQS leads to energy close to the middle of interval of possible values, rather than to a minimum energy. That is, it leads to kinetically rather than thermodynamically preferred structure.

The thermodynamically preferred distribution may be different (including different versions of the regular one) for different solid solutions (in the figure HfYN, HfTaN, HfMoN)

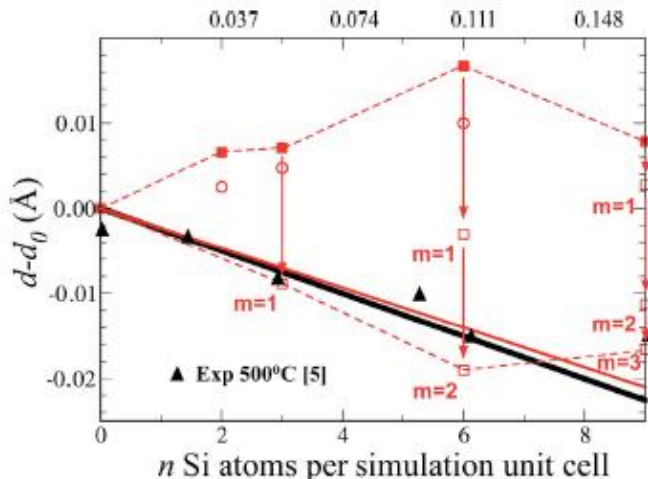


[M. Matas et al., Acta Mater. 206, 116628 (2021)]

Electroneutral substitution in (some) solid solutions

Electroneutral substitution (instead of 1:1 substitution):
preserved charge (given by number of val. el. without lonepairs)

Example 1: when replacing aluminium (3 el.) by silicon (4 el.) in
AlSiN, 4 atoms Al (12 el.) are replaced by 3 atoms Si (12 el.)
and one vacancy (figure: m next to $\square$ = number of vacancies)



APPLIED PHYSICS LETTERS 96, 071908 (2010)

Role of negatively charged defects in the lattice contraction of Al-Si-N

C. A. Pignedoli,¹ D. Passerone, H. J. Hug, A. Pélisson-Schecker, and J. Patscheider
Swiss Federal Laboratories for Materials Testing and Research, Empa, Dübendorf,
Zürich 8600, Switzerland

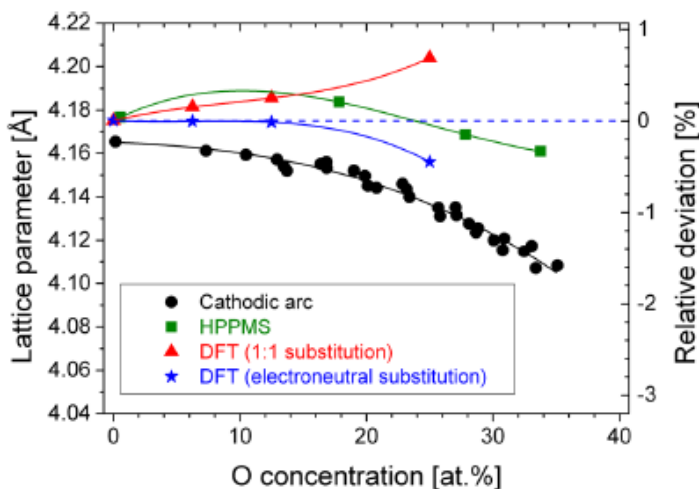
(Received 14 November 2009; accepted 22 January 2010; published online 17 February 2010)

Much better agreement with exp. than for 1:1 substitution (■)

Electroneutral substitution in (some) solid solutions

Electroneutral substitution (instead of 1:1 substitution):
preserved charge (given by number of val. el. without lonepairs)

Example 2: when replacing nitrogen (formal charge $-3e$) by oxygen ($-2e$) in TiAlON, VAlON, etc, electroneutrality is preserved by interstitial anions, or (more likely) cation vacancies



JOURNAL OF APPLIED PHYSICS 116, 093515 (2014)

Effect of oxygen incorporation on the structure and elasticity of Ti-Al-O-N coatings synthesized by cathodic arc and high power pulsed magnetron sputtering

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²Department of Physics and Astronomy, Uppsala University, Lägerhyddsvägen 1, S-75120 Uppsala, Sweden

³Oerlikon Balzers Coating AG, Iramali 18, LI-9496 Balzers, Principality of Liechtenstein

(Received 27 June 2014; accepted 25 August 2014; published online 5 September 2014)

Much better agreement with exp. than for 1:1 substitution

Phase transitions

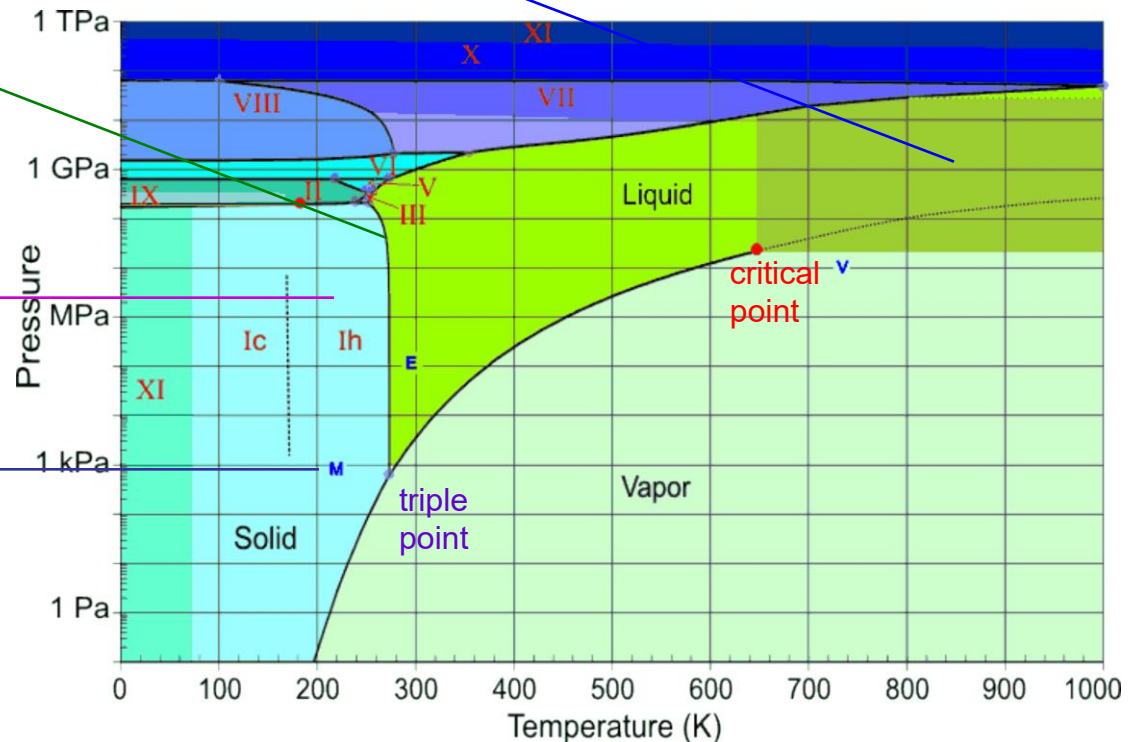
First a high-school figure (phase diagram of H_2O).

There is a supercritical fluid above the critical point (possibility to bypass critical point and change phase without phase transition)

Boundary solid-liquid is slightly tilted to the left due to the water anomaly (chapter 2)

Many phases of ice ("our" ice is I_h)

M, E, V =
Mars, Earth, Venus

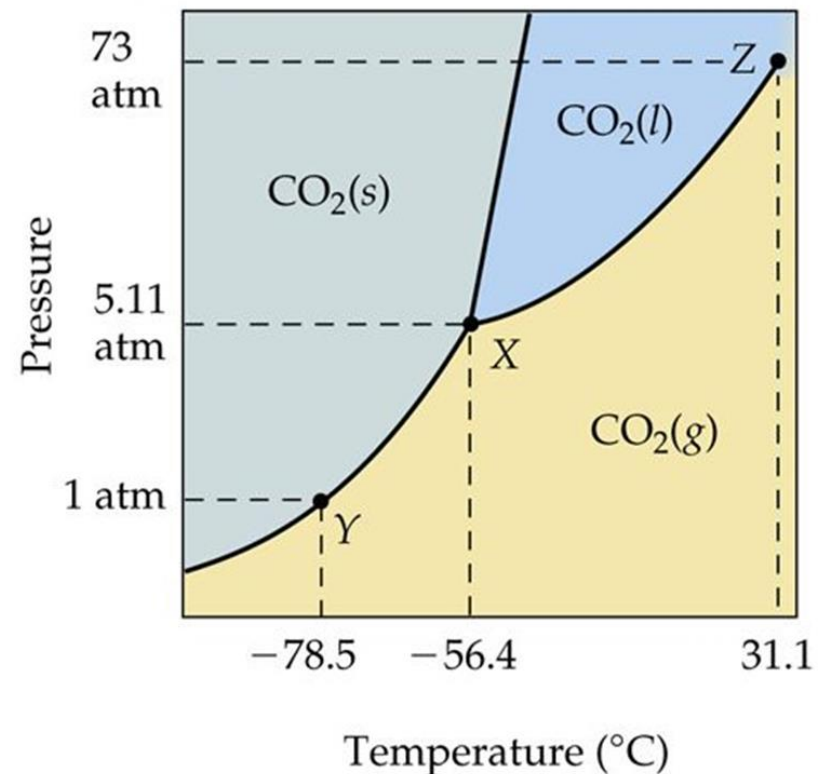
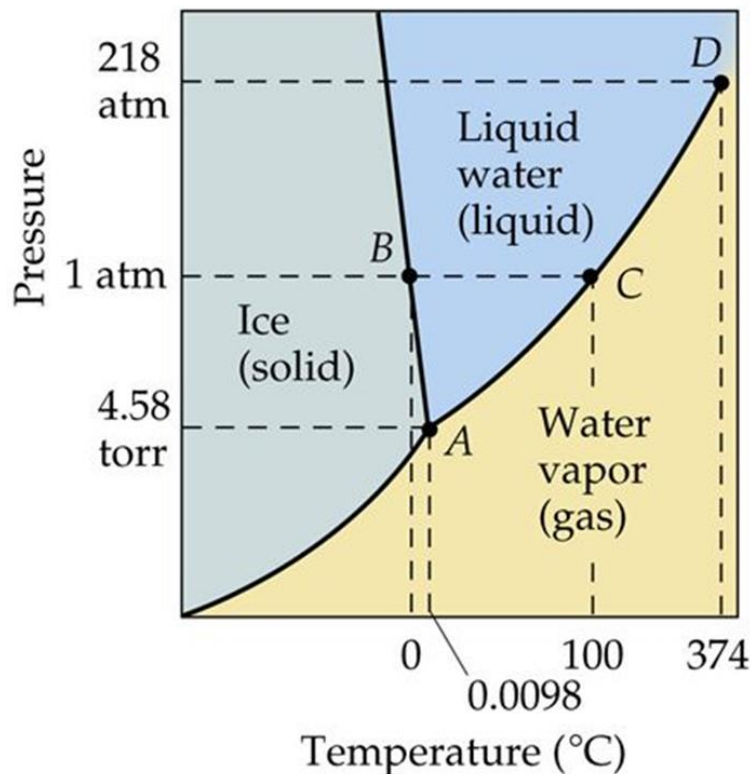


Phase transitions

Boundary solid-liquid is tilted to the left due to the water anomaly

It becomes more visible with non-linear axis

The same boundary for CO_2 (no H bonds) is tilted to the right



Phase transitions

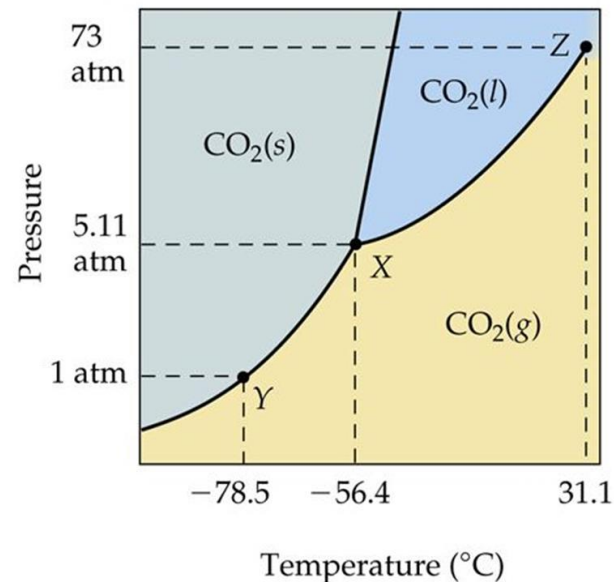
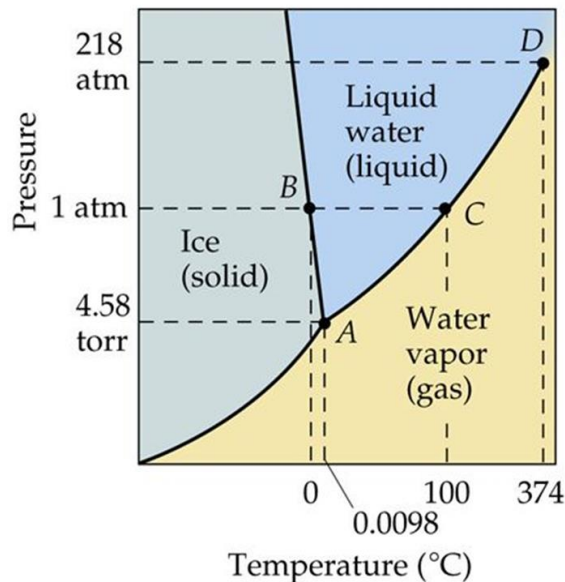
Clausius-Clapeyron equation: in an equilibrium of phases 1 and 2 (i.e. along solid lines representing phase transitions):

$$dG_1 = V_1 dp - S_1 dT = dG_2 = V_2 dp - S_2 dT$$

$$dp/dT = (S_2 - S_1)/(V_2 - V_1)$$

$dp/dT = L/T(V_2 - V_1)$ where L is latent heat,

therefore the sign of the slope depends on the sign of $(V_2 - V_1)$



Phase transitions

Classification from practical point of view

- transition between solid/liquid/gas (previous slide; part of physics of condensed state but let's focus on solids)
- change of number of phases (homogeneity): e.g. spinodal and binodal decomposition of solid solution 9-11 slides above
- change of atomic (crystallographic) structure: phases of ice 3 slides above, ferrite $\times$ austenite for Fe, etc., etc., etc.
- change of electronic structure at (almost) preserved atomic structure: change of ordering of spins due to a transition to another magnetic state, transition to superconducting state, ...

Phase transitions

Classification from thermodynamical point of view:

n -th order transition leads to a discontinuity of n -th derivative of free energy F (fixed volume) / free enthalpy G (fixed pressure) by some state quantity (such as temperature or intensity of external magnetic field)

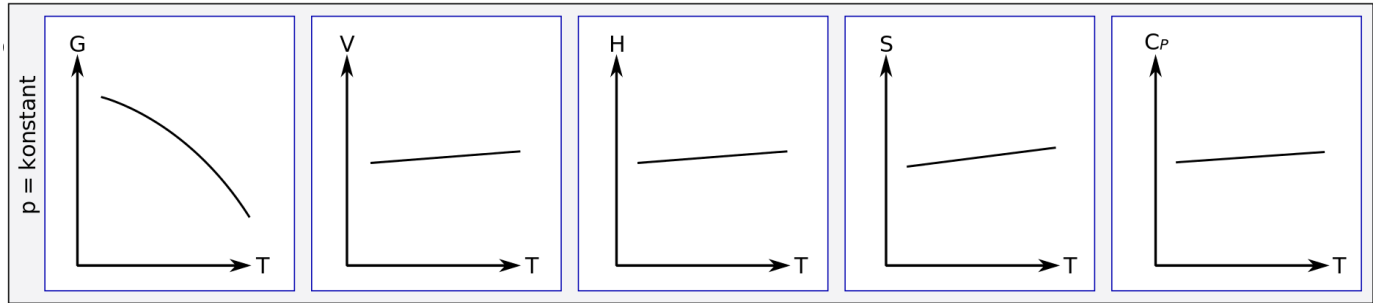
In praxis mainly $n = 1$ or 2

- 1st order transitions: already the 1st der. $\partial G / \partial T$ is discontinuous
- 2nd order transitions: only the 2nd der. $\partial^2 G / \partial T^2$ is discontinuous

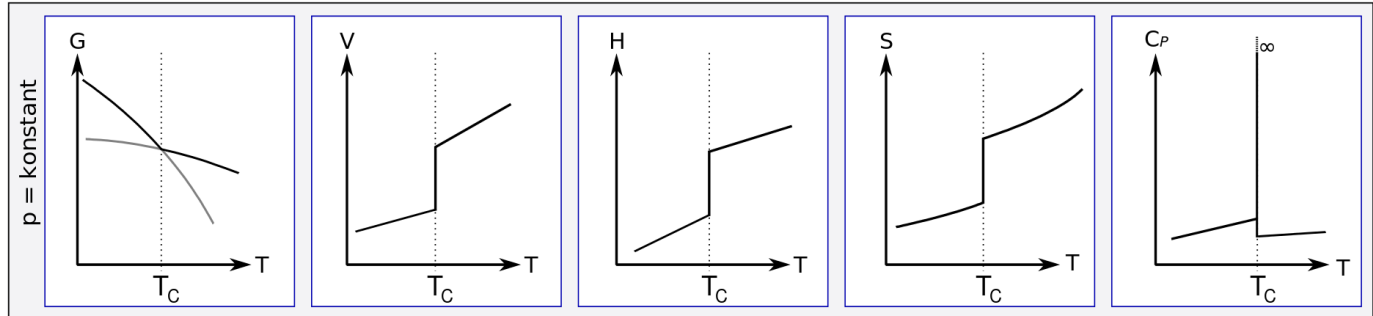
Phase transitions

- 1st order transitions: already the 1st der. $\partial G/\partial T$ is discontinuous
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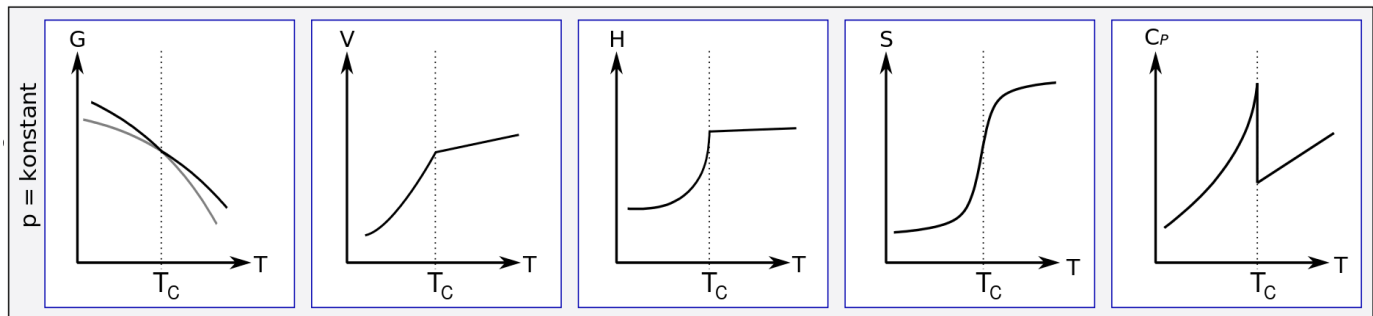
no transition



1st order transition



2nd order transition



Transitions of 1st order

already the 1st derivative is discontinuous: $\Delta \left[\frac{\partial^1(G)}{\partial(T)^1} \right]_P = \frac{\Delta H}{T_C} = -\Delta S \neq 0$



There is non-zero latent heat ΔH

Whole change can take place at a single temperature, but not immediately: the rate of heat transfer is finite, therefore both phases exist next to each other during phase transition

The transition does not have to take place (metastable phases)

Heat capacity diverges (transfer of ΔH at fixed T)

E.g. transitions between solid/liquid/gas state,
but also other phase transitions

Transitions of 2nd order

only the 2nd derivative is discontinuous: $\Delta \left[\frac{\partial^2 (G)}{\partial (T)^2} \right]_P = \frac{1}{T_C} \Delta \left(\frac{\partial H}{\partial T} \right)_P = \frac{\Delta C_P}{T_C} \neq 0$



Latent heat is zero

The changes with temperature are smooth ("continuous phase transitions"), but immediate at each of these temperatures.

There is not anything like metastable phase

Heat capacity changes abruptly ($\Delta C_p \neq 0$), but remains finite

E.g. change of magnetization (details in the next chapter 14): magnetization in itself is continuous, but susceptibility

$\chi = \partial M / \partial H = (-1/\mu_0 V) \cdot \partial^2 F(H, T) / \partial H^2$ is discontinuous

Transition of boiling water in snow

Boiling water thrown into dry air quickly evaporates, and at sufficiently low temperature ($\approx -25\text{ }^{\circ}\text{C}$) it becomes snow before falling on the ground (many videos on Youtube)



14) Magnetism

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Reminder of quantities



Magnesia district in Greece:
home of the tribe of Magnetes,
source of magnetic rocks, birthplace of
mythological (~900 BC) Magnes the
shepherd who allegedly discovered them

Magnetes

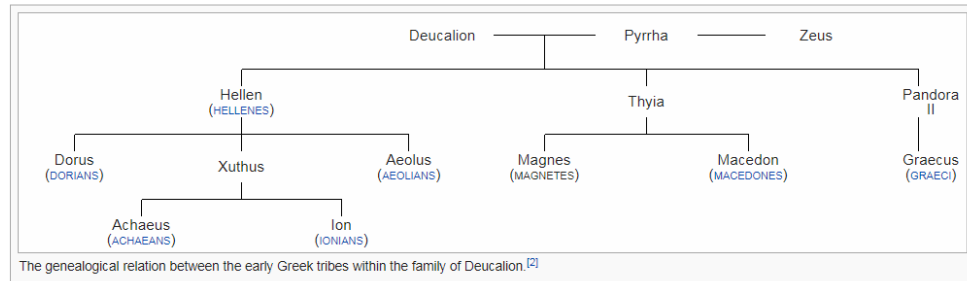
From Wikipedia, the free encyclopedia

The **Magnetes** (Greek: Μάγνητες) were an [ancient Greek](#) tribe. In book 2 of the *Iliad* [Homer](#) includes them in the Greek Army that is besieging [Troy](#), and identifies their homeland in [Thessaly](#), in part of what is still known as [Magnesia](#).^[1] They later also contributed to the [Greek colonisation](#) by founding two prosperous cities in Western [Anatolia](#), [Magnesia on the Maeander](#) and [Magnesia ad Sipylum](#).

Mythology [edit]

According to the [Hesiodic Catalogue of Women](#) (fr. 7), [Thyia](#), a daughter of [Deucalion](#), lay with [Zeus](#) and bore two sons: [Magnes](#) and [Makednos](#), the eponyms of the [Magnetes](#) and [Macedones](#), respectively. Within Thyia's extended family in the *Catalogue* are found the progenitors of several of the other early [Greek tribes](#). Her sister [Pandora II](#) (named after her grandmother, the famous [Pandora](#)) bore [Graecus](#) (also to Zeus). And their brother [Hellen](#), along with his three sons [Dorus](#), [Xuthus](#) (with his sons [Ion](#) and [Achaëus](#)) and [Aeolus](#), filled out the set of progenitors of the ancient tribes that formed the Greek/Hellenic nation.

Family tree [edit]



Moving charges lead to magnetism

The force between two infinite parallel conductors with charges $\tau_{1,2}$ per unit length is in vacuum equal to $F_s = \frac{1}{2\pi\epsilon_0} \frac{\tau_1\tau_2}{r}$ per unit length (integration of Coulomb law)

There are not any magnetic charges in the conductors. There are

- static protons, the proton charge in the rest frame connected to protons is τ^+ per unit length
- electrons moving with the velocity u , the electronic charge in the frame connected to electrons is $\tau^- (< 0)$ per unit length

In the laboratory rest frame (= frame connected to protons), the electrons are subject to length contraction, leading to electronic charge of $\tau^-/\sqrt{1-u^2/c^2} = \gamma\tau^-$ per unit length

The conductor is neutral in this frame, i.e. $\tau^+ + \gamma\tau^- = 0$ (the length contraction exactly compensates the increasing distance between electrons during their acceleration)

Moving charges lead to magnetism

The force between two infinite parallel conductors with charges $\tau_{1,2}$ per unit length is in vacuum equal to $F_s = \frac{1}{2\pi\epsilon_0} \frac{\tau_1\tau_2}{r}$ per unit length (integration of Coulomb law)

In the laboratory rest frame (= frame connected to protons), the electrons are subject to length contraction, leading to electronic charge of $\tau^-/\sqrt{1-u^2/c^2} = \gamma\tau^-$ per unit length. The conductor is neutral in this frame, i.e. $\tau^+ + \gamma\tau^- = 0$

In the frame connected to electrons, the protons are subject to length contraction, leading to proton charge of $\tau^+/\sqrt{1-u^2/c^2} = \gamma\tau^+$ per unit length. The conductor becomes slightly charged in this frame, with a total charge $\gamma\tau^+ + \tau^- = [1-\gamma^2]\tau^-$ per unit length.

Moving charges lead to magnetism

In the frame connected to electrons, the conductor becomes slightly charged, with a charge $\gamma\tau^+ + \tau^- = [1-\gamma^2]\tau^-$ per unit length

Electrons in one conductor are attracted to the slightly charged other conductor by the aforementioned electrostatic force

$$F_s = \frac{1}{2\pi\epsilon_0} \frac{\tau_1\tau_2}{r} = \frac{1}{2\pi\epsilon_0} \frac{\tau^-\tau^-(1-\gamma^2)}{r} = -\frac{1}{2\pi\epsilon_0} \frac{(\tau^-)^2 u^2}{r(c^2 - u^2)}$$

the electric current, represented in the rest frame by electrons with a charge density $\gamma\tau^-$ per unit length, is equal to $I = \gamma\tau^-u$

$$F_s = -\frac{1}{2\pi\epsilon_0} \frac{I^2}{r(c^2 - u^2)\gamma^2} = -\frac{1}{2\pi\epsilon_0} \frac{I^2(c^2 - u^2)}{r(c^2 - u^2)c^2} = -\frac{1}{2\pi\epsilon_0} \frac{I^2}{rc^2}$$

substitute $\epsilon_0 c^2 = 1/\mu_0$ and get the Ampere's force law

$$F_s = -\frac{\mu_0}{2\pi} \frac{I^2}{r}$$

Moving charges lead to magnetism

As shown above, magnetic force can be understood as an electrostatic force between charges respecting theory of relativity. The older empirical findings (Ampere's force law, Biot-Savart law, second summand of Lorentz's force as a change of the first one after in a different frame, ...) can be derived using STR.

This is not questioning the concept of magnetic field, nor the equality of $\mathbf{E}$ and $\mathbf{B}$ in the equations describing the EM waves (e.g. through vacuum which does not even contain any charges). The quantities $\mathbf{E} \cdot \mathbf{B}$ and $\mathbf{E}^2 - c^2 \mathbf{B}^2$ are relativistic invariants, i.e. there does not necessarily exist a frame where $\mathbf{B} = 0$.

The magnetism is weak for non-relativistic velocities: the ratio of magnetic and electrostatic force between charges with velocities $\mathbf{v}_1, \mathbf{v}_2$ (generalization of parallel currents on previous slides) is proportional to $\mathbf{v}_1 \cdot \mathbf{v}_2 / c^2$ ($\Leftrightarrow B \sim E/c^2 \Leftrightarrow$ second-order correction). However, it is important when it constitutes the only force.

Reminder of quantities

In general $\mathbf{B} = \mu_0 \mathbf{H} + \mu_0 \mathbf{M}$

$\mathbf{B}$ magnetic induction [T],

μ_0 permeability of vacuum [H/m]

$\mathbf{H}$ intensity of magnetic field [A/m]

$\mathbf{M}$ magnetization [A/m]

For weak fields we expect linear magnetics

$\Rightarrow \mathbf{M}$ is parallel to $\mathbf{H}$, $\mathbf{M} = \chi \mathbf{H}$ where χ is not tensor but scalar

$\Rightarrow \mathbf{B} = \mu \mathbf{H} = \mu_0 \mu_r \mathbf{H} = \mu_0 (1 + \chi) \mathbf{H}$

$\Rightarrow \chi = M/H$, or also $\chi = \partial M / \partial H$ or $\chi = \mu_0 \partial M / \partial B_0$
(equivalents for low χ , be careful about ferromagnetics)

μ permeability of the environment [H/m]

μ_r relative permeability of the environment [-]

χ **susceptibility** [-]

external field $B_0 = \mu_0 H$

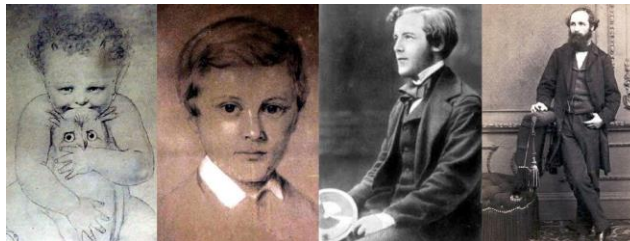
(does not matter for the aforementioned low χ : $\chi/[1+\chi] \approx \chi$)

Reminder of Maxwell equations

Name	E and B	E, B, D, and H
Coulomb's law of electrostatics, or Gauss's Law:	$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon}$	$\nabla \cdot \mathbf{D} = \rho$
Absence of magnetic monopoles:	$\nabla \cdot \mathbf{B} = 0$	$\nabla \cdot \mathbf{B} = 0$
Faraday's Law of Induction:	$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$	$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$
Ampère's Law, or the Biot-Savart Law, plus displacement current:	$\nabla \times \mathbf{B} = \mu \mathbf{J} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}$	$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}$

Consequence of Maxwell equations:

- assuming the absence of magnetic monopoles and
 - in a fixed electric field
- the only source of magnetic field (magnetic moments) is
- electrical current, i.e. **movement of electrical charges**



Reminder of Maxwell equations

Why the letters E , B , D , H , ... ?

Reminder of Maxwell equations

Why the letters E , B , D , H , ... ?

Maxwell denoted the necessary quantities alphabetically

Vector potential	A
Magnetic induction	B
Total electric current	C
Electric displacement	D
Electromotive force	E
Mechanical force	F
Velocity at a point	G
Magnetic force	H

(in the meantime C and G abandoned,
and some quantities renamed)

Magnetic moment

There are magnetic moments $\mathbf{m}$ associated with individual electrons & atoms, magnetization is given by their density:

$$\mathbf{M} = d\mathbf{m} / dV$$

Mechanical moment of a pair of forces M_{mech} (do not confuse with M) in external field B_0 (do not confuse with inside field B)

$$\mathbf{M}_{\text{mech}} = \mathbf{m} \times \mathbf{B}_0$$

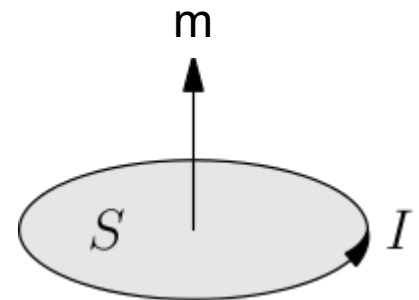
The resulting energy (after integration over angle)

$$\Delta E = -\mathbf{m} \cdot \mathbf{B}_0$$

For a current loop we can derive

$$\mathbf{m} = I \cdot \mathbf{S}$$

(sometimes directly given as a definition of $\mathbf{m}$)



Magnetic moment

There are magnetic moments $\mathbf{m}$ associated with individual electrons & atoms, magnetization is given by their density:

$$\mathbf{M} = d\mathbf{m} / dV$$

Mechanical moment of a pair of forces $\mathbf{M}_{\text{mech}}$ (do not confuse with M) in external field $\mathbf{B}_0$ (do not confuse with inside field $\mathbf{B}$)

$$\mathbf{M}_{\text{mech}} = \mathbf{m} \times \mathbf{B}_0$$

The resulting energy (after integration over angle)

$$\Delta E = -\mathbf{m} \cdot \mathbf{B}_0$$

for whole material $E = -V \cdot \mathbf{M} \cdot \mathbf{B}_0 = -V \cdot \mathbf{M} \cdot \mu_0 \cdot \mathbf{H}$,

to formulas 5 slides above ($\chi = \partial M / \partial H$, etc.) we can add

$$\chi = (-1/\mu_0 V) \cdot \partial^2 E(H) / \partial H^2, \text{ or even better (at finite temperature)}$$

$$\chi = (-1/\mu_0 V) \cdot \partial^2 F(H, T) / \partial H^2$$

Magnetism of solid materials is of quantum origin

Bohr-van Leeuwen theorem:

Magnetic field does not do work ($\mathbf{v} \times \mathbf{B}$ perpendicular to $\mathbf{v}$), change of external field therefore does not change the material state corresponding to the minimum energy $\Rightarrow$ does not change the distribution of velocities in the material, etc.



If the **total** electric current ($\Rightarrow$ magnetic moment) in a (non-rotating) material is zero without external magnetic field, it will stay zero also after switching the external field on ($\chi = 0$).

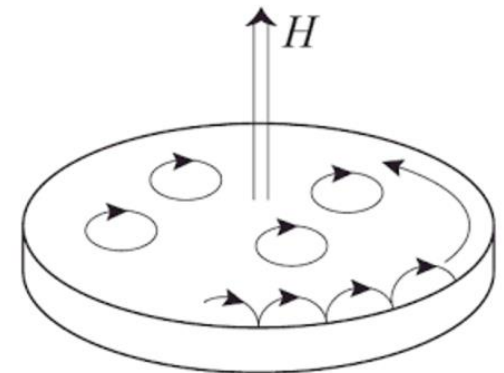
Magnetism of solid materials is of quantum origin

Bohr-van Leeuwen theorem:

From another point of view: electrons in magnetic field circulate with a frequency f , but

- internal currents ($\Rightarrow$ diamag. moments, $dm = -e.f.dS$) are exactly cancelled out by
- circumference current resulting from open orbits at the edge ($\Rightarrow$ paramagnetic moment with opposite orientation, $m = e.f.S$)

therefore again $\chi = 0$



Source of magnetism in solid mater.

As pointed out 4 slides above: the source of magnetic moments is **movement of electrical charges**

The important motions of charges in the microworld are

- circulating of electrons around atom core
- rotation of electrons, i.e. spin
- rotation of atom core: neglected here

Circulating of electron around atom core (particle point of view):

$$\mathbf{m} = I \cdot \mathbf{S} = -e \cdot f \cdot \pi r^2 = -e \cdot (v/2\pi r) \cdot \pi r^2 = -(e/2m_e) \cdot (m_e v r) = -(\mathbf{e}/2\mathbf{m}_e) \cdot \mathbf{L}$$

i.e. magnetic mom. and angular mom. are proportional

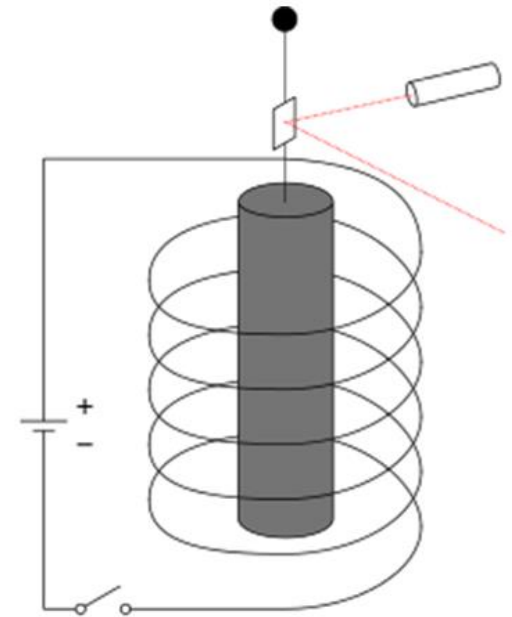
Typical value of angular momentum in the microworld is $\hbar$,
therefore typical value of magnetic moment is $\mu_B = e\hbar/2m_e$,
so called Bohr magneton

Exp. proofs of the direct proportion of magnetic mom. and angular mom.

Einstein - de Haas effect:

consequence of angular momentum

conservation: ferromagnetic cylinder starts to rotate after a change of its magnetization



Barnett effect:

the opposite of the aforementioned effect, i.e. magnetization caused by rotation

Relationship of magnetic momentum and angular momentum

Orbital angular momentum $L = \hbar\sqrt{l(l+1)}$ leads to (derived above)

$$m = -e/2m_e \cdot L$$

$$= \gamma_L \cdot L$$

where gyromagnetic ratio $\gamma_L = -e/2m_e$

$$= -\mu_B \sqrt{l(l+1)}$$

$$= -g_L \mu_B \sqrt{l(l+1)}$$

where gyromagnetic ratio $g_L = 1$

Spin angular momentum $S = \hbar\sqrt{s(s+1)}$ leads to (no derivation)

$$m = -e/m_e \cdot S$$

$$= \gamma_S \cdot S$$

where gyromagnetic ratio $\gamma_S = -e/m_e$

$$= -2\mu_B \sqrt{s(s+1)}$$

$$= -g_S \mu_B \sqrt{s(s+1)}$$

where gyromagnetic ratio $g_S = 2$

Quantities γ and g are both called gyromagnetic ratio (in the latter case also g-factor), g sometimes includes also the sign '-'

Relationship of magnetic momentum and angular momentum

Orbital angular momentum $L = \hbar\sqrt{l(l+1)}$ leads to
 $m = -g_L\mu_B\sqrt{l(l+1)}$ where gyromagnetic ratio $g_L = 1$

Spin angular momentum $S = \hbar\sqrt{s(s+1)}$ leads to
 $m = -g_S\mu_B\sqrt{s(s+1)}$ where gyromagnetic ratio $g_S = 2$

Transition from electron (quantum numbers j, l, s) to atom (quantum numbers J, L, S , do not confuse with momenta $\mathbf{J}, \mathbf{L}, \mathbf{S}$):

Total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ leads to

$$m = -g_J\mu_B\sqrt{J(J+1)}$$

where g_J (Lande g-factor) is not surprisingly between g_L and g_S

$$g_J = 1 + [\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2] / 2\mathbf{J}^2 = 1 + [J(J+1) + S(S+1) - L(L+1)] / 2J(J+1)$$

Relationship of magnetic momentum and angular momentum

Transition from electron (quantum numbers j, l, s) to atom (quantum numbers J, L, S , do not confuse with momenta $\mathbf{J}, \mathbf{L}, \mathbf{S}$):

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Reminder of Hund rules:

- 1) maximization of S
- 2) maximization of L
- 3) $J = |L - S|$ for lower than half occupation of the top shell,
 $J = L + S$ for higher than half (for exactly half $L = 0$)

Relationship of magnetic momentum and angular momentum

Total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ leads to

$$m = -g_J \mu_B \sqrt{J(J+1)}$$

where g_J (Lande g-factor) is not surprisingly between g_L and g_S

$$g_J = 1 + [\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2] / 2\mathbf{J}^2 = 1 + [J(J+1) + S(S+1) - L(L+1)] / 2J(J+1)$$

Sounds very theoretical,
but even a student of KFY
may need it in his papers

cell are discussed. The criterion of success is to obtain an energy minimum corresponding to the experimental low-temperature ferromagnetic moment of Ho atoms $m = 6.5 \mu_B$ [56] or $\approx 7.0 \mu_B$ [4] in bulk HoN. This value is well below the maximum ordered moment $g_J \mu_B = 10.0 \mu_B$ [15,21,56] and between other m values of $3.2 \mu_B$ reported for thin-film HoN [3] and $8.9 \mu_B$ assuming long-range spiral ordering (difficult to describe by first-principle calculations) rather than ferromagnetic ordering [15]. The most probable cause of this quenching of magnetic moment are low-temperature crystal-field interactions [57]. While experimental issues such as unwanted oxidation or presence of N vacancies have been proven to affect magnetic properties of RE nitrides as well [58,59], a case can be made that the similarity of the aforementioned independently reported m values of 6.5 and $7.0 \mu_B$ supports the former as the main cause. The described low-temperature $m = 6.5\text{--}7.0 \mu_B$ per Ho atom is not to be confused with high-temperature paramagnetic $m = 10.3 \mu_B$ [6], $10.7 \mu_B$ [56], or $10.8 \mu_B$ [15] per Ho atom (close to the theoretical value $g_J \mu_B / [J(J+1)] = 10.6 \mu_B$ [16]).

[M. Matas et al., *Comp. Mater. Sci.* 230, 112537 (2023)]

Direction of magnetic momentum

Orbital angular momentum $L = \hbar\sqrt{l(l+1)}$ leads to

$$m = -g_L\mu_B\sqrt{l(l+1)} \quad (\text{amplitude})$$

$$m_z = -g_L\mu_B m_l \quad (\text{projection to the direction of } \mathbf{B})$$

where $m_l = -l, (-l+1), \dots, l$

(specifics of quantum mechanics: projection of the angular momentum to any direction is lower than its value ... ok)

Similarly for the spin angular momentum

(S, g_S, m_S [for electron $\pm 1/2$, for atom more general])

Similarly for the total angular momentum

(J, g_J, m_J)

Magnetic phenomena

Diamagnetism: consequence of the effect of external field on **trajectories** of electrons (each electron contributes separately, even when total $m = 0$ for all electrons associated with an atom)

i.e. this phenomenon has strongly different mechanism from the following ones, but it is called similarly because it also affects χ

Paramagnetism: consequence of the effect of external field on **vectors on magnetic moments** of atoms, if they are non-zero and **do not interact with each other**, and free electrons

Ferro-/antiferro-/ferrimagnetism: consequence of energetical preference to **order magnetic moments** of atoms, if they are non-zero and **do interact with each other**, without external field

Magnetic phenomena

Diamagnetism: consequence of the effect of external field on **trajectories** of electrons (each electron contributes separately, even when total $m = 0$ for all electrons associated with an atom)

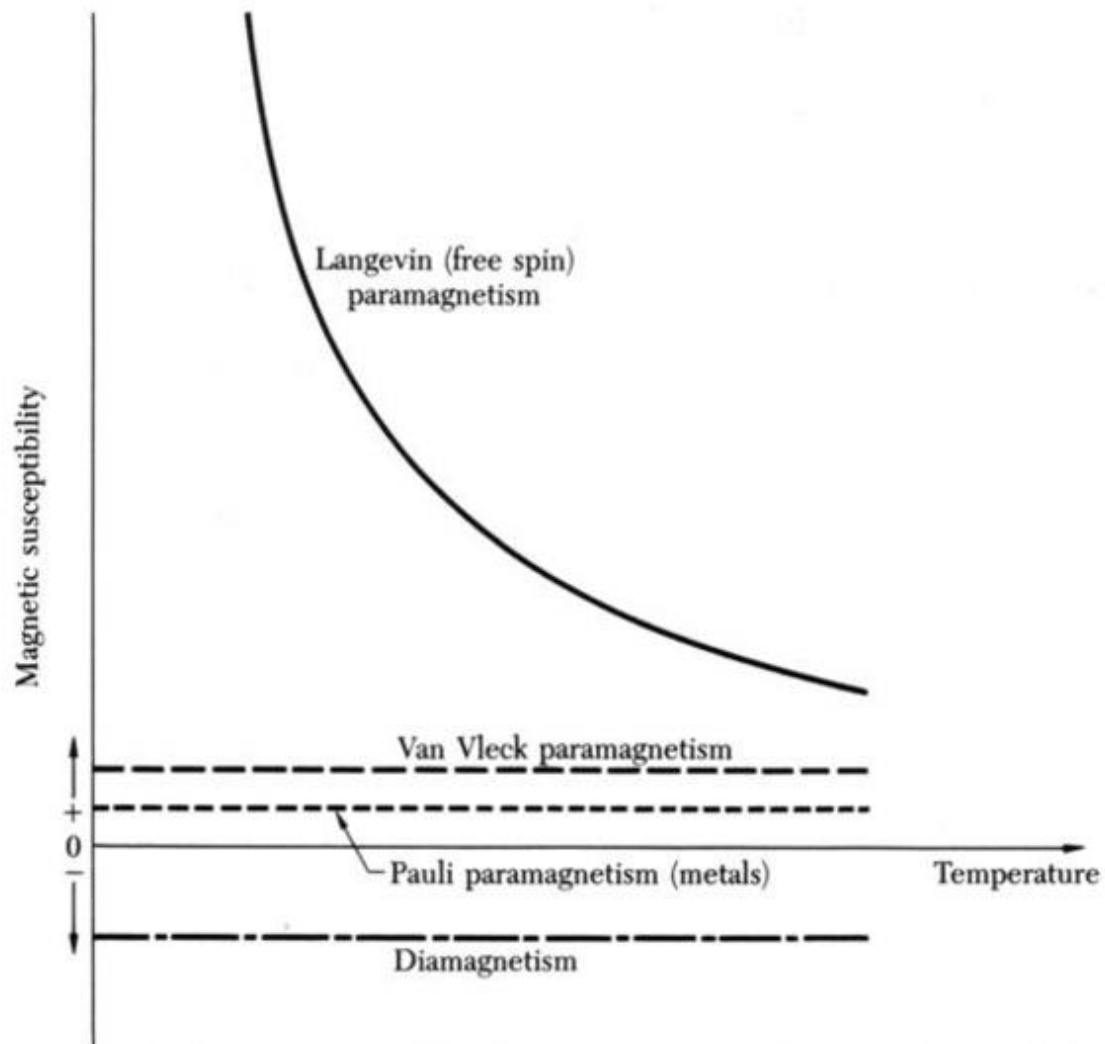
- contribution of localized electrons (Langevin+Larmor)
- contribution of free electrons (Landau)

Paramagnetism: consequence of the effect of external field on **vectors on magnetic moments** of atoms, if they are non-zero and **do not interact with each other**, and free electrons

- contribution of atoms (Langevin+Curie)
- contribution of free electrons (Pauli)

We are talking about magnetic moment **after** the atom is inserted into mag. field, i.e. after excitation caused by that (van Vleck)

Magnetic phenomena



Langevin diamagnetism

Localized electrons, circulating around the atom cores with a radius ρ (i.e. not metals)

First approach: switching the magnetic field on gives rise to a tangential electric field (Faraday law) $E \cdot 2\pi\rho = -d/dt (B \cdot \pi\rho^2)$

the moment of electric force acting on circulating electron is $-e \cdot E \cdot \rho = e \cdot \rho^2/2 \cdot dB/dt$

moment of force = speed of change of angular momentum, so $dL/dt = e \cdot \rho^2/2 \cdot dB/dt$



$$\Delta L = e \cdot \rho^2/2 \cdot B$$

7 slides above $m = -e/2m_e \cdot L$, therefore

$$\Delta m = -e/2m_e \cdot \Delta L = -e^2 \rho^2 B / 4m_e$$

Langevin diamagnetism

Localized electrons, circulating around the atom cores with a radius ρ (i.e. not metals)

First approach (previous slide):

$$\Delta \mathbf{m} = -e/2m_e \cdot \Delta L = -\mathbf{e}^2 \rho^2 \mathbf{B} / 4m_e$$

Second approach: insertion into magnetic field $\mathbf{B}$ leads to a precession with angular velocity $\omega = e\mathbf{B}/2m_e$ (Larmor formula, no derivation)



$$\Delta \mathbf{m} = \Delta I \cdot S = -e \cdot eB/2m_e \cdot 1/2\pi \cdot \pi \rho^2 = (\text{again}) -\mathbf{e}^2 \rho^2 \mathbf{B} / 4m_e$$

Langevin diamagnetism

Formula derived (two different approaches) above:

$$\Delta m = -e^2 \rho^2 B / 4m_e$$

It is desirable to replace $\rho^2 = x^2 + y^2$ by a mean value:

$$\Delta m = -e^2 \langle \rho^2 \rangle B / 4m_e$$

For spherical atom it is desirable to replace distance from z-axis ($\rho^2 = x^2 + y^2$) by distance from the middle of atom ($r^2 = x^2 + y^2 + z^2$):

$$\Delta m = -e^2 \langle \rho^2 \rangle B / 4m_e = -e^2 \cdot 2/3 \langle r^2 \rangle \cdot B / 4m_e = -e^2 \langle r^2 \rangle B / 6m_e$$

For whole material (atomic density N , Z electrons per atom):

$$M = -NZe^2 \langle r^2 \rangle B / 6m_e$$

$$\chi = -NZe^2 \langle r^2 \rangle \mu_0 / 6m_e$$

Langevin diamagnetism

Formulas derived above:

$$\Delta m = -e^2 \rho^2 B / 4m_e$$

$$M = -NZe^2 \langle r \rangle^2 B / 6m_e$$

$$\chi = -NZe^2 \langle r \rangle^2 \mu_0 / 6m_e$$

The derivation is valid for weak fields (contribution to the angular velocity of electron circulating around atom core is low compared to the angular velocity before switching B on, etc.)

The derivations are classical, but specifically for Langevin diamagnetism the quantum derivations lead to the same formula

Langevin diamagnetism

Rare case when material properties do not depend predominantly on valence electrons, but on **all** electrons (Z in the formula $\chi = -NZe^2\langle r \rangle^2\mu_0/6m_e$)



It is not surprising, that the **heaviest** $\pm$ stable element, **bismuth**, is at the same time **most diamagnetic** (pyrolytic carbon, i.e. modified graphite, has higher χ only perpendicularly to graphitic planes, not isotropically)

A standard periodic table of elements. The element Bismuth (Bi), with atomic number 83, is circled in blue. It is located in the p-block, group 15, period 6.

Material $\blacklozenge$	$\chi_v (\times 10^{-5} \text{ (SI units)}) \blacktriangle$
Superconductor	-10^5
Pyrolytic carbon	-40.9
Bismuth	-16.6
Mercury	-2.9
Silver	-2.6
Carbon (diamond)	-2.1
Lead	-1.8
Carbon (graphite)	-1.6
Copper	-1.0
Water	-0.91

table from wikipedia

Landau diamagnetism

Contribution of free electrons (metals, or also semimetals)

The effect is clearly proportional to the number of free electrons, i.e. the density of states (per E and V) at the Fermi level $g(E_F)$

After derivation of the constant of proportionality (skipped)

$$\chi = -\mu_B^2 \mu_0 g(E_F)/3$$

or alternative forms

$$\chi = -e^2 \mu_0 \sqrt{(2m_e E_F)/12\pi^2 m_e \hbar}$$

$$\chi = -e^2 \mu_0 k_F / 12\pi^2 m_e$$

Reminder of equations for electronic gas with a density N :

radius of Fermi sphere $k_F = (3\pi^2 n)^{1/3}$

Fermi level $E_F = \hbar^2 k_F^2 / 2m_e$

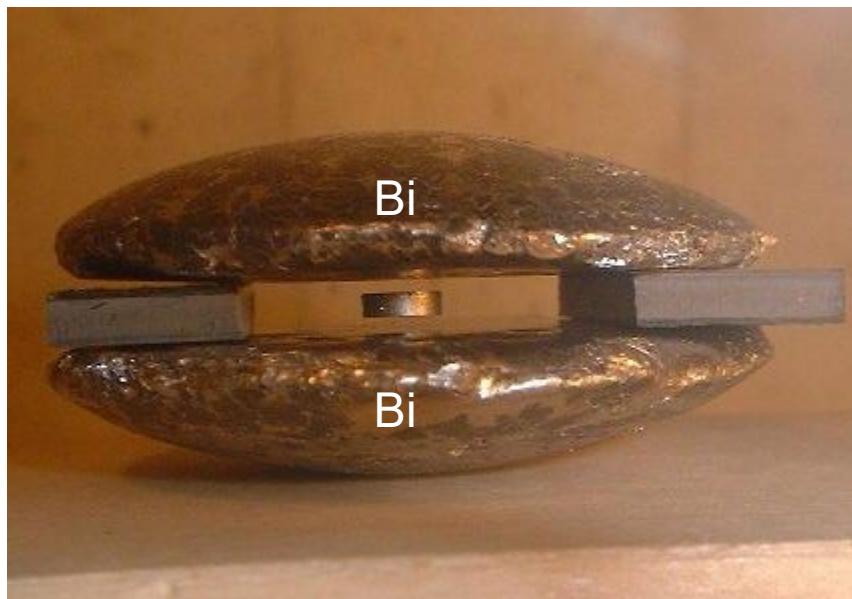
density of states / V $g(\varepsilon) = 1/2\pi^2 \cdot (2m_e/\hbar^2)^{3/2} \cdot \sqrt{\varepsilon}$

Diamagnetism - summary

- Weakens the magnetic field ($\Leftrightarrow$ in inhomogeneous B the force is towards the region of lower B): minus sign of χ
- Effect exist always, all electrons of all atoms contribute to it
- Effect is weak (especially compared to ferromagnetism)
- Effect is dominant in materials where most electrons are paired, many shells completely filled

Levitation

First possibility: levitating material is ferromagnetic (see the figure) or paramagnetic (e.g. videos with O_2 between poles of a magnet). Stabilization in a space using a diamagnetic material (often bismuth mentioned above) is necessary.



from instructions at USA server:

It can be obtained by taking bismuth shot from shotgun shells. They are a special kind that use bismuth shot instead of lead shot, to prevent lead poisoning to birds in hunting areas. ...

For obvious reasons, be sure to remove the bismuth shot from the shells before trying to melt it.

Levitation

Second possibility: levitating material is diamagnetic, typically something containing predominantly diamagnetic H_2O ... e.g. a frog (see the figure). Repelled by all walls of strong (e.g. 16 T) hollow magnet, i.e. no need for further stabilization.



Langevin paramagnetism

Turning of magnetic moments of individual atoms (if they are non-zero, i.e. not in all materials) towards external field direction

Atom has non-zero magnetic moment $m = -g_J \mu_B \sqrt{J(J+1)}$

Projection to $\mathbf{B}$ is $m_z = -g_J \mu_B m_J$ where $m_J = -J, (-J+1), \dots, J$

Before switching $\mathbf{B}$ on the positive and negative values of m_J are equally probable $\Rightarrow \langle m_z \rangle = 0$

After switching $\mathbf{B}$ on the probability of individual states is proportional to $\exp(-E/k_B T)$, where $E = -\mathbf{m} \cdot \mathbf{B}$ (above) $\Rightarrow \langle m_z \rangle \neq 0$

Langevin paramagnetism

Projection to $\mathbf{B}$ is $m_z = -g_J \mu_B m_J$ where $m_J = -J, (-J+1), \dots, J$

After switching $\mathbf{B}$ on the probability of individual states is proportional to $\exp(-E/k_B T)$, where $E = -\mathbf{m} \cdot \mathbf{B}$ (above) $\Rightarrow \langle m_z \rangle \neq 0$

example for $L=0$ a $S=J=0.5 \Rightarrow g_J=g_S=2, m_J=\pm 0.5$:

$$\langle m_z \rangle = [\mu_B e^{\mu_B B/k_B T} - \mu_B e^{-\mu_B B/k_B T}] / [e^{\mu_B B/k_B T} + e^{-\mu_B B/k_B T}] = \mu_B \cdot \tanh(\mu_B B/k_B T)$$

$T = 300$ K: $\tanh$ is 0.5 for gigantic $B = 250$ T $\Rightarrow$ we can assume weak fields $\Rightarrow \tanh(\mu_B B/k_B T) \cong \mu_B B/k_B T$

$$M \cong N \cdot \mu_B \cdot (\mu_B B/k_B T) = N \mu_B^2 B/k_B T$$

$$\chi \cong N \mu_B^2 \mu_0 / k_B T$$

Langevin paramagnetism

example for $L=0$ a $S=J=0.5 \Rightarrow g_J=g_S=2, m_J=\pm 0.5$:

$$\langle m_z \rangle = [\mu_B e^{\mu_B B/k_B T} - \mu_B e^{-\mu_B B/k_B T}] / [e^{\mu_B B/k_B T} + e^{-\mu_B B/k_B T}] = \mu_B \cdot \tanh(\mu_B B/k_B T)$$

$$\chi \cong N \mu_B^2 \mu_0 / k_B T$$

general value of J :

$$\langle m_z \rangle = g_J J \mu_B \cdot \{ (2J+1)/2J \cdot \text{ctgh}[(2J+1)/2J \cdot x] - 1/2J \cdot \text{ctgh}(1/2J \cdot x) \}$$

Brillouin function $B_J(x)$; $x = g_J J \mu_B B / k_B T$

again approximation for weak fields

(low x , i.e. low magnetic energy compared to thermal energy):

$$\chi \cong N \mu_B^2 \mu_0 g_J^2 J(J+1) / 3 k_B T$$

(for $J=0.5$ and $g_J=2$ we get the previous formula)

Langevin paramagnetism

example for $L=0$ a $S=J=0.5 \Rightarrow g_J=g_S=2, m_J=\pm 0.5$:

$$\langle m_z \rangle = [\mu_B e^{\mu_B B/k_B T} - \mu_B e^{-\mu_B B/k_B T}] / [e^{\mu_B B/k_B T} + e^{-\mu_B B/k_B T}] = \mu_B \cdot \tanh(\mu_B B/k_B T)$$

$$\chi \cong N \mu_B^2 \mu_0 / k_B T$$

general value of J :

$$\langle m_z \rangle = g_J \mu_B \cdot \{ (2J+1)/2J \cdot \text{ctgh}[(2J+1)/2J \cdot x] - 1/2J \cdot \text{ctgh}(1/2J \cdot x) \}$$

$$\chi \cong N \mu_B^2 \mu_0 g_J^2 J(J+1) / 3 k_B T$$

classical limit

transition from sum to integral, or substitute $J \rightarrow \infty$

before the simplification which assumed low product $J \cdot B$

$$\langle m_z \rangle = g_J \mu_B \cdot \{ \text{ctgh}[x] - 1/x \} \quad \text{where again } x = g_J \mu_B B / k_B T$$

when x is low (despite high J), we get the previous formula

$$\chi \cong N \mu_B^2 \mu_0 g_J^2 J^2 / 3 k_B T \quad (J^2 \text{ instead of } J(J+1) \text{ is OK for } J \rightarrow \infty)$$

Curie law

From the aforementioned formula for $\langle m_z \rangle$ (incl. $\langle m_z \rangle \sim B$!) we got
$$\chi = M\mu_0/B = N\langle m_z \rangle\mu_0/B \cong N\mu_B^2\mu_0g_J^2J(J+1)/3k_B T$$



Curie law know in the form $\chi = C/T$

Curie - Weiss law

From the aforementioned formula for $\langle m_z \rangle$ (incl. $\langle m_z \rangle \sim B$!) we got
 $\chi = M\mu_0/B = N\langle m_z \rangle\mu_0/B \cong N\mu_B^2\mu_0g_J^2J(J+1)/3k_B T$



Curie law known in the form $\chi = C/T$

If the atoms (their d-electrons) interact (non-zero exchange energy), the consequence is additional **Weiss field** λM

(at low temperatures this field leads to ordering of magnetic moments - details below, now we are talking about the paramagnetic state of the same materials at high temperatures)

Curie - Weiss law

Curie law known in the form $\chi = C/T$

If the atoms (their d-electrons) interact (non-zero exchange energy), the consequence is additional **Weiss field** λM



$$\langle m_z \rangle \sim B \quad \text{converts to} \quad \langle m_z \rangle \sim B + \lambda M$$

$$M\mu_0/B = C/T \quad \text{converts to} \quad M\mu_0/(B + \lambda M) = C/T$$

$\chi = M\mu_0/B$ is however still valid, after combining both equations

$$\chi = C/(T - C\lambda/\mu_0)$$



Curie - Weiss law

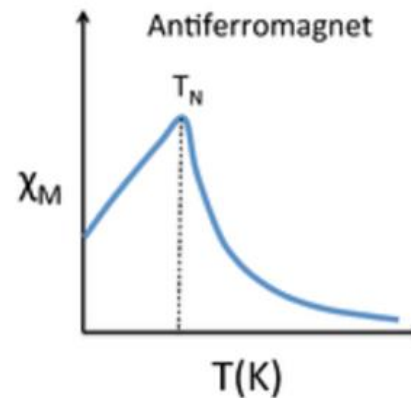
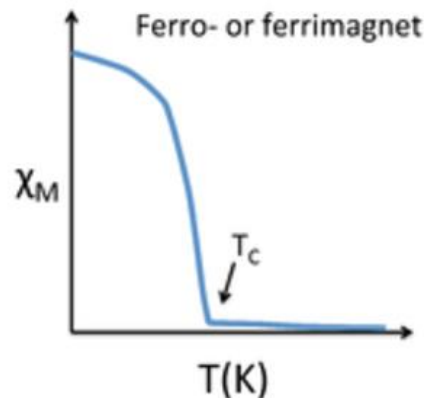
Curie - Weiss law

$$\chi = C/(T - C\lambda/\mu_0)$$

Curie - Weiss law, depending on the sign of λ known as

$$\chi = C/(T - T_C) \quad (\text{Curie temperature } T_C, \text{ positive exchange } E, \text{ ferromagnetics})$$

$$\chi = C/(T + T_N) \quad (\text{Neel temperature } T_N, \text{ negative exchange } E; \text{ antiferromagnetics})$$



$T_{C(N)}$ above which a material is paramagnetic and T from the formula for χ are not exactly equal, therefore also $\chi = C/(T - \Theta)$

Curie law - orbital quenching

After quantifying $\chi = N\mu_B^2\mu_0 g_J^2 J(J+1)/3k_B T = C/T$ we get

- good agreement for elements except transition metals
- **bad** agreement for transition metals and **real L**
- **good** agreement for transition metals and **L=0**

Reason: for d-electrons of transition metals the crystal field is more important than spin-orbit coupling $\Leftrightarrow$ rules the 3. Hund rule (valid for isolated atom) out, sets $\langle L_z \rangle = 0$

Example for ion Cu^{2+}

valence configuration $3d^9$, $S = 0.5$, $L = 2$, $J = 2.5$

$$g_J \sqrt{J(J+1)} = 3.55$$

$$g_S \sqrt{S(S+1)} = 1.73$$

experiment : 1.83

Pauli paramagnetism

Reorientation of magnetic moments ($\Leftrightarrow$ spins)
of free electrons towards the direction of external field

Reminder of the aforementioned stuff:

- free electron has $m_z = -g_S\mu_B m_S$ where $g_S = 2$ and $m_S = \pm 1/2$
- with B the electronic energy changes of $E = -\mathbf{m} \cdot \mathbf{B}$
(decreases for spins oriented like the field and vice versa)

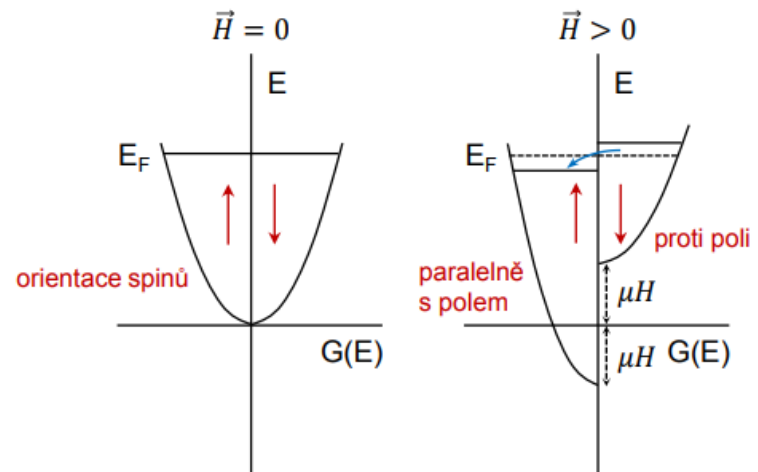
Both orientations share the same Fermi level $\Rightarrow$ with B the number of spins oriented like the field increases and vice versa

$$N_{\uparrow} = N/2 \cdot [1 + \mu_B g(E_F) B]$$

$$N_{\downarrow} = N/2 \cdot [1 - \mu_B g(E_F) B]$$

$$M = \mu_B (N_{\uparrow} - N_{\downarrow}) = \mu_B^2 g(E_F) B$$

$$\chi = \mu_B^2 \mu_0 g(E_F)$$



Paramagnetism - summary

- Strengthens the magnetic field ($\Leftrightarrow$ in inhomogeneous B the force is towards the region of higher B): minus sign of χ
- Effect does not exist always, most importantly magnetic moment cannot follow the direction of B if they are zero
- If the (especially Langevin) paramagnetism takes place, it is at common temperatures stronger than diamagnetism (therefore we call the materials - in sum - paramagnetic)
- for the (dominant) Langevin paramagnetism, sometimes - under simplification - also for whole paramagnetism, holds Curie law $\chi = C/T$,
or Curie-Weiss law $\chi = C/(T-T_C)$

Landau diamagnetism

×

Pauli paramagnetism

effect on trajectories of free electrons (regardless the spin):

$$\chi_{\text{Landau_diamagnetism}} = -\mu_B^2 \mu_0 g(E_F)/3 \quad (15 \text{ slides above})$$

effect on change of spins of free electrons:

$$\chi_{\text{Pauli_paramagnetism}} = \mu_B^2 \mu_0 g(E_F) \quad (2 \text{ slides above})$$

$$\text{i.e. } \chi_{\text{Pauli_paramagnetism}} = -3 \times \chi_{\text{Landau_diamagnetism}}$$

sum of both effects says that the electronic gas is paramagnetic

Landau diamagnetism

×

Pauli paramagnetism

i.e. $\chi_{\text{Pauli_paramagnetism}} = -3 \times \chi_{\text{Landau_diamagnetism}}$

sum of both effects says that the electronic gas is paramagnetic

This is not to say that the presence of electronic gas (presence of Pauli paramagnetism, independently of that of Langevin) guarantees an overall paramagnetism of a conductive material.

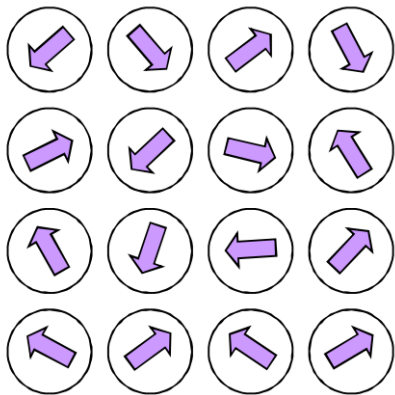
E.g. Cu, Ag, Au are excellent conductors, but diamagnetic: at the absence of Langevin, only conducting electrons contribute to paramagnetism (≈ 1 per atom), while all electrons contribute to diamagnetism (29, 47, 79 per atom Cu, Ag, Au)

Ferromagnetism

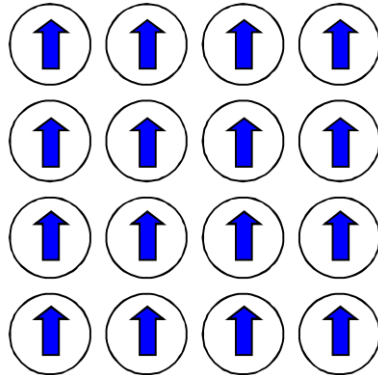
+ antiferromagnetism, ferrimagnetism

Possible ordering of neighbouring magnetic moments

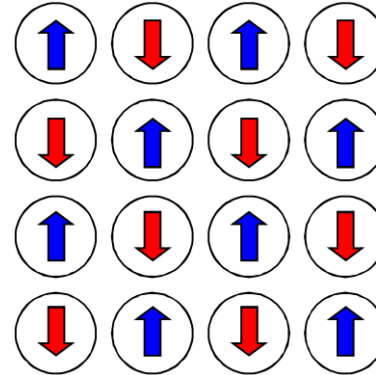
- same direction: ferromagnetic
- opposite direction, equal moments in both sublattices: antiferromagnetic
- opposite directions, different moments in both sublattices: ferrimagnetic



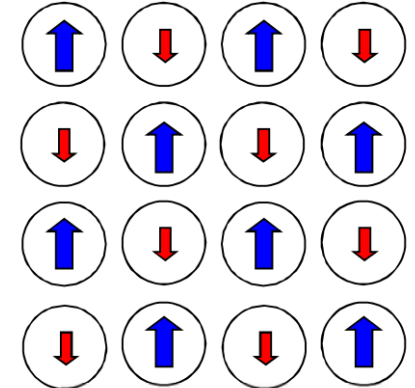
Paramagnetic



Ferromagnetic



Antiferromagnetic



Ferrimagnetic

Ferromagnetism

+ antiferromagnetism, ferrimagnetism

First a reminder of Langevin paramagnetism:

$$\langle m_z \rangle = g_J \mu_B \cdot \left\{ \frac{(2J+1)}{2J} \operatorname{ctgh} \left[\frac{(2J+1)}{2J} x \right] - \frac{1}{2J} \operatorname{ctgh} \left(\frac{1}{2J} x \right) \right\},$$

$$M/M_{\text{saturation}} = \frac{(2J+1)}{2J} \operatorname{ctgh} \left[\frac{(2J+1)}{2J} x \right] - \frac{1}{2J} \operatorname{ctgh} \left(\frac{1}{2J} x \right)$$

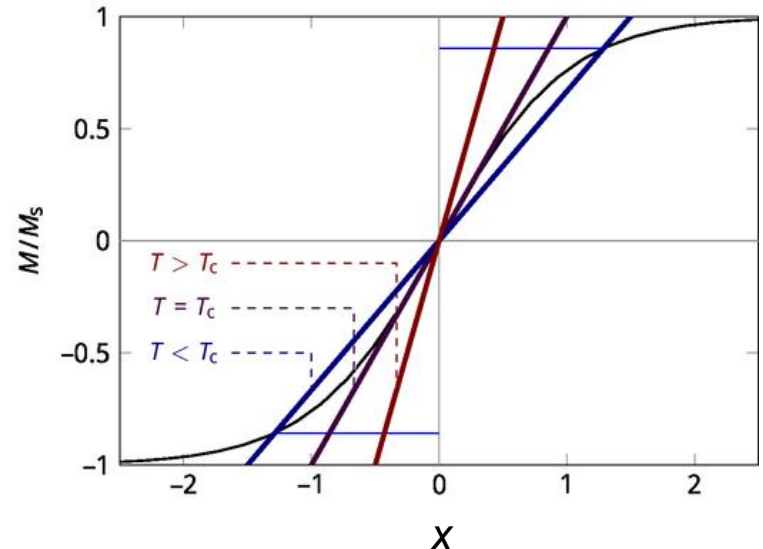
where $x = g_J \mu_B B / k_B T$

Weiss model: as pointed out above, ferromagnet can be described as a paramagnet (Langevin) with additional internal field λM , i.e. $x = g_J \mu_B (B + \lambda M) / k_B T$

Brill. function and line constitute 2 equations for 2 variables M , x

Graphical solution for $B = 0$:

at $T < T_c$ there is a solution with $M \neq 0$ (decreases with T)

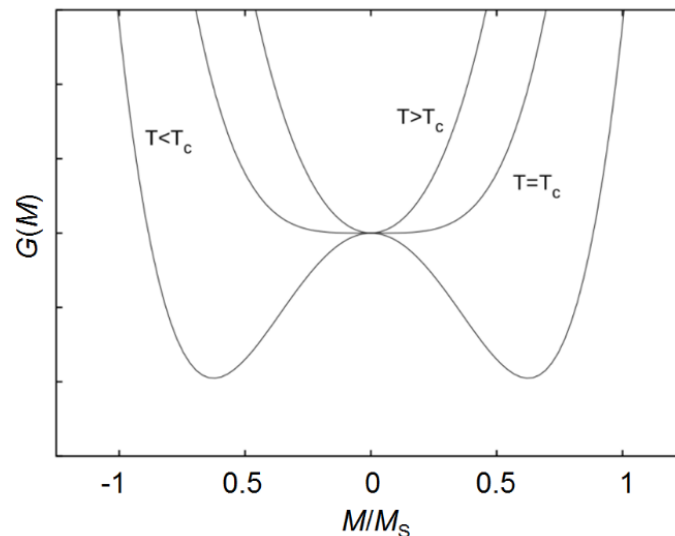
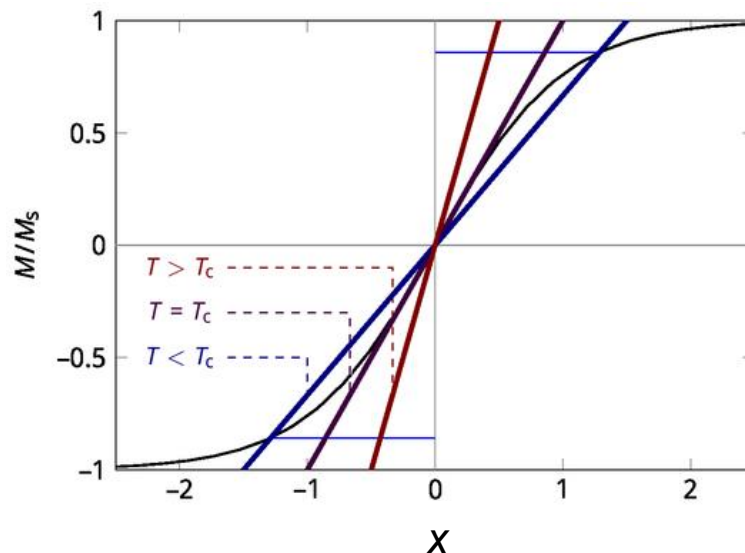


Ferromagnetismus

+ antiferromagnetismus, ferimagnetismus

Graphical solution for $B = 0$:
at $T < T_C$ there is a solution
with $M \neq 0$ (decreases with T)

The solution with $M \neq 0$ not
only exists, it also constitutes
a minimum of free enthalpy
(while the state with $M = 0$ is
below T_C metastable, contrary to
first-order transitions there is not
even a local minimum)



Ferromagnetism (when happens)

Previous slide shows that the ordering of magnetic moments can take place. It can exist below temperature which increases with increasing absolute value of (Weiss) exchange energy.

When is this value high? See chapter 2.

For lower line number the orbitals do not overlap that much $\Rightarrow$ interact weakly $\Rightarrow$ electrons do not have to end up in the same covalent bonding orbital $\Rightarrow$ can choose spin $\Rightarrow$ magnetism.

Periodic table showing elements and their magnetic properties. The table is color-coded to indicate magnetic behavior:

- Red circle highlights Cr, Mn, and Fe in the 3d transition metal series.
- Blue circle highlights Fe, Co, and Ni in the 3d transition metal series.
- Red circle highlights Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb in the lanthanide series.
- Blue circle highlights Gd, Tb, Dy, Ho, Er, Tm in the lanthanide series.

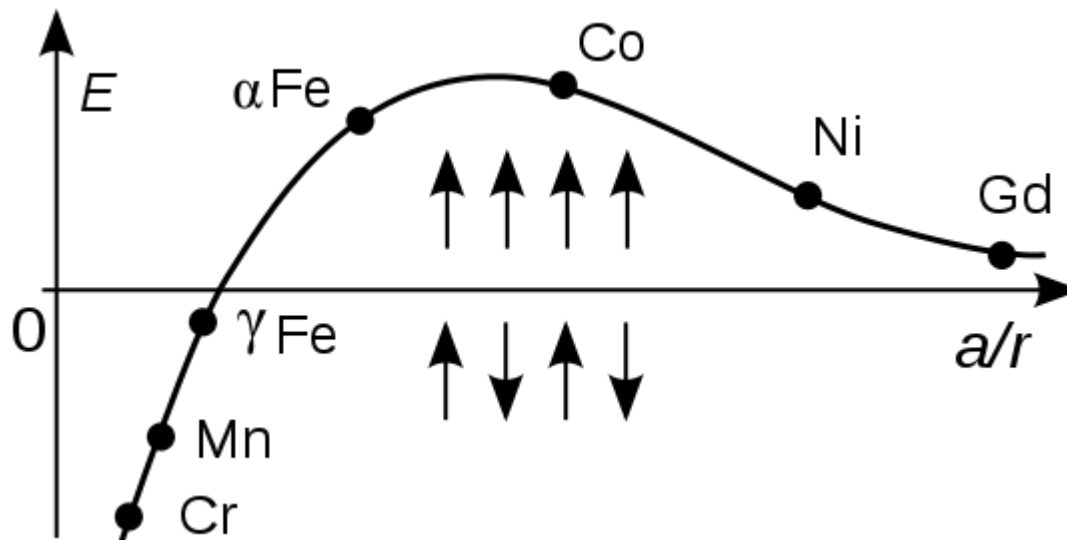
Cr, Mn, ... : antiferromagnetic
Fe, Co, Ni, ... : ferromagnetic

figure from chapter 2

Ferromagnetism (when happens)

Previous slide shows that the ordering of magnetic moments can take place. It can exist below temperature which increases with increasing absolute value of (Weiss) exchange energy.

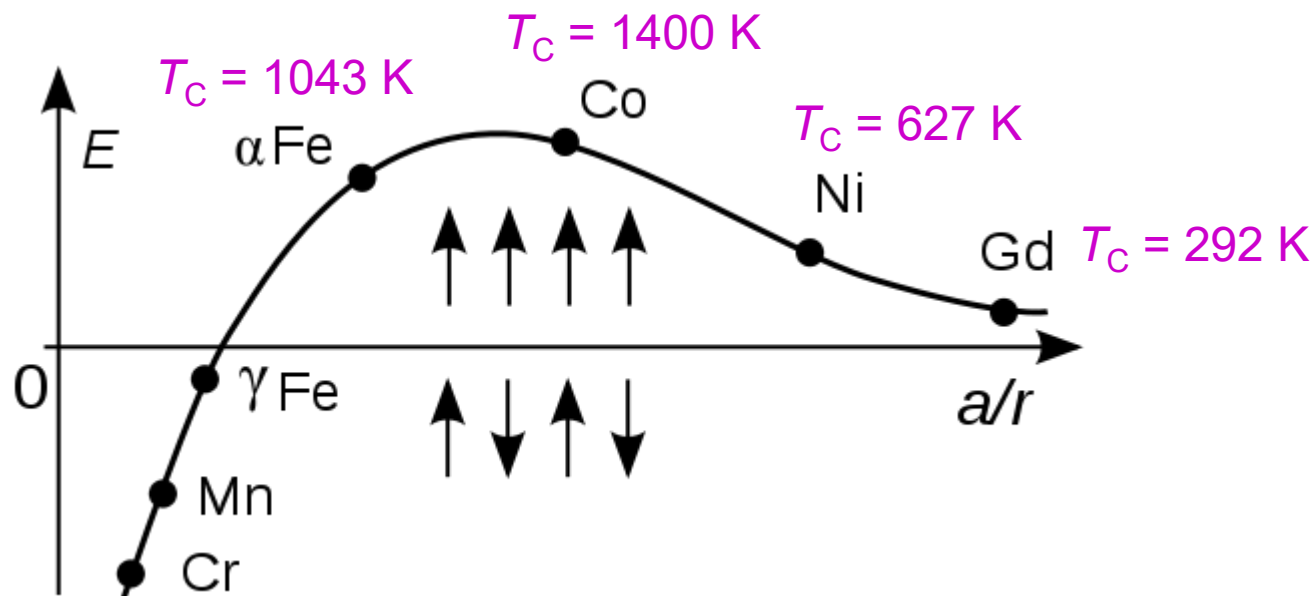
Within the first line of transition metals: dependence of exchange energy on the ratio of interatomic distance (a) and radius of 3d orbital (r) gives **Bethe-Slater curve** (ferro / antiferromag. ordering for positive/negative exchange energy)



Ferromagnetism (when happens)

Within the first line of transition metals: dependence of exchange energy on the ratio of interatomic distance (a) and radius of 3d orbital (r) gives **Bethe-Slater curve** (ferro / antiferromag. ordering for positive/negative exchange energy)

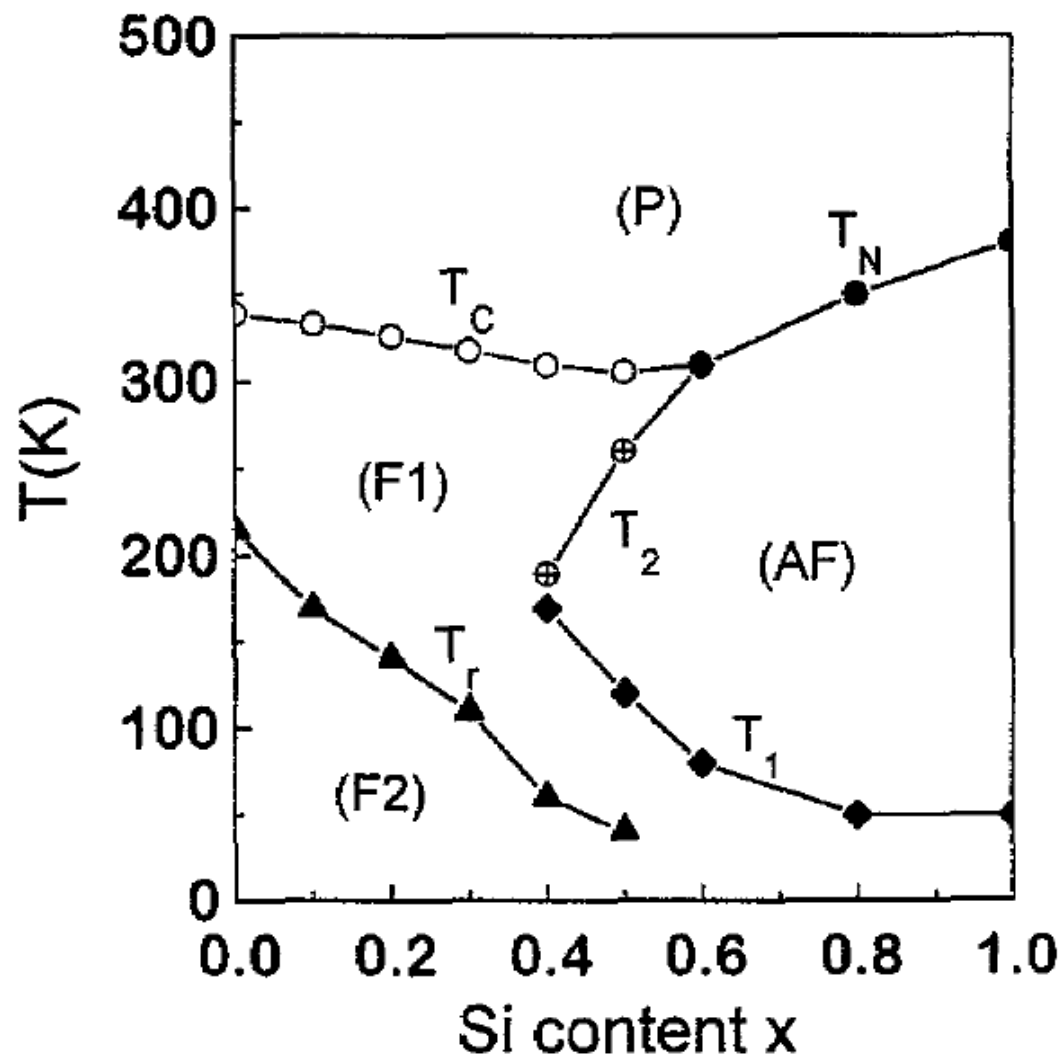
Monotonic dependence of Curie temperature on E



Sometimes it is not that simple

In some materials the magnetic ordering changes with temperature more than once.

Often 2× (AF-F-P),
e.g. for NdMn_2GeSi
(middle composition
in the figure) even
4× (F2-F1-AF-F1-P)



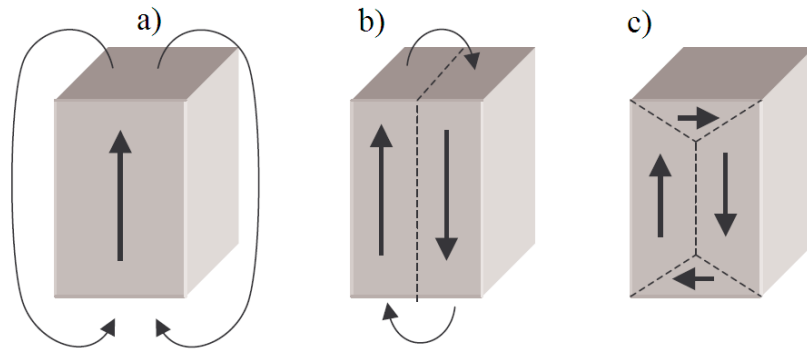
$\text{NdMn}_2(\text{Ge}_{1-x}\text{Si}_x)_2$

[Y. Wang et al, J. Alloy. Compd. 257, 19 (1997)]

Domain structure

If the spontaneous ordering of magnetic moments begins at more places simultaneously, their orientation does not have to be everywhere the same. At least two opposite directions along the same "easy axis" (see below). **Domain structure** forms

- energetically non-preferred from the exchange int. point of view
- energetically preferred due to saving energy needed to form magnetic field outside the material (see figure)

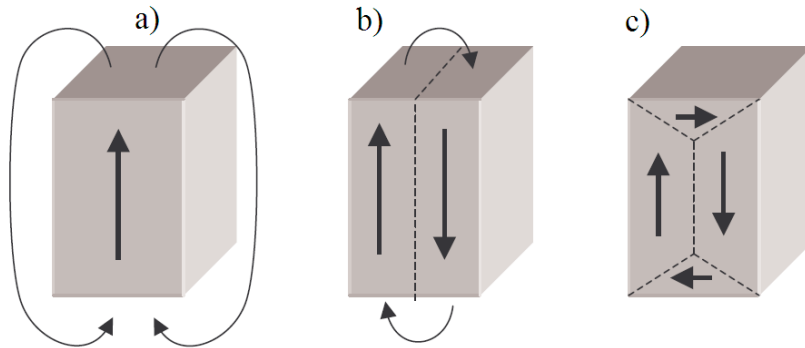


Thus, there is a domain size which is energetically most preferred. The real domain size (depending on magnetic, mechanical, thermal history) can be different.

Domain structure

If the spontaneous ordering of magnetic moments begins at more places simultaneously, their orientation does not have to be everywhere the same. Domain structure forms.

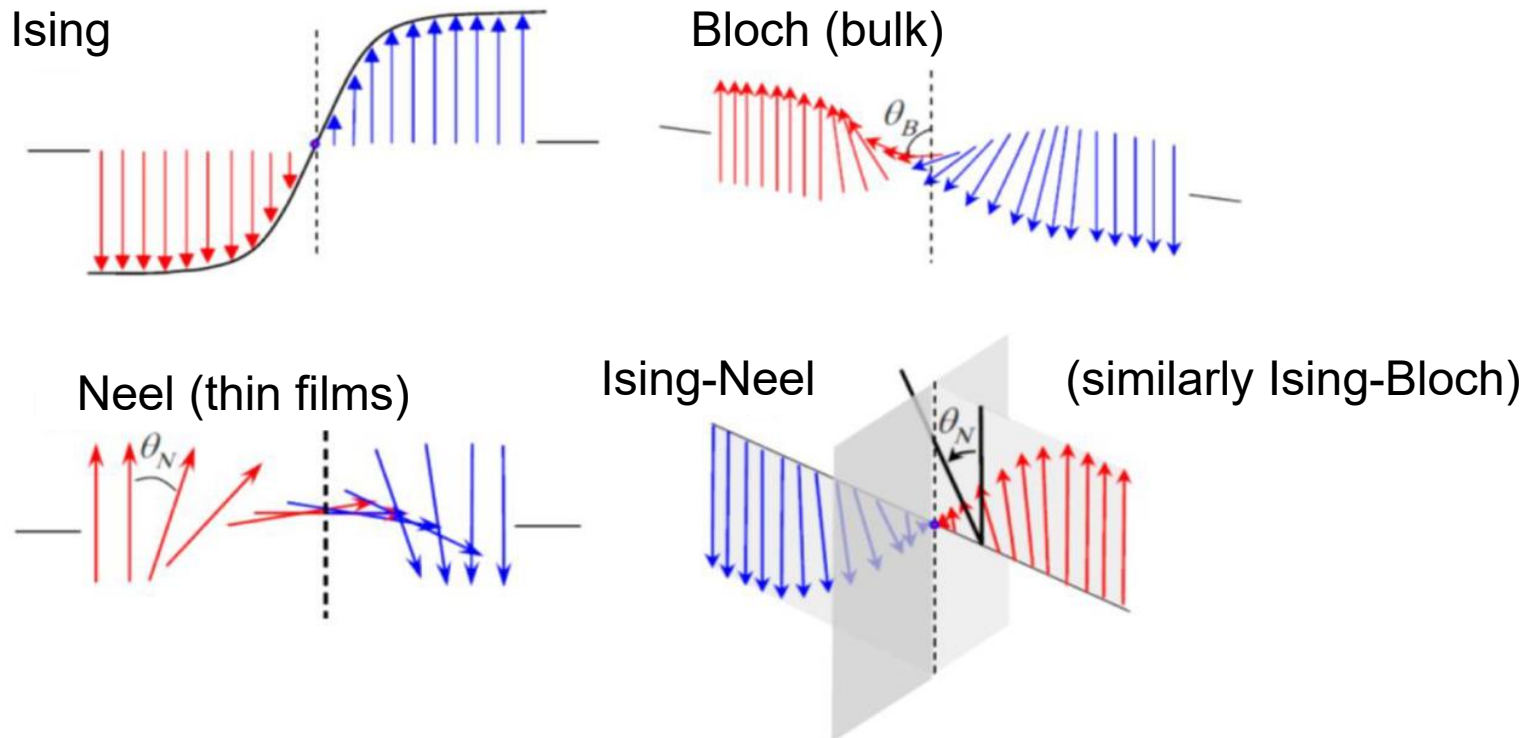
While individual domains have (below T_C) non-zero microscopic magnetization shown 6 slides above, the macroscopic magnetization can be zero.



Domain structure

If the spontaneous ordering of magnetic moments begins at more places simultaneously, their orientation does not have to be everywhere the same. Domain structure forms.

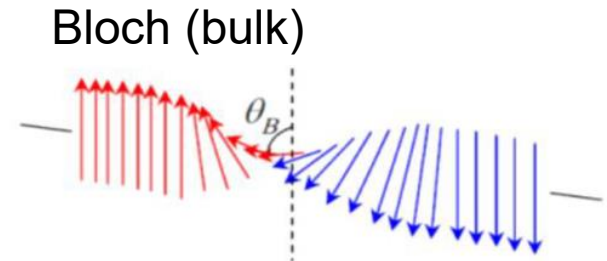
Various domain borders (e.g. depending on sample size):



Domain structure

If the spontaneous ordering of magnetic moments begins at more places simultaneously, their orientation does not have to be everywhere the same. Domain structure forms.

If there is a small angle φ (so small that $\cos \varphi \approx 1 - \varphi^2/2$) between two spins S , the exchange energy is proportional to $S^2 \varphi^2$. If the rotation of π is realized in N steps, the total exchange energy is lowered to $S^2 \pi^2 / N$ (iron: $N \approx 300$).



Magnetization curve of monocrystal

Spin-orbit coupling (let alone other effects) $\Rightarrow$ spin depends on shape of orbitals $\Rightarrow$ spin depends on its orientation in crystal $\Rightarrow$ magnetic properties of crystalline materials are anisotropic.
Mag. is easy along **easy axis**, difficult along **hard axis**.

During magnetization the spins

- 1) first order along such an easy axis which is relatively most parallel to the external field (growth of domains of this orientation and vice versa; weak external field is sufficient),
- 2) after that, the spins (domains) rotate from the approximately correct to the exactly correct direction (strong field needed)

bcc Fe: easy axis [100], hard axis [111]

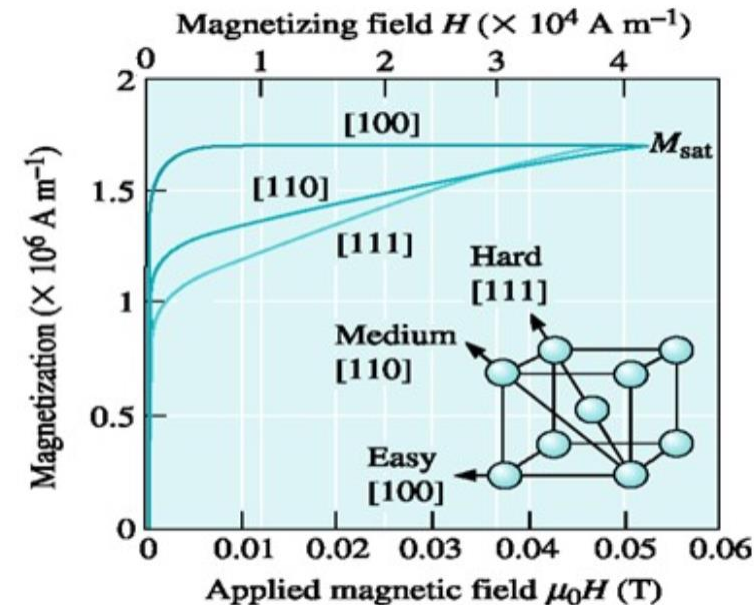
fcc Ni: easy axis [111], hard axis [100]

hcp Co: easy axis [0001], hard axis [10-10]

Magnetization curve of monocrystal

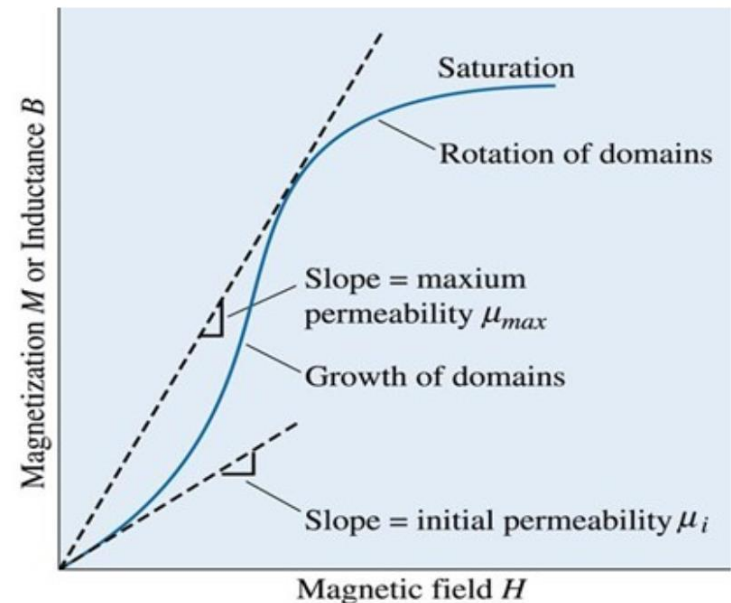
bcc Fe: easy axis [100], hard axis [111] - see the figure
(α -Fe, ferrite: up to 912 °C, incl. ferromagnet up to 770 °C)

- [100] (easy axis): magnetization caused by low external field almost corresponds to the final magnetization
- [110]: magnetization (to [100]) caused by low external field well corresponds to the final / $\sqrt{2}$
- [111]: magnetization (to [100]) caused by low external field well corresponds to the final / $\sqrt{3}$



Mag. curve of real material

- 1) The first part of the curve (very weak fields) is linear and reversible (the domain borders stop at the first defect)
- 2) The middle faster-than-linear part (Rayleigh law $M \sim H^2$) represents the growth of "approximately correctly" oriented domains. The material contains grain borders, dislocations, impurities, etc. The moving domain borders need energy to overcome them, therefore this is non-reversible.
- 3) The final slower-than-linear part represents the turning of domains to the correct direction

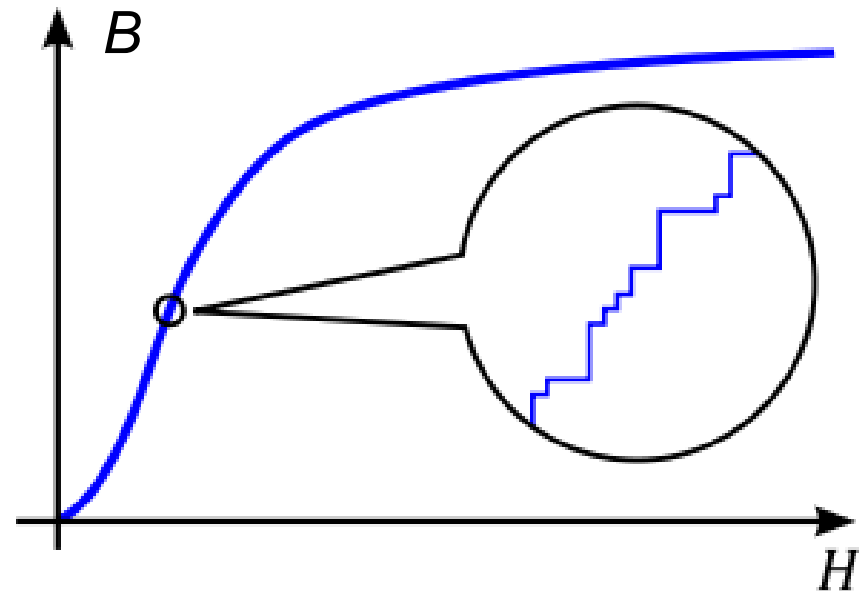


Mag. curve of real material

- 2) The middle faster-than-linear part (Rayleigh law $M \sim H^2$) represents the growth of "approximately correctly" oriented domains. The material contains grain borders, dislocations, impurities, etc. The moving domain borders need energy to overcome them, therefore this is non-reversible.

Overcoming of individual defects means that this part actually happens in steps - see the figure.

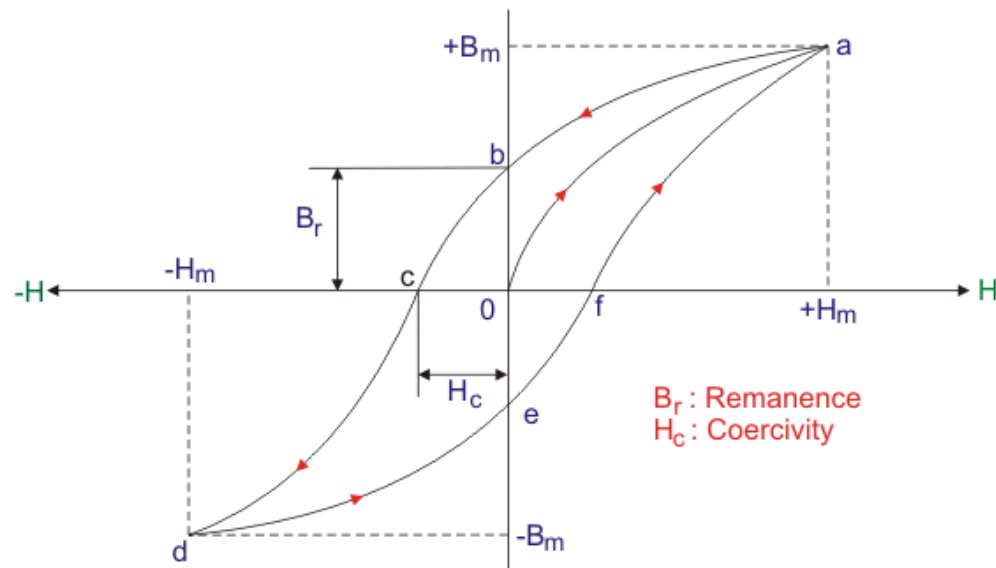
The overcoming of individual defects can be registered as cracking (Barkhausen effect).



Hysteresis curve

Formation, movement and perishment of domain walls is differently difficult in different mater. This defines how easily the domain structure changes with the magnetic field. Quantities:

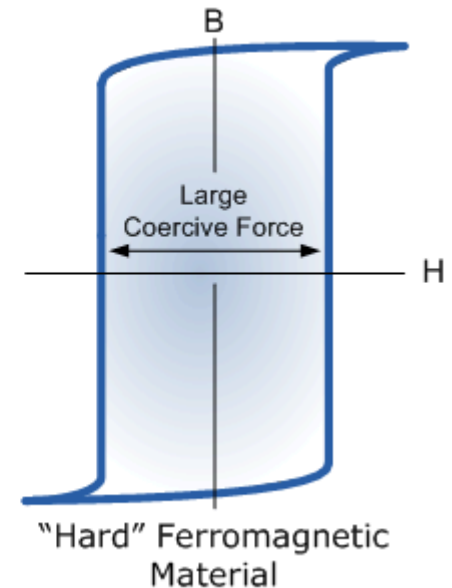
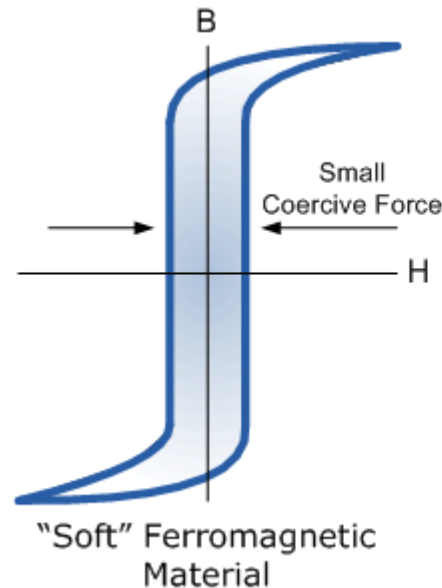
- B_r (remanent / residual magnetization after switching the external field off), or also ratio of B_r and a saturation value B_m
- H_c (coercitive field, needed to eliminate magnetization in the opposite direction), or also ratio of H_c and a saturation value H_m



Hysteresis curve

Formation, movement and perishment of domain walls is differently difficult in different mater. This defines how easily the domain structure changes. Ferromagnets can be divided to

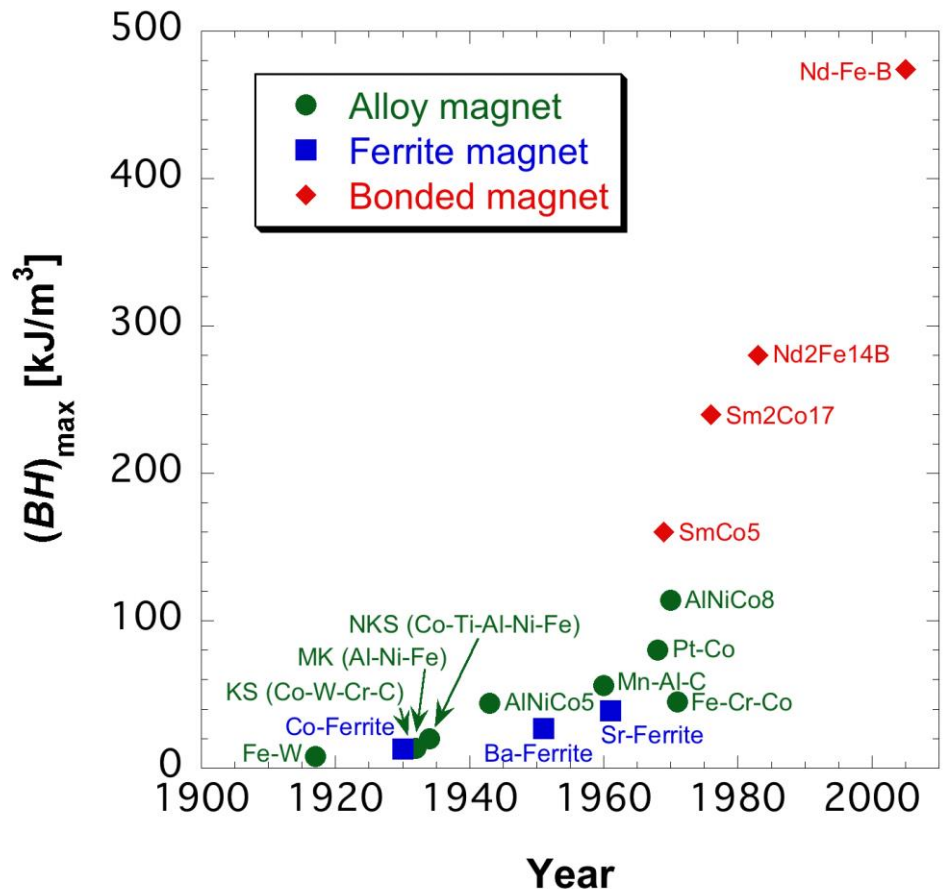
- Soft (low H_C):
e.g. transformer cores
- Hard (high H_C):
e.g. magnetic memories



Hysteresis curve

Formation, movement and perishment of domain walls is differently difficult in different mater. This defines how easily the domain structure changes. Ferromagnets can be divided to

- Soft (low H_C):
e.g. transformer cores
- Hard (high H_C):
e.g. magnetic memories



Ferromagnetism - summary

- Significantly (orders of mag.) strengthens the magnetic field (e.g. for 99.8% Fe $\chi = 5\,000$, for 99.95% Fe $\chi = 200\,000$)
- Can be described as paramagnetism with an additional internal Weiss field
- Exists up to Curie (ferro-, ferri-) or Neel (antiferro-) temperature, paramagnetism above it
- Domain structure (compromise between the energy of exchange interaction and energy needed to form field outside)
- Hysteresis curve (narrow/wide for soft/hard ferromagnets)

Magnetic force

A magnet does not only magnetize ferromagnetic (and to a lesser extent paramagnetic) materials around, it also attracts them. However, the force on charged particle (see also the reminder at the beginning of the chapter) $\mathbf{F} = q.(\mathbf{v} \times \mathbf{B})$ changes only the direction of its velocity, not the size of its velocity.

So where does the ability of magnets to lift objects (change the size of velocity of systems of charged particles) come from?

Magnetic force

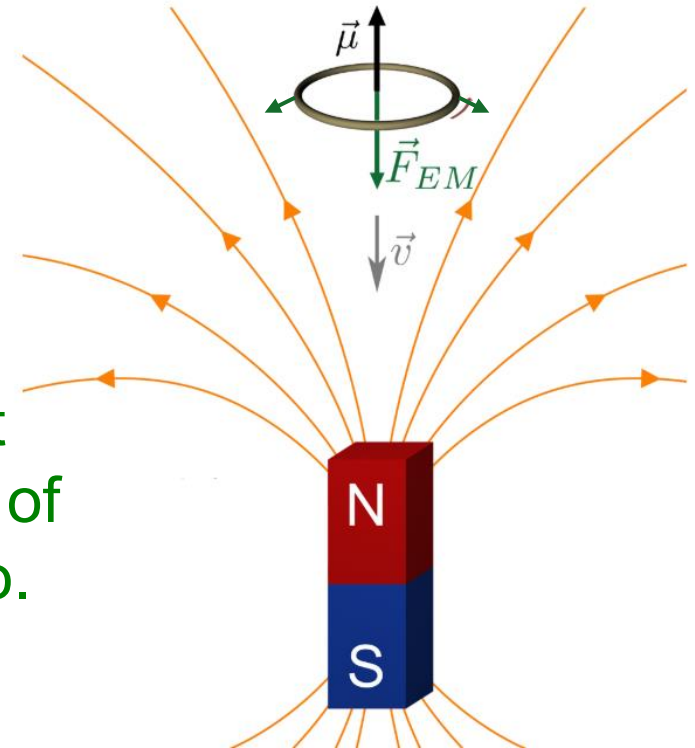
So where does the ability of magnets to lift objects (change the size of velocity of systems of charged particles) come from?

The above holds for free particles and/or particles in a homogeneous field.

When lifting objects,

- the particles inside are not free (to put it simple, they circulate around a fixed axis) and
- they are in inhomogeneous field.

Thus, the total force acting on a current loop (see the figure, showing elements of the total force at two points) is non-zero.

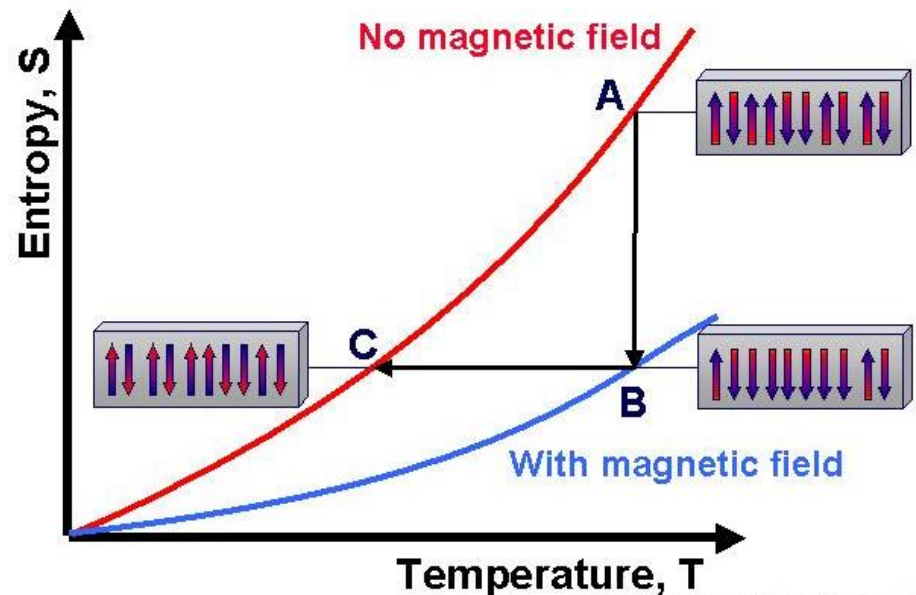


Adiabatic demagnetization

The entropy can be lowered

- (i) by lowering the temperature (at given external mag. field) or
- (ii) by ordering the spins (at given temperature)

By combining izotermic magnetization followed by adiabatic demagnetization, we can (on a one-time basis) cool the material
< 1 mK (electronic paramagnet)
<1 nK (nuclear paramagnet)



15) Superconductivity

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

Special fields

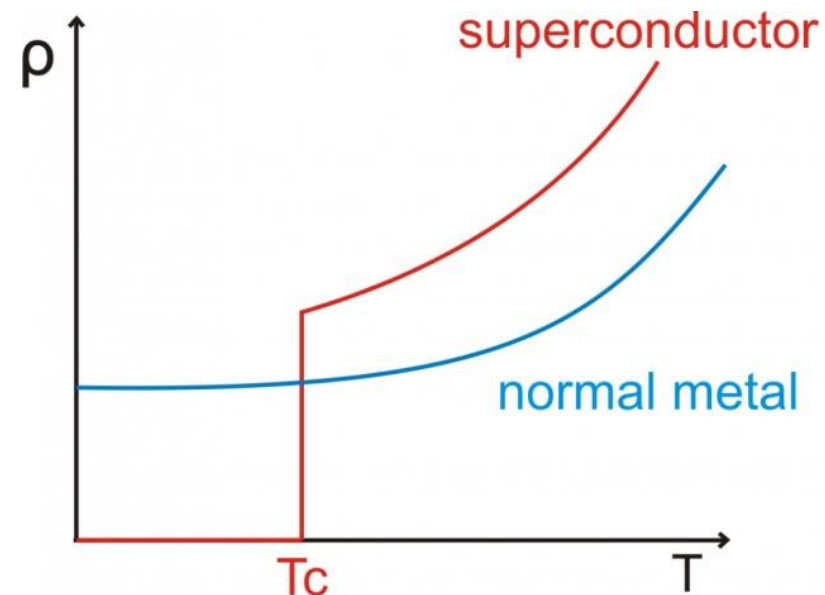
- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

What characterizes superconductivity

Superconductive state of some mat. below the critical temp. (T_C)

⇒ electrical resistivity drops to zero (not only towards zero)
checked with error $< 10^{-25} \Omega\text{m} \Leftrightarrow$ decay time $> 100\,000$ years

⇒ relative permeability drops to zero
(not only slightly below 1 like in normal diamagnetics),
i.e. the material becomes an ideal diamagnetic,
expels the magnetic field
(Meissner - Ochsenfeld effect)



What characterizes superconductivity

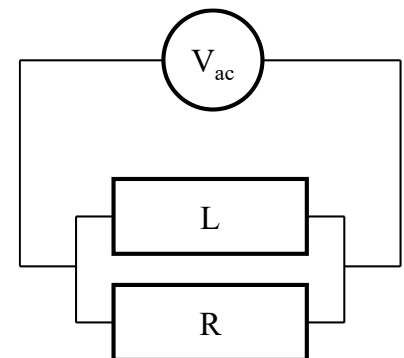
Superconductive state of some mat. below the critical temp. (T_C)

⇒ electrical resistivity drops to zero

⇒ relative permeability drops to zero

Notes about the first of these effects

- Ohm law $I = U/R = U/0$ does not mean that the current through a superconductor can be infinite ($\leq \approx 10^{10} \text{A/m}^2$), see also below
- the zero dc resistivity does not change the fact that it takes non-zero time to accelerate electrons with non-zero mass, i.e. superconductor still has non-zero kinetic inductance (e.g. for 1 kHz $\omega L \approx 10^{-12} R_{\text{normal}}$)



What characterizes superconductivity

Superconductive state of some mat. below the critical temp. (T_c)

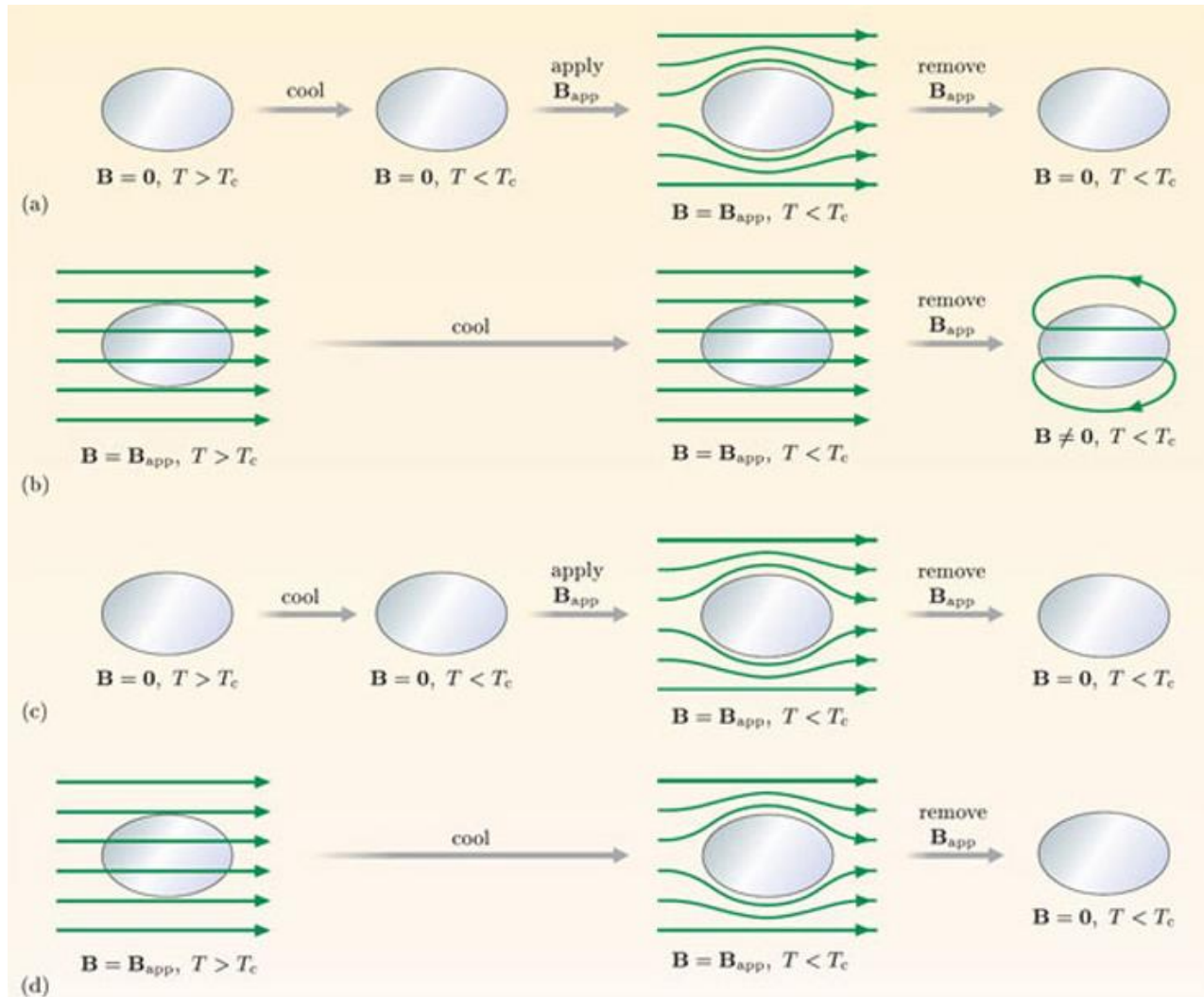
⇒ electrical resistivity drops to zero

⇒ relative permeability drops to zero

Notes about the second of these effects

- do not confuse expulsion of mag. field from a superconductor with an EM induction (magnetic field induces currents, which give rise to a magnetic field with an opposite sign)
- thus, for a supercond. state we need not only low temperature, but also sufficiently low magnetic field (so it can be expelled)
- there is a possibility to trap magnetic field inside material, if its surface cools down (becomes superconducting) first

Superconductor × perfect conductor



Perfect conductor
(flux **conserving**):
final state **does**
depend on the
order of cooling
and switching B_{app}

Superconductor
(flux **expelling**):
final state **does**
not depend on the
order of cooling
and switching B_{app}

Penetration depth of B

First of all a reminder of Maxwell equations

Name	$\mathbf{E}$ and $\mathbf{B}$	$\mathbf{E}$, $\mathbf{B}$, $\mathbf{D}$, and $\mathbf{H}$
Coulomb's law of electrostatics, or Gauss's Law:	$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon}$	$\nabla \cdot \mathbf{D} = \rho$
Absence of magnetic monopoles:	$\nabla \cdot \mathbf{B} = 0$	$\nabla \cdot \mathbf{B} = 0$
Faraday's Law of Induction:	$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$	$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$
Ampère's Law, or the Biot-Savart Law, plus displacement current:	$\nabla \times \mathbf{B} = \mu \mathbf{J} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}$	$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}$

The field B inside a superconductor is zeroed by shielding currents circulating in a surface layer of low but non-zero thickness. Thus, B does not drop to zero, but smoothly approaches zero at a distance corresponding to this thickness.

Penetration depth of B

usual equation of motion $m.d\mathbf{v}/dt = q\mathbf{E} - m\mathbf{v}/\tau$
converts to $m.d\mathbf{v}/dt = q\mathbf{E}$

in parallel, the flux density $\mathbf{j} = -nq\mathbf{v}$
so $d\mathbf{j}/dt = nq^2/m.\mathbf{E}$

(first London eq. : both perfect conductor and superconductor)
and $\text{rot } d\mathbf{j}/dt = nq^2/m.\text{rot } \mathbf{E}$

third Maxwell equation $\text{rot } \mathbf{E} = -d\mathbf{B}/dt$
so $\text{rot } d\mathbf{j}/dt = -nq^2/m.d\mathbf{B}/dt$
and $\text{rot } \mathbf{j} = -nq^2/m.\mathbf{B}$

(second London eq. : only superconductor)

based on the experience with superconductors, we have chosen zero integration constant (the first L. equation says that the term $\text{rot } \mathbf{j} + nq^2/m.\mathbf{B}$ is constant, for superconductors it is zero)

Penetration depth of B

third Maxwell equation

$$\text{rot } \mathbf{E} = -d\mathbf{B}/dt$$

so

$$\text{rot } d\mathbf{j}/dt = -nq^2/m.d\mathbf{B}/dt$$

and

$$\text{rot } \mathbf{j} = -nq^2/m.\mathbf{B}$$

(second London eq. : only superconductor)

fourth Maxwell equation

$$\mathbf{j} = 1/\mu_0 . \text{rot } \mathbf{B} \text{ (pro } d\mathbf{E}/dt = 0)$$

so

$$1/\mu_0 . \text{rot rot } \mathbf{B} = -nq^2/m.\mathbf{B}$$

and

$$1/\mu_0 . (\text{grad div } \mathbf{B} - \Delta\mathbf{B}) = -nq^2/m.\mathbf{B}$$

second Maxwell equation

$$\text{div } \mathbf{B} = 0$$

so

$$\Delta\mathbf{B} = \mu_0 nq^2/m.\mathbf{B} = (1/\lambda^2).\mathbf{B}$$

solution in 1D

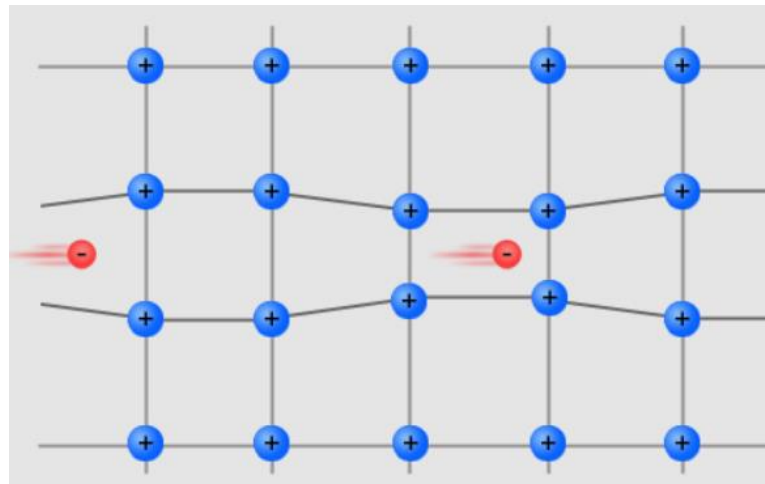
$$\mathbf{B} = \mathbf{B}_{\text{app}} e^{-(x/\lambda)}$$

i.e. B penetrates to (decays within) $\lambda = \sqrt{(m/\mu_0 nq^2)} = \text{tens nm}$

BCS theory of superconductivity

John Bardeen, Leon Cooper a John Robert Schrieffer
Nobel prize 1972 (J.B. the only winner of two NCs for physics)

Principle: pairs of electrons (more pairs with decreasing temp.) create bonded **Cooper pairs**. Electrons (despite Coulombian repulsion) are bonded in that way that they share the same lattice vibration, same phonon). Another point of view: the first electron deforms the lattice of cations during its movement, locally increases their concentration, this attracts the other el. .



BCS theory of superconductivity

First electron deforms the lattice of cations during its movement, locally increases their concentration, this attracts the other electron.

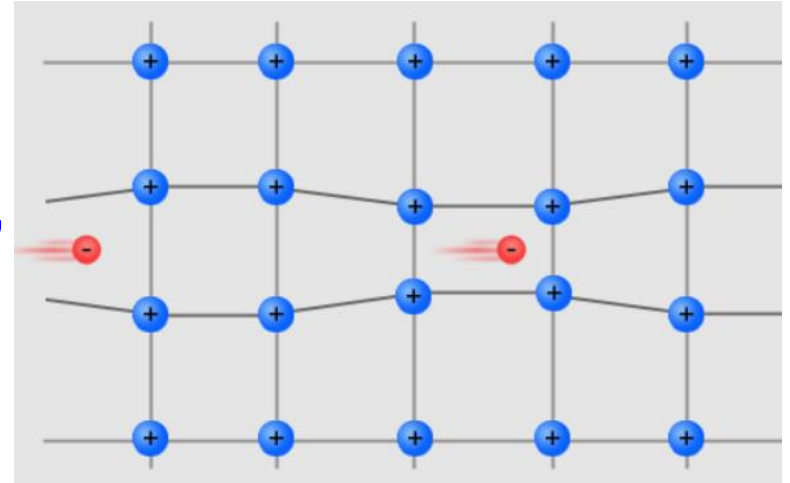
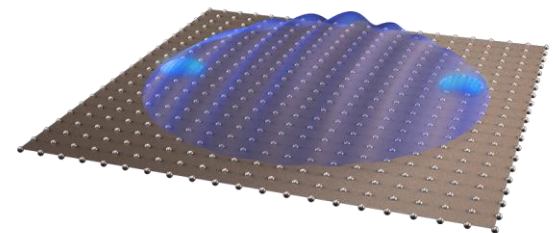
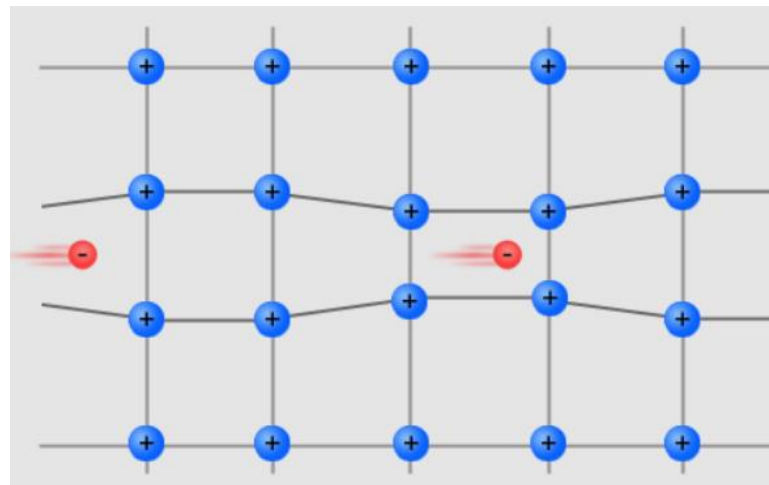


Figure is illustrative: in general, electrons do not have velocities parallel to the line connecting them, instead they orbit around each other shifted by half of the circle (opposite velocities). At the same time the circle center moves $\Rightarrow$ electrical current.



BCS theory of superconductivity

First electron deforms the lattice of cations during its movement, locally increases their concentration, this attracts the other electron.



Strong reaction to the electron passage (electron-phonon coupling) is necessary, which harms normal conductivity

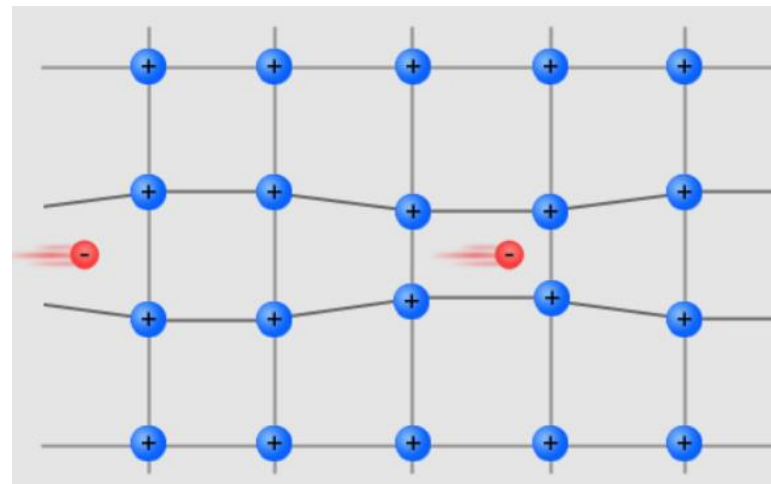


best conductors (Cu, Ag, Au, ...)
do not exhibit superconductivity

[illegible]

BCS theory of superconductivity

First electron deforms the lattice of cations during its movement, locally increases their concentration, this attracts the other electron.



Reaction to the el. passage must constitute the main deformation (not lost in normal thermal vibrations)
⇒ low-temperature phenomenon

1																	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
1	H	IIA																III A	IV A	V A	VI A	VII A	He														
2	3	Li	4	Be																	5	B	6	C	7	N	8	O	9	F	10	Ne					
					■ BLUE = AT AMBIENT PRESSURE ■ GREEN = ONLY UNDER HIGH PRESSURE																																
3	11	Na	12	Mg	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar																					
					III B	IV B	V B	VI B	VII B	VIII		IX	X	XI	XII																						
4	19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr	
5	37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe	
6	55	Cs	56	Ba	57	*La	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn	
7	87	Fr	88	Ra	89	+Ac	104	Rf	105	Ha	106	107	108	109	110	111	112																				

* Lanthanide Series

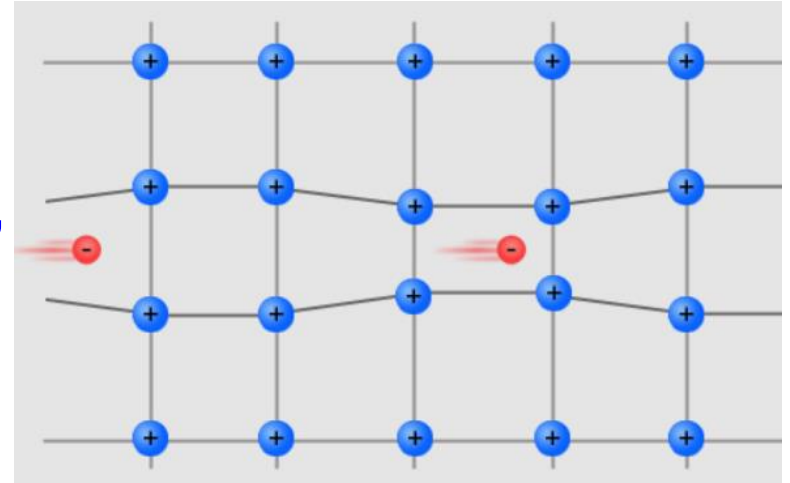
58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

+ Actinide Series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

BCS theory of superconductivity

First electron deforms the lattice of cations during its movement, locally increases their concentration, this attracts the other electron.



The lattice reacts in $2\pi/\omega_D$

$$\approx 10^{-13} \text{ s}$$

Electron moves by velocity

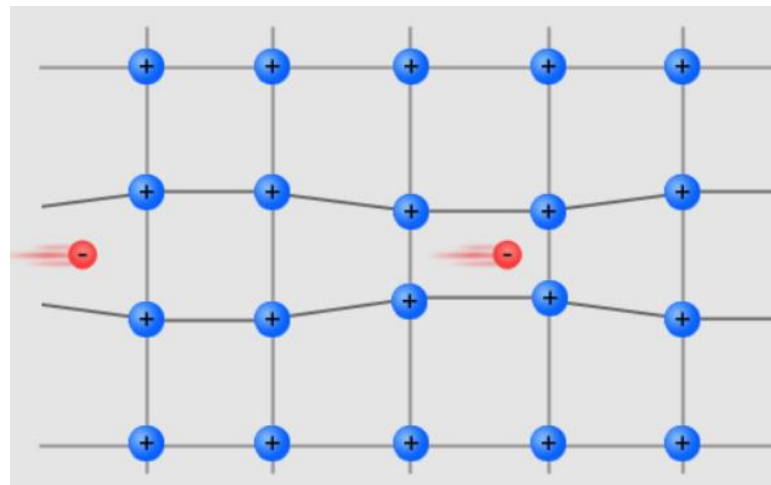
$$\approx 10^6 \text{ ms}^{-1}$$

Distance of electrons bonded in this way is **$\approx 10^{-7} \text{ m} = 100 \text{ nm}$**

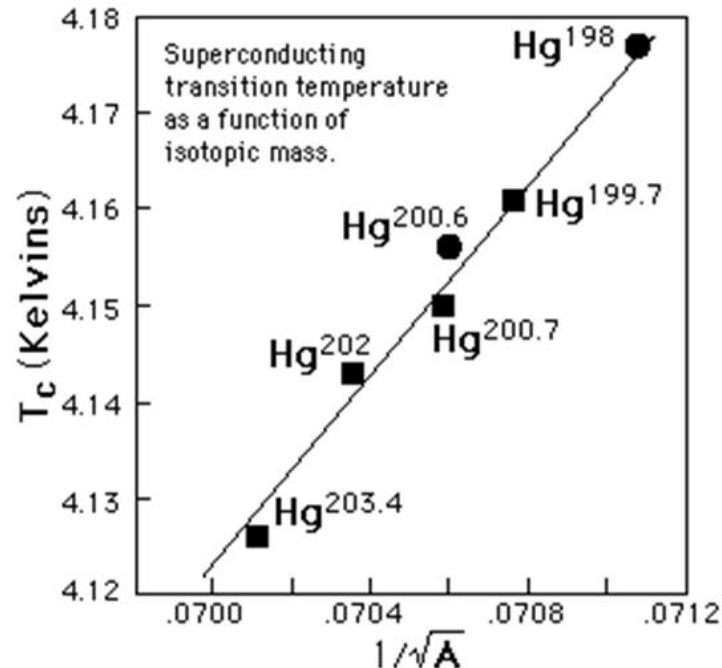
(more than the distance to another conductive electron not included in the Cooper pair, i.e. the pairs overlap)

BCS theory of superconductivity

First electron deforms the lattice of cations during its movement, locally increases their concentration, this attracts the other electron.



Isotope effect: for given element in given structure, lighter isotopes exhibit stronger reaction to electron passage $\Rightarrow$ easier formation of C. pair $\Rightarrow$ higher T_C . Agrees with BCS theory, contrary to efforts to explain supercond. electronically.



BCS theory of superconductivity

Principle: pairs of electrons form bonded **Cooper pairs**

They are quasiparticles (not unprecedented - note e.g. the holes in semiconductors and their effective mass) with integer spin 0 or 1, usually 0 (electrons with opposite spins bond better)

Conductive electrons above T_C : fermions, each in own state, scatter on lattice defects independently of each other

Cooper pairs below T_C : bosons, condense in single shared ground state, scattering would have to happen to all of them at once (extremely unlikely) - **therefore superconductivity**

BCS theory of superconductivity

Cooper pairs below T_C : bosons

More precisely quasibosons:

- they remember that they are system of fermions, i.e. like any other system of any other number of fermions must have antisymmetric wavefunction with respect to exchange of electrons (not to be confused with exchange of whole C. pairs)
- contrary to other systems of fermions they are extremely delocalized (the aforementioned electronic distance on the order of hundreds nm), so in praxis they often behave like bosons in that way that they condense in a single state, i.e. ignore Pauli principle

Quasiparticles

The Cooper pair is the last quasiparticle introduced here - a good opportunity to summarize all of them

Quasiparticles in the narrow sense. Resemble real particles.

- electron (different dispersion rel. - chapter 7 - than free one)
- hole (not even exists as a free one)
- exciton (bound state of electron and hole, which do not conduct current but keep close to each other after the excitation)
- Cooper pair (bound state of two electrons)

Quanta of energy related to a collective excitation of many particles. Do not resemble real particles in the background.

- phonon (correlated movement of atoms, chapter 2)
- plasmon (correlated movement of electrons, chapter 10)
- magnon (correlated movement of spin moments)

BCS theory of superconductivity

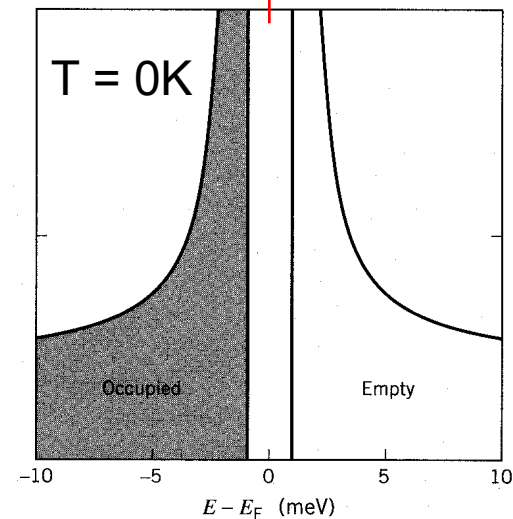
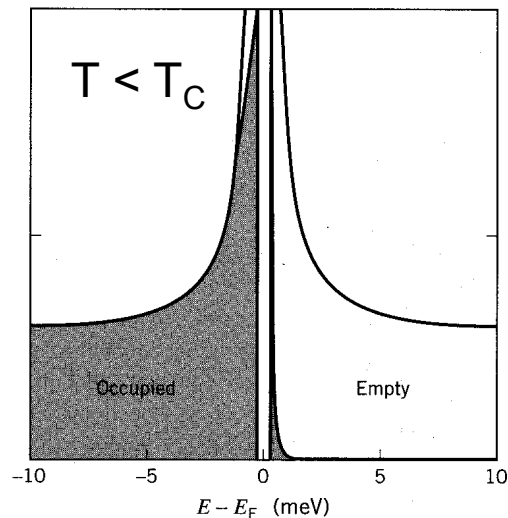
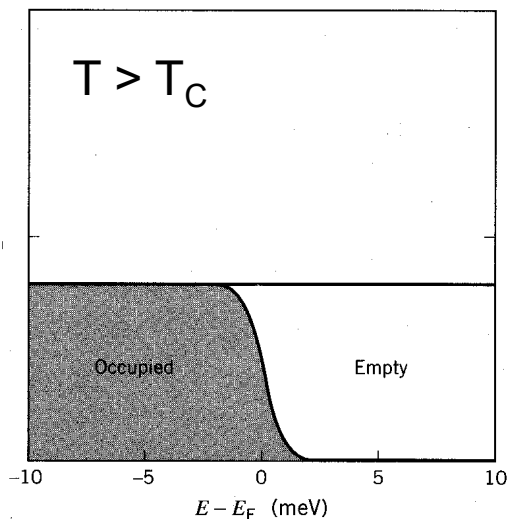
After the transition to the superconductive state, band gap opens. Its width 2Δ corresponds to bonding energy of C. pair.

$$2\Delta(0\text{K}) = 3.53k_{\text{B}}T_{\text{C}}, \text{ for example}$$

$$\text{Al} \quad 2\Delta = 0.34 \text{ meV} = 3.3kT_{\text{C}} \quad (T_{\text{C}} = 1.2 \text{ K})$$

$$\text{YBa}_2\text{Cu}_3\text{O}_{7-x} \quad 2\Delta = 30 \text{ meV} = 4.0kT_{\text{C}} \quad (T_{\text{C}} = 92 \text{ K, or } >100 \text{ K})$$

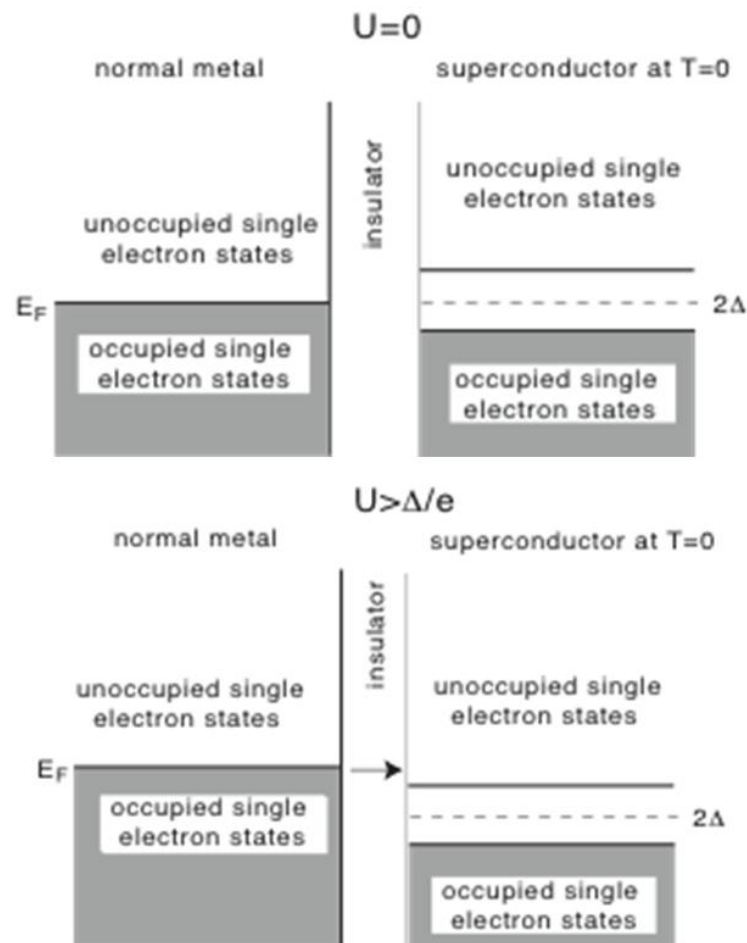
$$2\Delta(T) = 2\Delta(0\text{K}).(1-[T/T_{\text{C}}]^2)$$



BCS theory of superconductivity

After the transition to the superconductive state, band gap opens. Its width 2Δ corresponds to bonding energy of C. pair.

Measurement (in parallel to optical methods) using the voltage which, due to the shift of Fermi level, leads to tunneling from metal to superconductor: NIS junction



BCS theory of superconductivity

After the transition to the superconductive state, band gap opens. Its width 2Δ corresponds to bonding energy of C. pair.

Density of electrons in Cooper pairs is $g(E_F) \cdot \Delta$ where g is the density of states, after the condensation their energy drops on the average of 0.5Δ , i.e. the total energy of $1/2 g(E_F) \cdot \Delta^2$

Density of magnetic field energy is $1/2 B^2 / \mu_0$



$$B_C = \sqrt{[\mu_0 \cdot g(E_F)] \cdot \Delta}$$

Critical current

Thus, the current through superconductor is limited not only because it is realized by finite number of electrons moving by finite velocity, but also for more fundamental reasons

Current I through a wire of diameter r induces mag. field on its surface $H_l = I/(2\pi r)$. Superconductivity disappears for $H_l > H_c$.



$$I_c = 2\pi r H_c = 2\pi r B_c / \mu_0$$

Values like 10^{10}A/m^2 , but not infinity

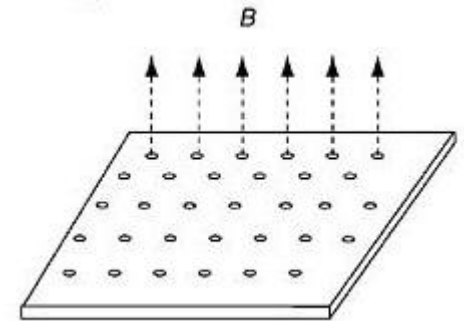
Types of superconductivity

Type I (straightforward case described by the BCS theory)

- typically pure metals
- first order phase transition (latent heat)
- uncompromising relationship to magnetic field:
can expel strong fields (ideal diamagnetic),
but once it cannot the superconductivity disappears

Type II (even more useful - higher critical temp. and mag. field)

- typically alloys
- second order phase transition
- smoother relationship to magnetic field :
only weak fields can be expelled from whole
volume, which is followed by a wide range
of fields expelled from part of the volume (so called **vortices**,
parallel non-supercond. cylinders, appear), superconductivity
between vortices disappears only for very strong fields

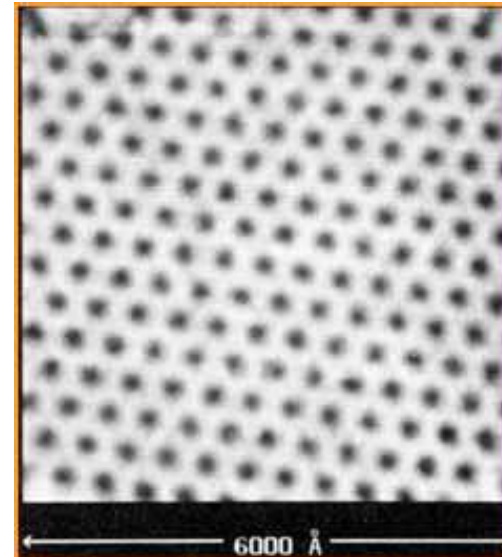


Types of superconductivity

Type II

- only weak fields can be expelled from whole volume, wide range of fields expelled from part of the volume (**vortices**), supercond. between vortices disappears for very strong fields

hexagonal lattice of vortices
(STM; ordering disappears
with increasing external field)



[H.F. Hess et al., Phys. Rev. Lett. 62, 214 (1989)]

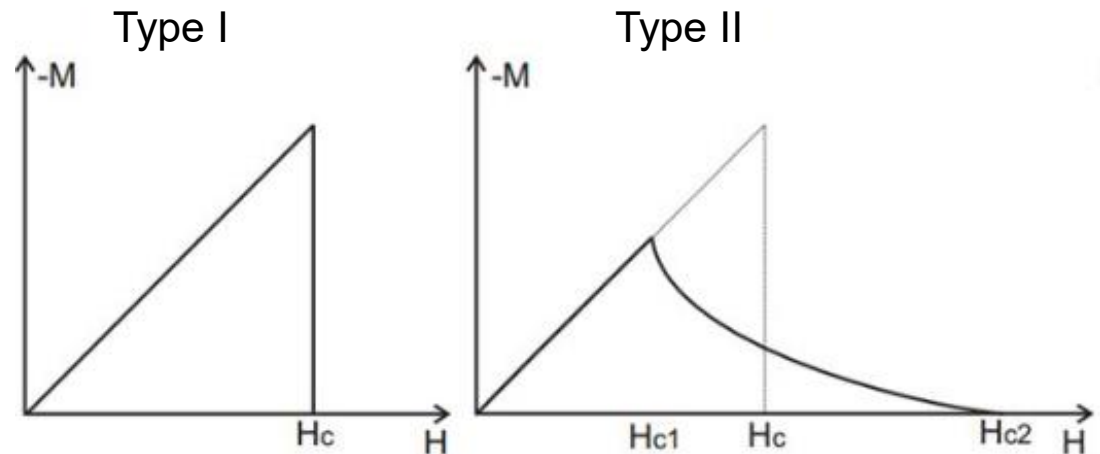
Types of superconductivity

Type I

- can expel strong fields (ideal diamagnetic), but once it cannot the superconductivity disappears

Type II

- only weak fields can be expelled from whole volume, wide range of fields expelled from part of the volume (**vortices**), supercond. between vortices disappears for very strong fields



Types of superconductivity

Type I

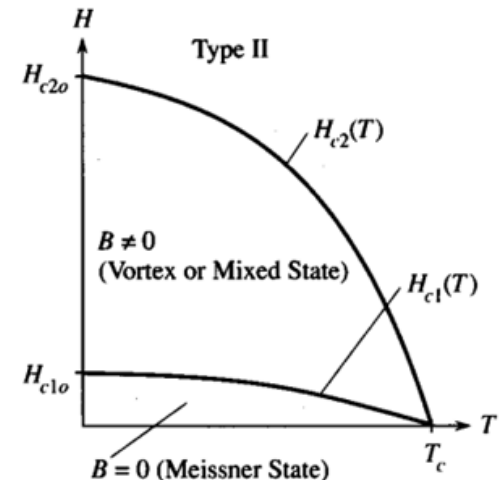
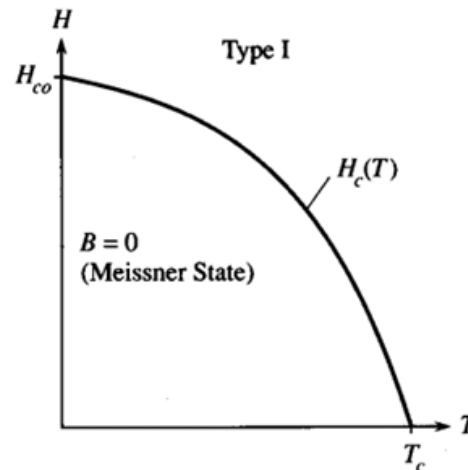
- can expel strong fields (ideal diamagnetic), but once it cannot the superconductivity disappears

Type II

- only weak fields can be expelled from whole volume, wide range of fields expelled from part of the volume (**vortices**), supercond. between vortices disappears for very strong fields

critical fields obviously depend on temperature, for type I

$$H_C = H_{C0}(1-[T/T_C]^2)$$

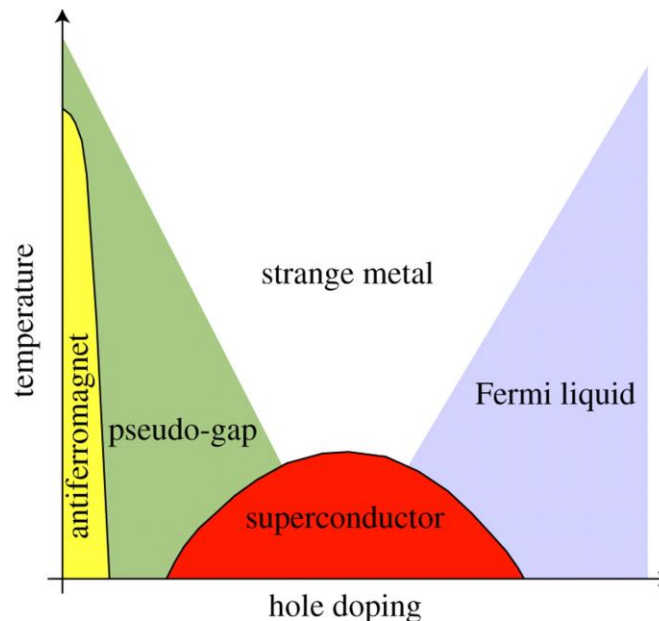


Type II superconductivity

Principle is still the same: role of Cooper pairs

Details are more complicated:

- Cooper pairs rather formed by holes
- role of antiferromagnetic ordering and magnetic interactions in general (movement of the first electron induces a wave of spin fluctuations, this attracts the other electron)



Ginzburg-Landau theory

Penetration depth of magnetic field λ (see above): lower $\lambda \Rightarrow$ energetically expensive expulsion of B from larger volume

Coherence length of Cooper pairs ξ , i.e. how far from the boundary reaches their wavefunction its maximum:
lower $\xi \Rightarrow$ energetically preferred formation of more C. pairs

Coherence length is different quantity than the aforementioned size of Cooper pairs (distance of electrons of hundreds nm), although the order of magnitude is often the same

Relationship with uncertainty relations:

$$\delta p \cdot \delta x \approx \hbar$$

$$\delta E / v_F \cdot \delta x \approx \hbar$$

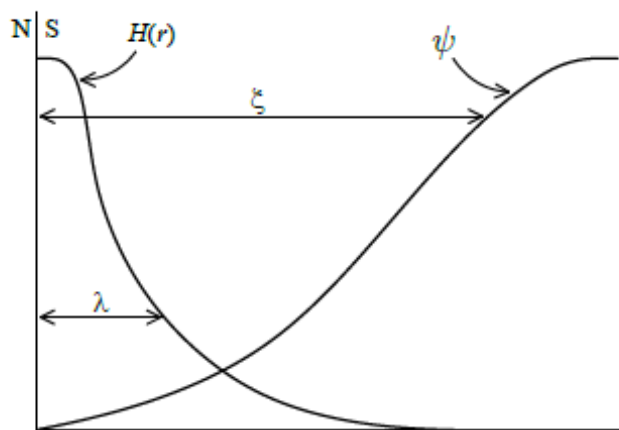
$$\Delta / v_F \cdot \xi \approx \hbar$$

Ginzburg-Landau theory

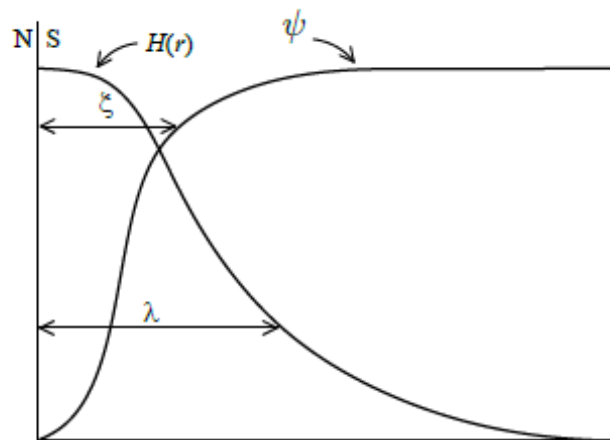
Penetration depth of magnetic field λ (see above): lower $\lambda \Rightarrow$ energetically expensive expulsion of B from larger volume

Coherence length of Cooper pairs ξ , i.e. how far from the boundary reaches their wavefunction its maximum: lower $\xi \Rightarrow$ energetically preferred formation of more C. pairs

The energetical cost of the boundary and in turn the supercond. type is decided by the Ginzburg-Landau parameter $\kappa = \lambda/\xi$



(a) $\kappa \ll 1$



(b) $\kappa \gg 1$

Ginzburg-Landau theory

Penetration depth of magnetic field λ (see above): lower $\lambda \Rightarrow$ energetically expensive expulsion of B from larger volume

Coherence length of Cooper pairs ξ , i.e. how far from the boundary reaches their wavefunction its maximum:
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The energetical cost of the boundary and in turn the supercond. type is decided by the Ginzburg-Landau parameter $\kappa = \lambda/\xi$

$\lambda/\xi < 1/\sqrt{2}$: energy of boundary is positive, i.e. system tries to minimize them (type I superconductors)

$\lambda/\xi > 1/\sqrt{2}$: energy of boundary is negative, i.e. system forms as many of them as possible ($\Rightarrow$ vortices in type II supercond.)

Ginzburg-Landau theory

$\lambda/\xi < 1/\sqrt{2}$: energy of boundary is positive, i.e. system tries to minimize them (type I superconductors)

$\lambda/\xi > 1/\sqrt{2}$: energy of boundary is negative, i.e. system forms as many of them as possible ($\Rightarrow$ vortices in type II supercond.)

same examples as above (where only 2Δ and T_C were given)

Al (type I)

$$2\Delta = 0.34 \text{ meV}$$

$$T_C = 1.2 \text{ K}$$

$$\xi = 1600 \text{ nm}$$

$$\lambda = 50 \text{ nm}$$

$$\mu_0 H_C = 0.01 \text{ T}$$

YBa₂Cu₃O_{7-x} (type II)

$$2\Delta = 30 \text{ meV}$$

$$T_C = 92 \text{ K}$$

$$\xi = 15 \text{ nm}$$

$$\lambda = 200 \text{ nm}$$

$$\mu_0 H_C = 150 \text{ T}$$

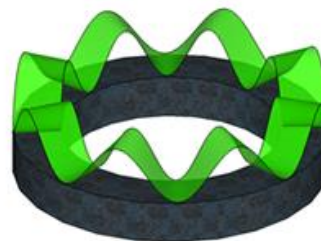
Quantized magnetic flux

Contrary to localized electrons (wave packets), Cooper pairs are described by a wave which is everywhere at once

While a localized wave can change its phase after an orbit, continuous wave cannot



not this way



but this way

In parallel, if a magnetic flux Φ goes through (is trapped in) a ring, wavefunction of charged particle changes after orbiting this ring by factor $e^{(iq\Phi/\hbar c)}$

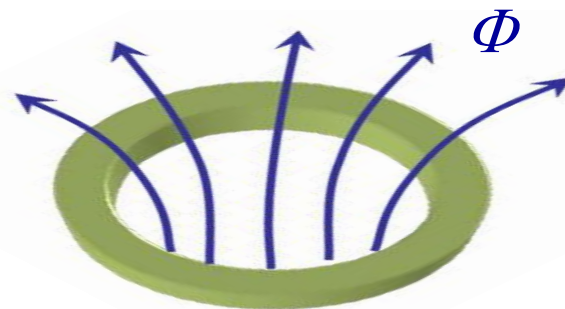
Quantized magnetic flux

In parallel, if a magnetic flux Φ goes through (is trapped in) a ring, wavefunction of charged particle changes after orbiting this ring by factor $e^{(iq\Phi/\hbar c)}$

Therefore it must hold $q\Phi/\hbar c = 2\pi n$
where for Cooper pair $q = 2e$
(sign does not matter now)



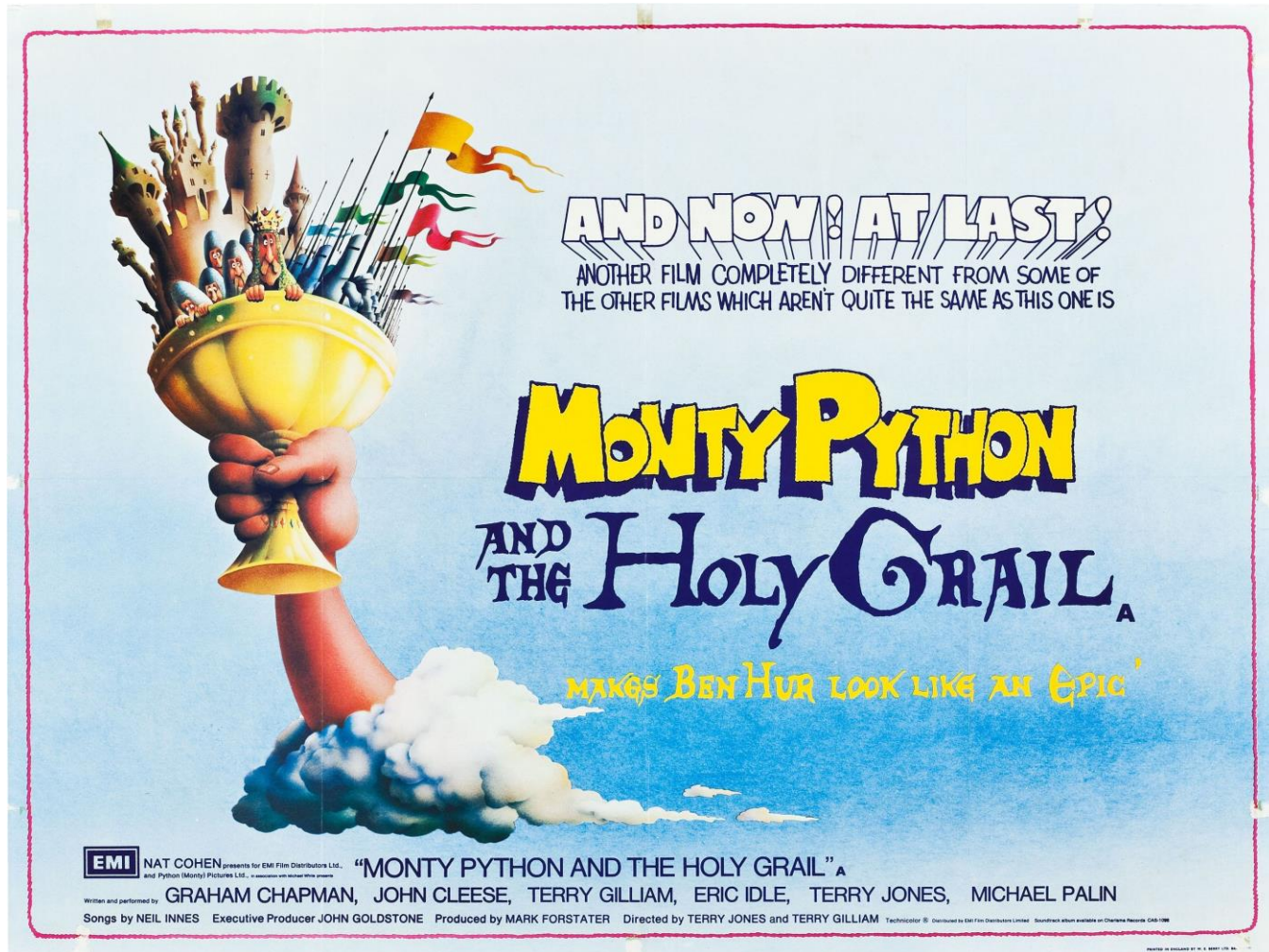
$$\Phi = n \cdot \pi \hbar c / e = n \cdot hc / 2e = n \cdot 2 \times 10^{-15} \text{ Tm}^2$$



I.e. magnetic flux, not quantized in other cases, is quantized inside a superconducting ring. Magnetic flux through vortices in a type II superconductor constitutes a crucial example.

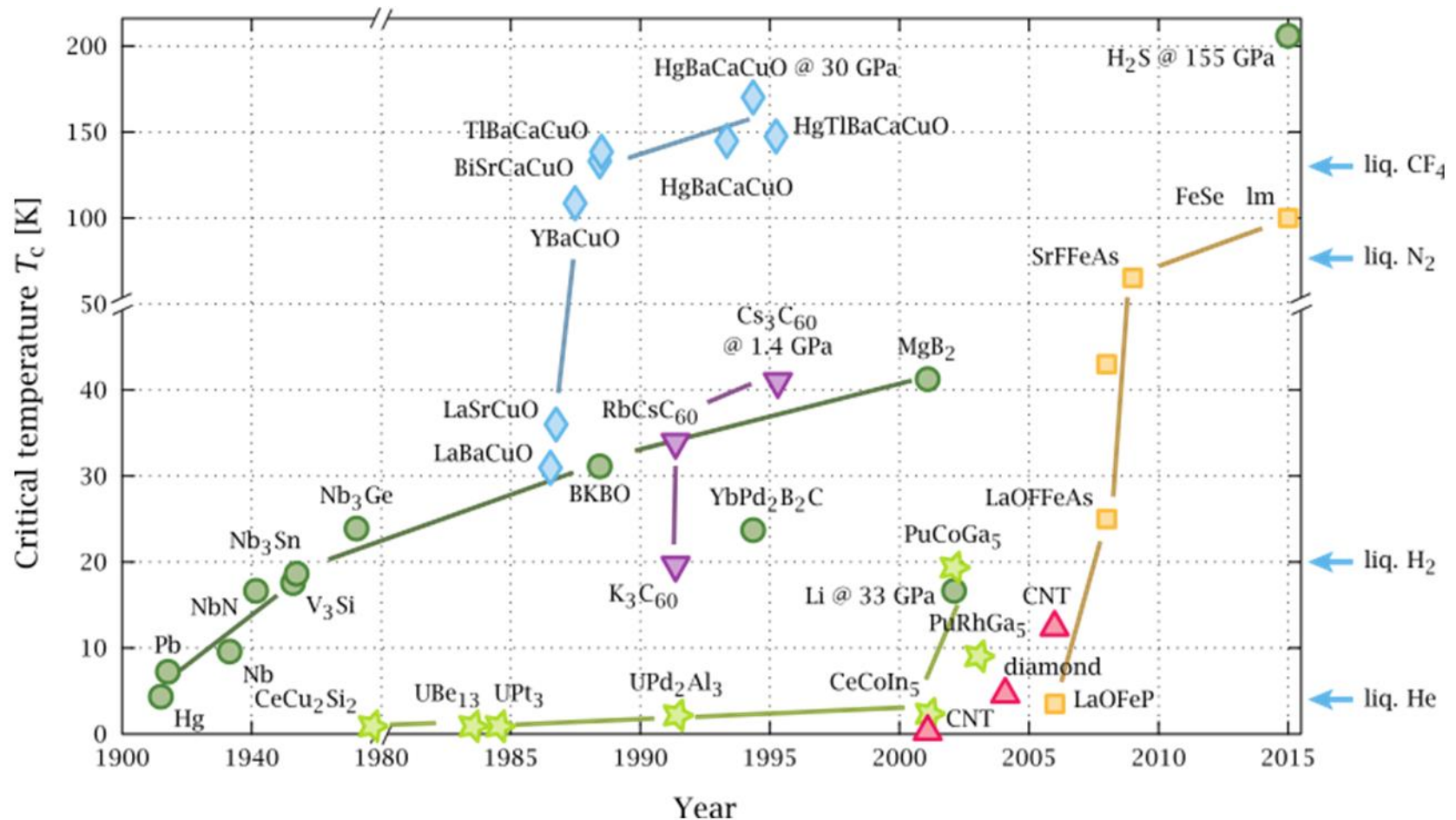
High-temperature superconductivity

One of holy grails of modern physics



High-temperature superconductivity

Transition to cuprates was a key step forward which extended the practical usefulness (Bednorz and Mueller: LaBaCuO 1986, NP 1987), especially YBaCuO with T_c above liquid N₂



High-temperature superconductivity

Superconductors of I. type (except metal hydrogen): $T_C < 40$ K

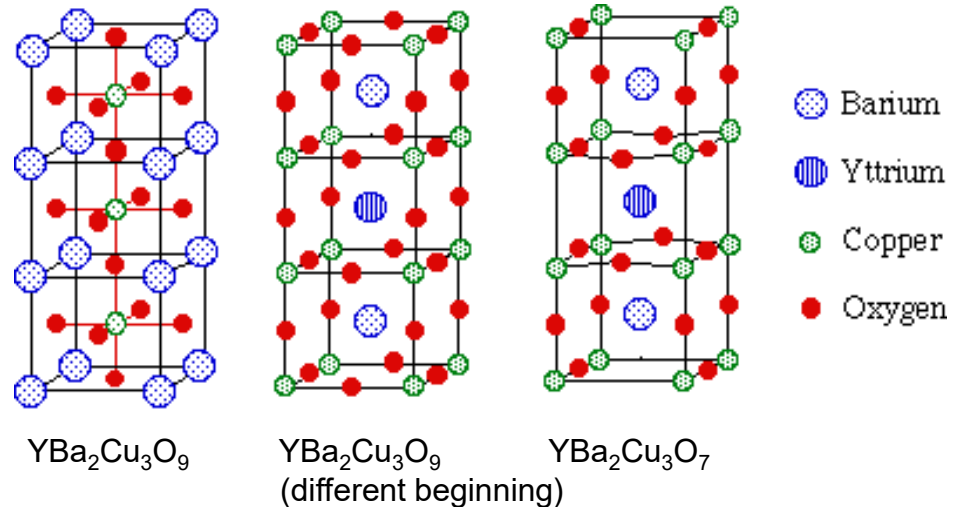
Superconductors of II. type: disadvantages below, but higher T_C

YBaCuO and other cuprates (blue diamonds on previous slide) are perovskites with oxygen vacancies (that's why $\text{YBa}_2\text{Cu}_3\text{O}_7$ or $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ instead of $\text{YBa}_2\text{Cu}_3\text{O}_9$), superconductivity takes place in planes CuO

⇒ anisotropy

⇒ lower maximum current

⇒ ceramics, not wires



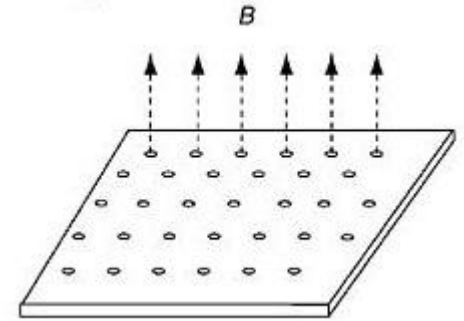
Levitation and flux pinning

Thanks to **type II** superconductors, train (**MagLev**) can levitate in even more sophisticated way than frog (previous chapter)



Levitation and flux pinning

Magnetic field penetrates to a type II superconductor in the form of vortices, which are immovable (role of impurities)

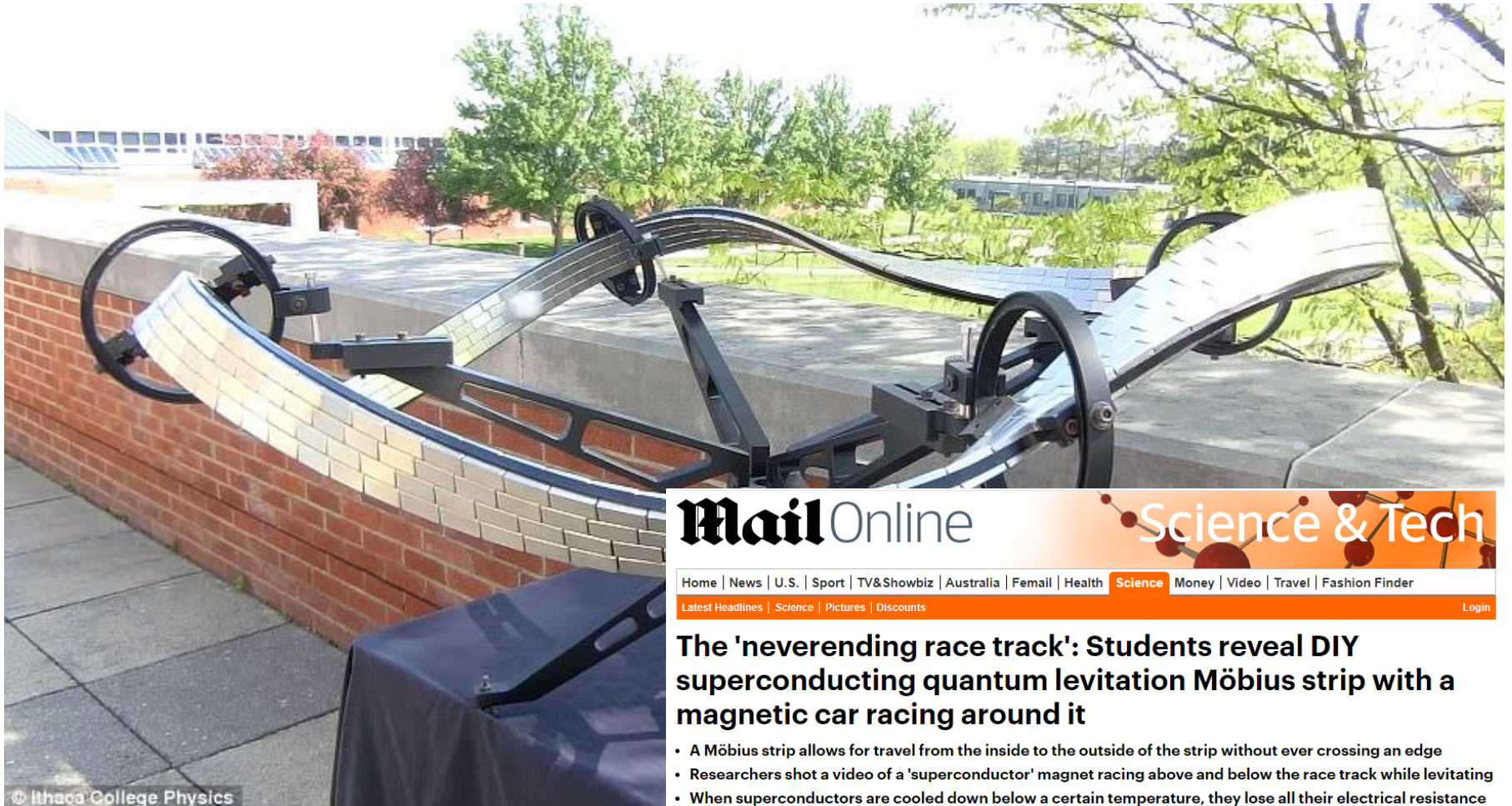


Vortices, and in turn whole material, are therefore pinned in space (at a fixed distance from external magnet)

Distance = distance in any direction, not only above the magnet (rail) but also below the rail or next to a side rail

Levitation and flux pinning

Distance = distance in any direction, not only above the magnet (rail) but also below the rail or next to a side rail



OK, last example of levitation



16) Amorphous materials

Atomic structure

- 1) Introduction, crystal structure
- 2) Bonding in solid materials
- 3) Vibrations and thermal properties
- 4) Classical calculations

Electronic structure

- 5) Role of free electrons
- 6) Band structure
- 7) Semiconductors
- 8) Quantum calculations

Functional properties

- 9) Mechanical properties
- 10) Optical properties
- 11) Photoinduced properties
- 12) Other functional properties

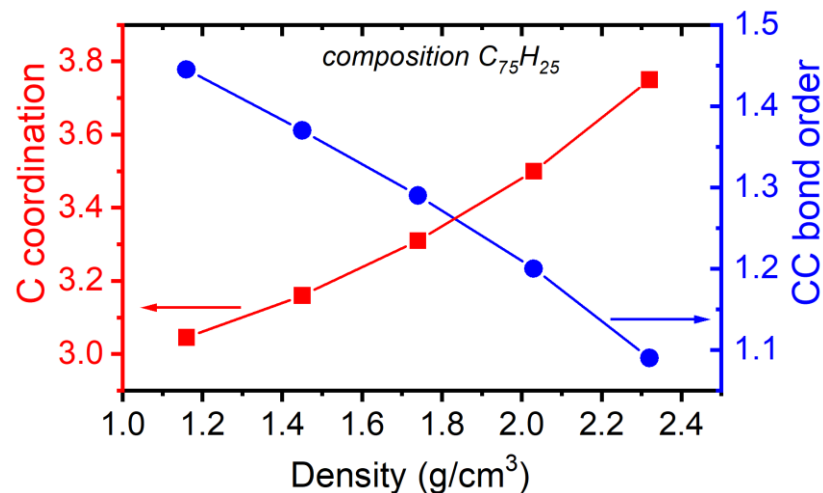
Special fields

- 13) Thermodynamics and solid solutions
- 14) Magnetism
- 15) Superconductivity
- 16) Amorphous materials

Structure and properties are not defined by the word amorphous

Example 1:

characteristics of amorphous C:H (coordination number, bond ratio C-C/C=C/C≡C, the resulting properties, ...) can be different for the same composition (figure: **depending on density**)

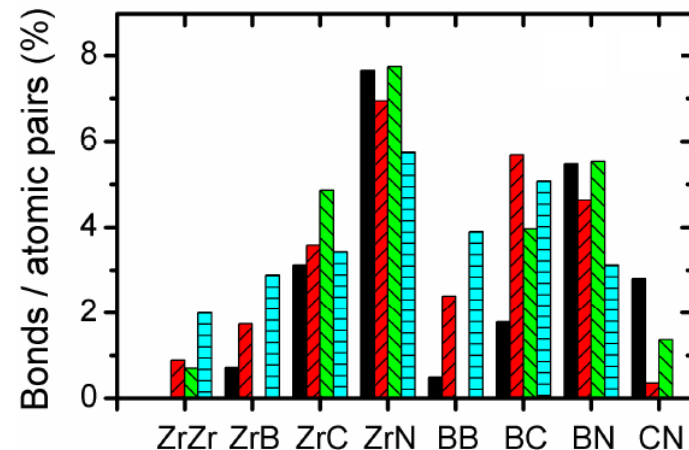


[J. Houska et al., Surf. Coat. Technol. 203, 3770 (2009)]

Structure and properties are not defined by the word amorphous

Example 2:

The **ratio of individual bonds** in multicomponent materials **does not correspond to a random distribution of atoms in space** (different preferences for bonding of different pairs of elements)



[J. Houska et al., Thin Solid Films 542, 225 (2013)]

useful criterion (figure): ratio of the actual and the maximum number of bonds (pairs of atoms)
⇒ strong preference towards preferential formation of Zr-N bonds in ZrBCN

Types of amorphous materials

By bond type

- covalent (e.g. a-SiC)
- ionic (e.g. a-Al₂O₃)
- metallic (e.g. a-ZrCu)
- combinations in the case of mixed character of bonds

Until now the same as for crystalline materials

Types of amorphous materials

By composition

- 1) compositions corresponding to a stable (or at least not too metastable) crystalline phase / solid solution



crystallization is easy (does not require segregation)



amorphous material forms (freezes) in a case of fast cooling from molten state (in a case of bulk material), low temperature (in a case of atom-by-atom growth), etc.

Types of amorphous materials

By composition

- 1) compositions corresponding to a stable (or at least not too metastable) crystalline phase / solid solution
- 2) compositions which require preliminary diffusion and the resulting segregation before "at least some" crystallization



amorphous phase has independent (more independent than in point 1) meaning - the corresponding solution exists as homogeneous only in the amorphous state

Types of amorphous materials

By composition

- 1) compositions corresponding to a stable (or at least not too metastable) crystalline phase / solid solution
- 2) compositions which require preliminary diffusion and the resulting segregation before "at least some" crystallization

Example: cryst. of Si_3N_4 ($\diamond$) and Si (∇) in $\text{Si}_{42}\text{B}_{11}\text{C}_2\text{N}_{45}$. Requires a lot of, diffusion, i.e. only at high temperature (and not at all in $\text{Si}_{32}\text{B}_{12}\text{C}_3\text{N}_{53}$).

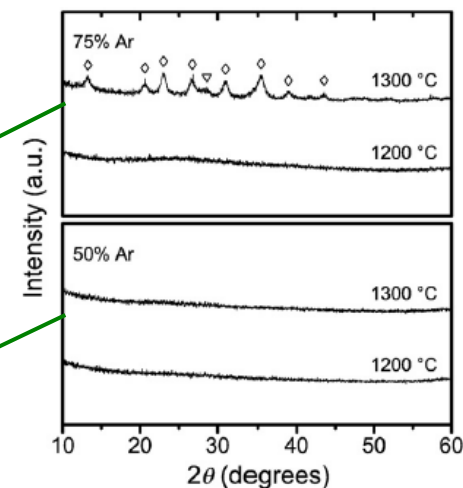


Fig. 5. X-ray diffraction patterns taken from Si-B-C-N coatings after annealing in helium to 1200 °C and 1300 °C. The coatings were prepared with 50% and 75% Ar fraction in the nitrogen–argon gas mixture. In the case of the coating prepared with the 75% Ar fraction, α - Si_3N_4 ($\diamond$) and Si (∇) reflections are observed.

[J. Capek et al., *Surf. Coat. Technol* 203, 466 (2008)]

Annealing, cooling, glass transition

P.W. Anderson (NP 1977): *The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition*

VIEWPOINTS | THE FUTURE

Through the Glass Lightly

+ See all authors and affiliations

Science 17 Mar 1995:
Vol. 267, Issue 5204, pp. 1615-1616
DOI: 10.1126/science.267.5204.1615-e

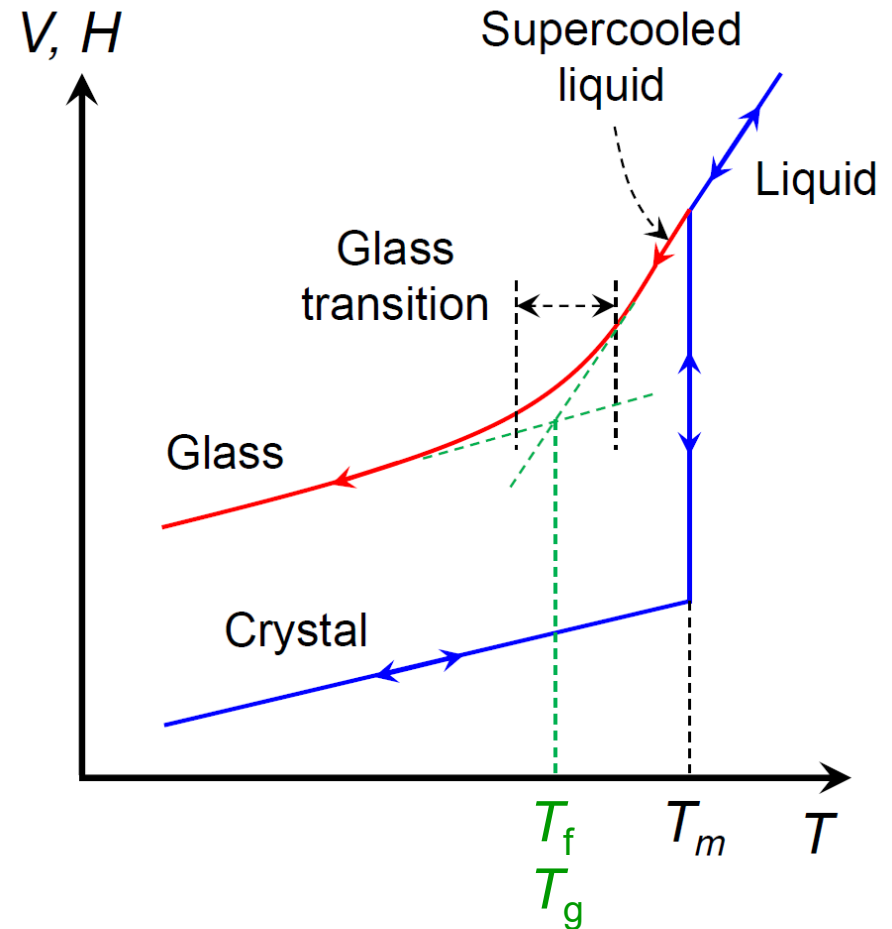
Annealing, cooling, glass transition

Crystalline material exhibits uniquely defined melting temperature T_m

Quantities like V and H abruptly change at this temperature

First order phase transition (latent heat)

see chapter 13 for classification of phase transitions

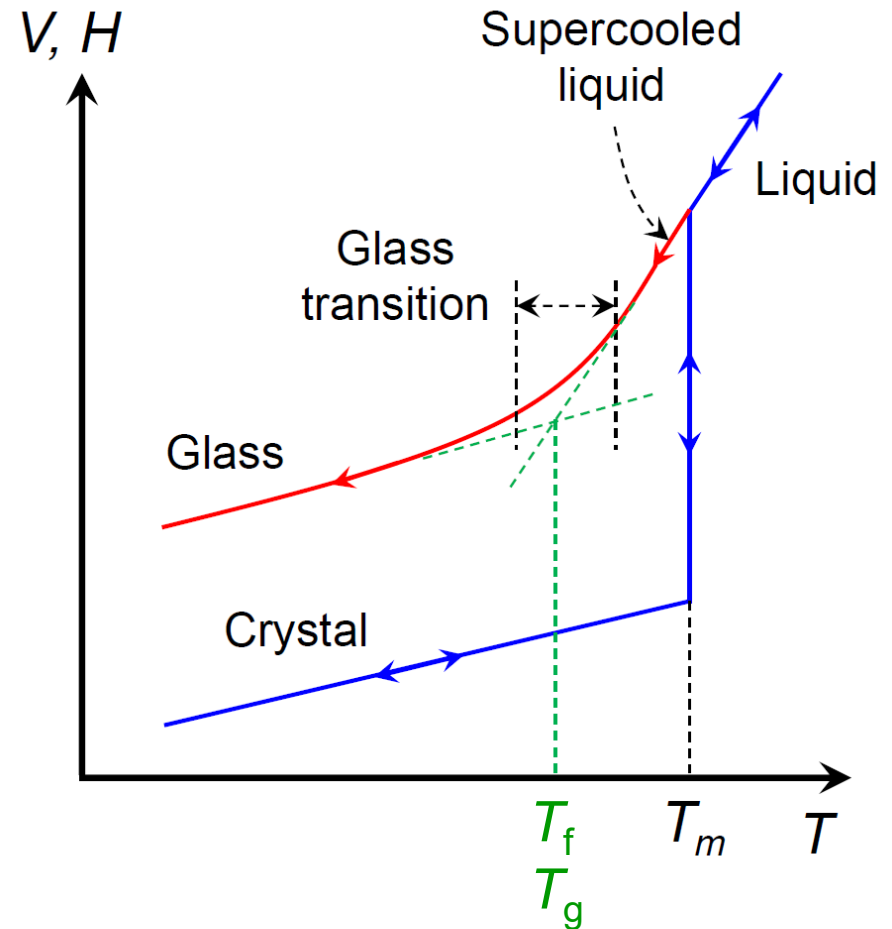


Annealing, cooling, glass transition

Amorphous material exhibits only an approximate / fictitious melting temperature T_f

Quantities like V and H change smoothly

Not phase transition in a narrow sense of the word (between two energetical minima: the only true minimum is crystal), if we take it as one it is of second order (pseudo-second-order)



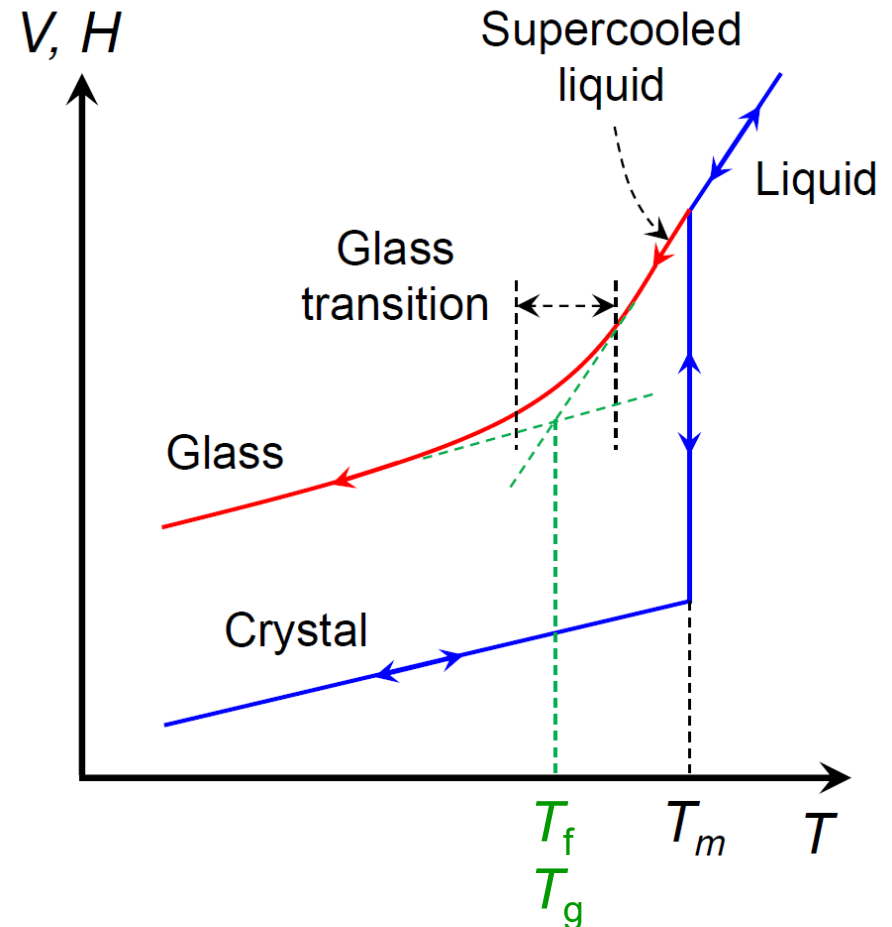
Annealing, cooling, glass transition

Amorphous material exhibits only an approximate / fictitious melting temperature T_f

Quantities like V and H change smoothly

Not phase transition in a narrow sense of the word (between two energetical minima)

Another quantity is temperature of glass transition T_g : sometimes overlaps with T_f , sometimes corresponds to viscosity 10^{12} Pa.s



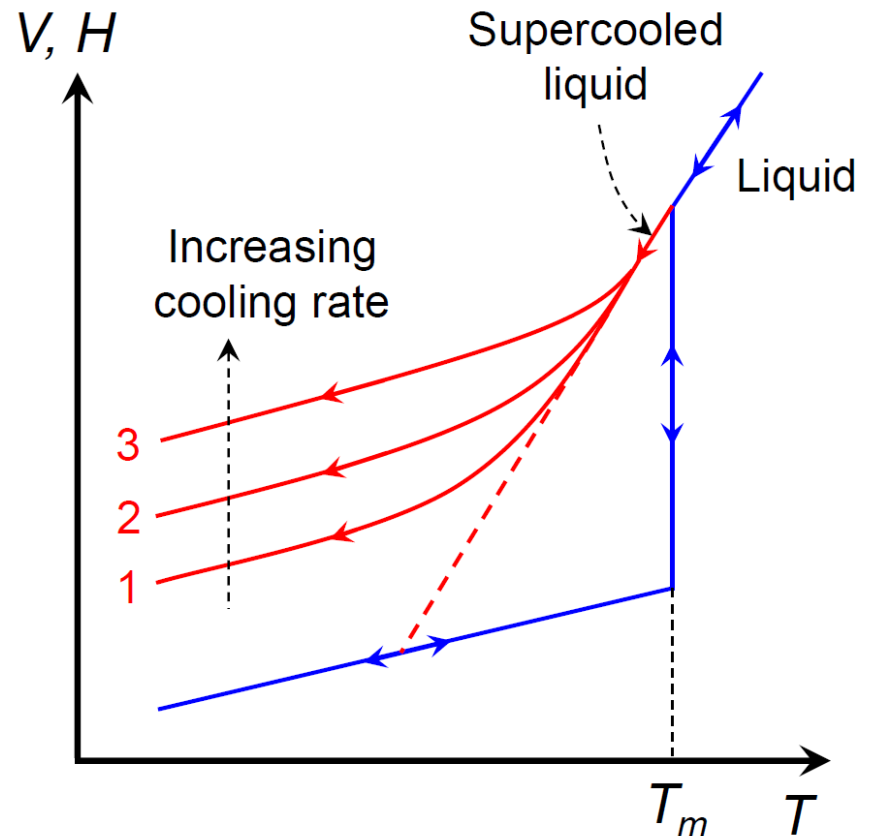
Annealing, cooling, glass transition

Amorphous material exhibits only an approximate / fictitious melting temperature T_f , V and H change smoothly

Value of T_f , and especially the structure and properties of the resulting material, depend on the cooling rate

For infinitely low cooling rate (if the material remains homogeneous and amorphous) we would get "**ideal glass**"

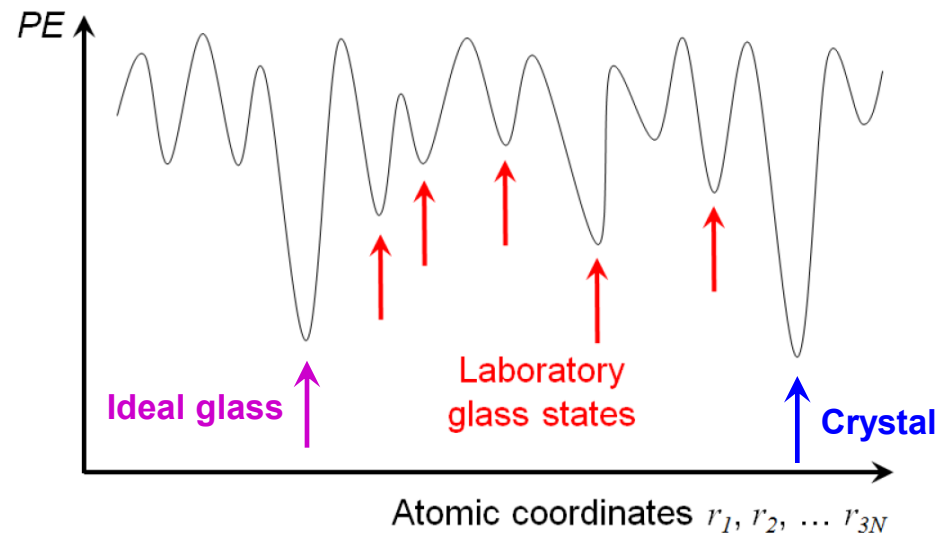
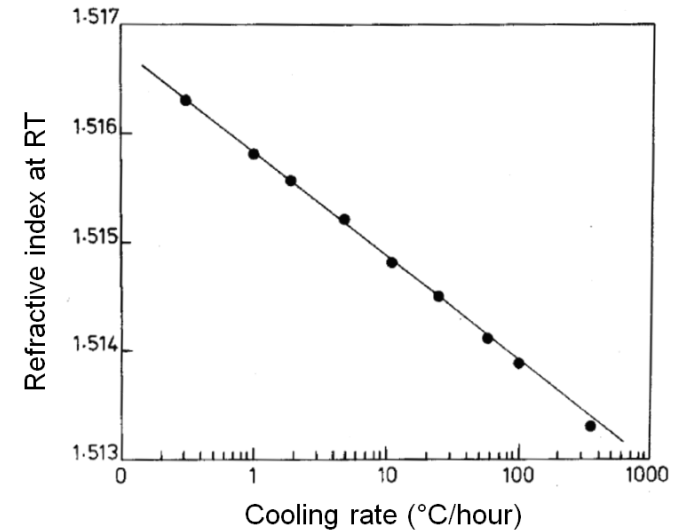
The slope of tangent - - - - of the dependence $V(T)$ leading to ideal glass: thermal expansion of supercooled liquid



Annealing, cooling, glass transition

Value of T_f , and especially the structure and properties of the resulting material, depend on the cooling rate

For infinitely low cooling rate (if the material remains homogeneous and amorphous) we would get "ideal glass"



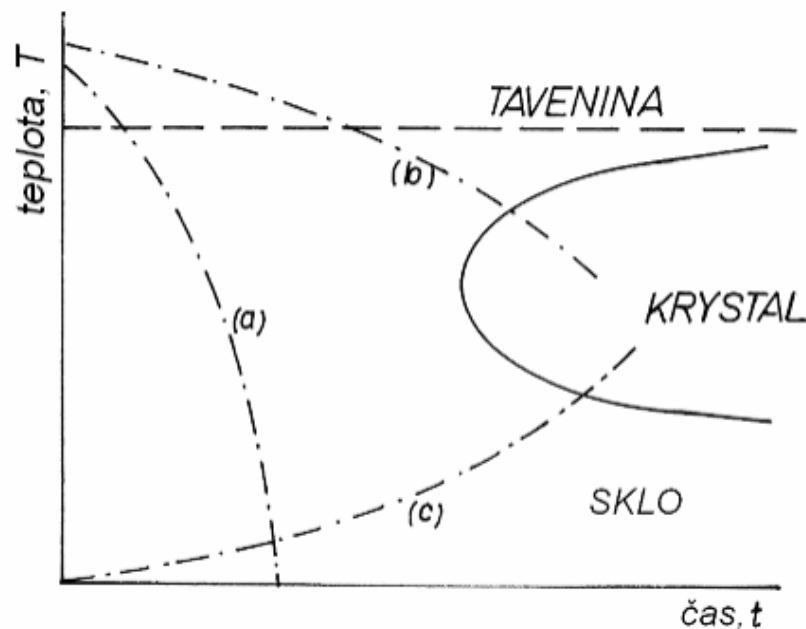
Annealing, cooling, glass transition

mainly for compositions crystallizing without segregation

(a) formation of glass

(b) formation of crystal
from melt

(c) formation of crystal
from glass



Annealing, cooling, glass transition

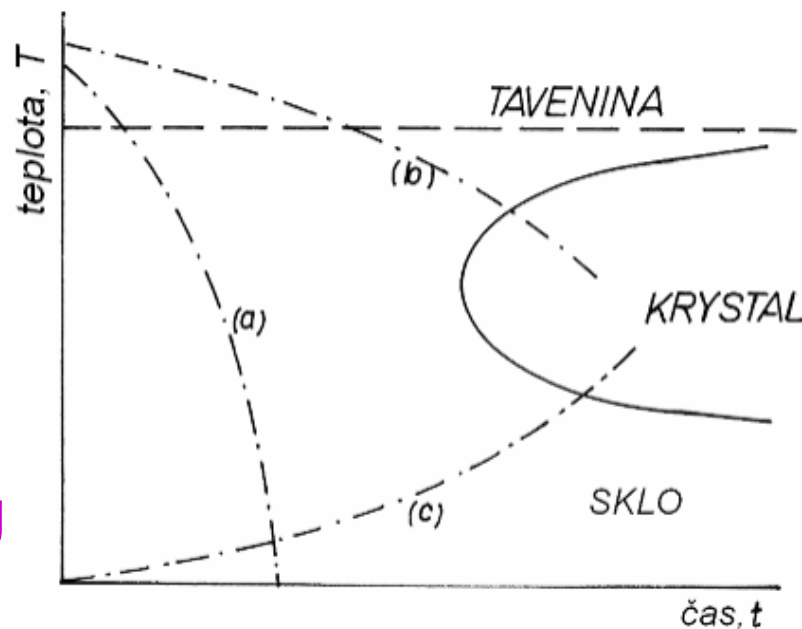
mainly for compositions crystallizing without segregation

It can happen that amorphous material has melting (glass transition) temperature not only below the melting temperature of crystalline material, but also below the temperature leading to crystallization during annealing (at some given heating rate)



The first thing which happens during annealing is **temporary** melting (softening), then crystallization, then **permanent** melting

The term glass in this context refers only to those amorphous materials which exhibit this behavior during annealing



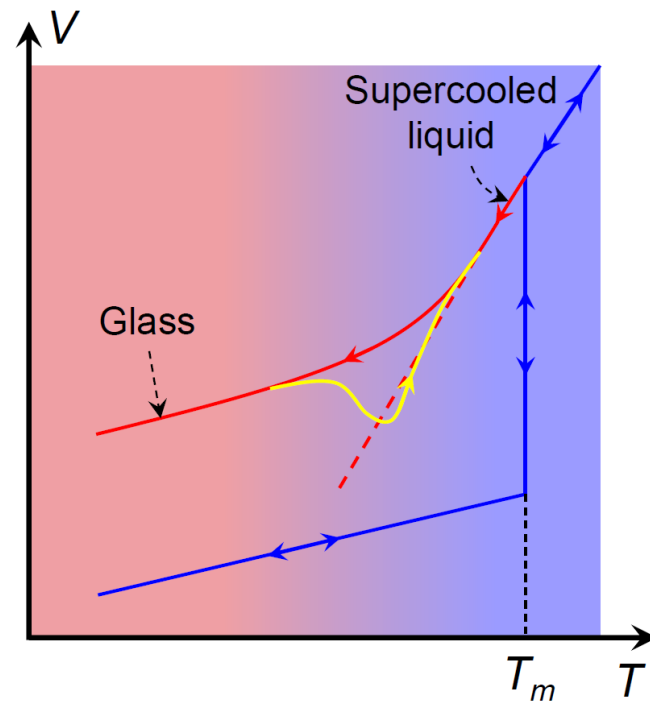
Annealing, cooling, glass transition

mainly for compositions crystallizing without segregation

It can happen that amorphous material has melting (glass transition) temperature not only below the melting temperature of crystalline material, but also below the temperature leading to crystallization during annealing (at some given heating rate)



The first thing which happens during annealing is temporary melting (softening), then crystallization (**note minimum of the yellow dependence $V(T)$**), then permanent melting



Annealing, cooling, glass transition

Which homework (except cooking) requires creating a melt?

Ironing

At the transition temperature between melt and glass, bonds between material's building blocks break and form:

For metals & ceramics the blocks are individual atoms

For textiles the blocks are whole polymer molecules, after breaking of bonds between them (only van der Waals bonds $\Rightarrow$ low temperature is enough) we get "melt" and can straight them by iron's pressure

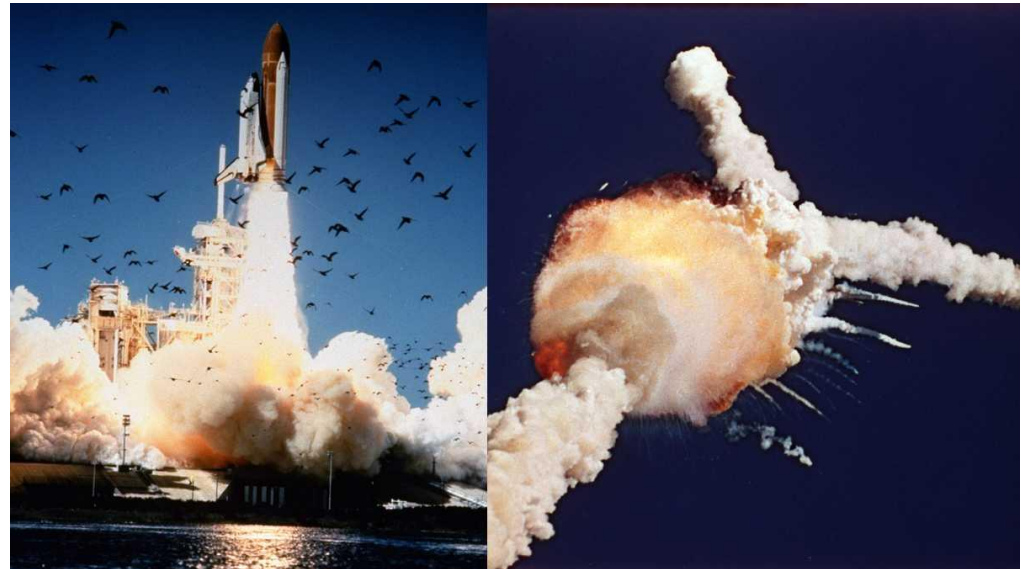


O-rings and space flights

Similarly for other polymer materials, for example

- poly(methyl methacrylate) (acrylic glass) is at room temperature just below glass transition
- rubber is at room temperature above glass transition ...
but not sufficiently above: the fate of space shuttle Challenger

"Not coincidentally, that moment also involved the most celebrated member of the Rogers Commission: the brilliant, irascible, and incurably curious Nobel Prize-winning physicist Richard Feynman. Feynman took a small rubber O-ring and piched it in the middle with a little steel clamp. He then placed the clamped O-ring in a glass of ice water. With the TV cameras running, Feynman pulled his experiment from the water with a flourish and removed the clamp. Much like our earlier wood block and rubber band test, Feynman's O-ring did not immediately snap back to its original "O" shape. **Having been chilled below its glass transition**, it needed lots more time to react. It was a smoking-gun moment, and it left many Americans with this conclusion: the Challenger crashed because its O-rings got too cold."



28.1.1986, -1°C

Composition of amorph. metal oxides

There are materials with (preferred) composition in crystalline state given by small integers corresponding to the number of corresponding positions in the lattice (random example: SiC), but in amorphous state there can be any composition ($a\text{-Si}_x\text{C}_y$)

But there are also materials with preferred composition given by small integers also in amorphous state (random ex: $a\text{-Al}_2\text{O}_3$); other compositions are understood as understoichiometric and lead to qualitatively different properties. Why so?

Composition of amorph. metal oxides

There are materials which can have any composition in amorphous state ($a\text{-Si}_x\text{C}_y$)

But there are also materials with preferred composition given by small integers also in amorphous state ($a\text{-Al}_2\text{O}_3$). Why so?

The first case corresponds to materials forming covalent bonds, in $a\text{-Si}_x\text{C}_y$ any needed number of bonds SiSi, CC and SiC.

Composition of amorph. metal oxides

But there are also materials with preferred composition given by small integers also in amorphous state (a-Al₂O₃). Why so?

The second case corresponds to materials forming ionic bonds - oxygen (6 val. el.) takes all metal electrons, within the efforts to complete the valence shell (8 el. including 2 taken). This leads to stoichiometries like Al₂O₃, (Ti/Zr/Hf)O₂, (V/Nb/Ta)₂O₅, ZnO (10 el. in full d-orbital of Zn do not play any role), etc.

In such energetically preferred state the maximum possible band gap opens (from another point of view: once the highly electronegative oxygen gets the required 8 electrons, it happily holds them, it does not let them to go back to the world and conduct current or absorb light there).

All of this holds independently of the crystallinity / amorphicity

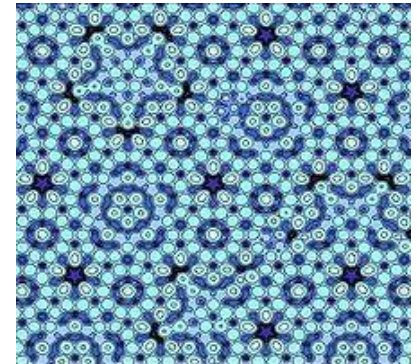
Ordering of amorphous structures

Long range order - translation symmetry

- only in crystals

Long range order - rotational symmetry

- in most crystals
- in quasicrystals (which do not have translational symmetry): popular curiosity (including NP), but after decades still limited applications



Short range order (preferred bond lengths, preferred coordination numbers, etc.) is similar in amorphous and crystalline materials (differences are on the same order as between individual crystalline phases)

Is there anything like **medium range order**?

Medium range order

network ring statistics

Network ring: closed chain of bonds between atoms

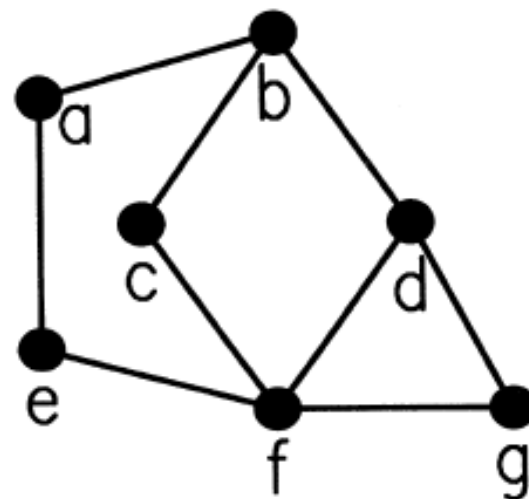
Shortest path (SP) network ring: ring with no shortcut over it (shortest path - or one out of several equally long shortest paths - between each two atoms is part of the ring)

2D example: SP rings are

- abcfea
- abdfea
- bdfcb
- dgfd

SP rings are not

- bdgfc (there is shortcut between d-f)
- abdgfea (there are shortcuts between b-f and d-f)



[D.S. Franzblau, Phys. Rev. B 44, 4925, (1991)]

Medium range order

network ring statistics

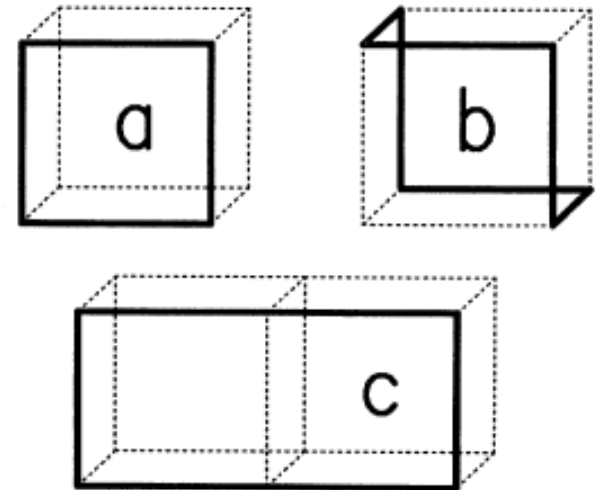
Network ring: closed chain of bonds between atoms

Shortest path (SP) network ring: ring with no shortcut over it (shortest path - or one out of several equally long shortest paths - between each two atoms is part of the ring)

3D example: the only SP rings in simple cubic cell are

- length 4 in fig. (a); 3 per atom, and
- length 6 in fig. (b); 4 per atom.

The ring in fig. (c) is not SP ring



[D.S. Franzblau, Phys. Rev. B 44, 4925, (1991)]

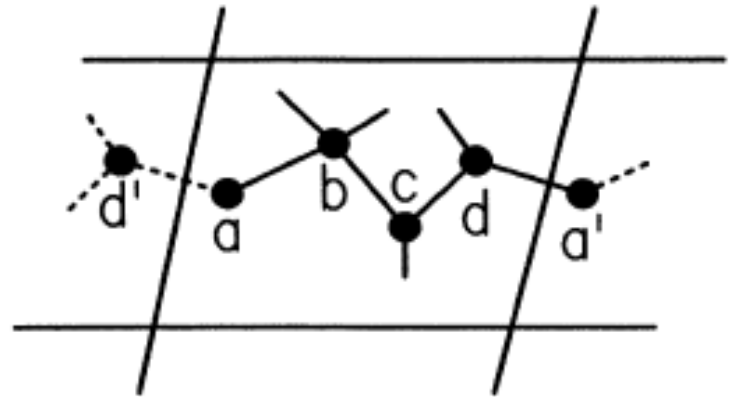
Medium range order

network ring statistics

Network ring: closed chain of bonds between atoms

Shortest path (SP) network ring: ring with no shortcut over it (shortest path - or one out of several equally long shortest paths - between each two atoms is part of the ring)

Periodic cell (atom a corresponds to a'): be careful about the fact that 'abcda' is not ring (let alone SP ring)



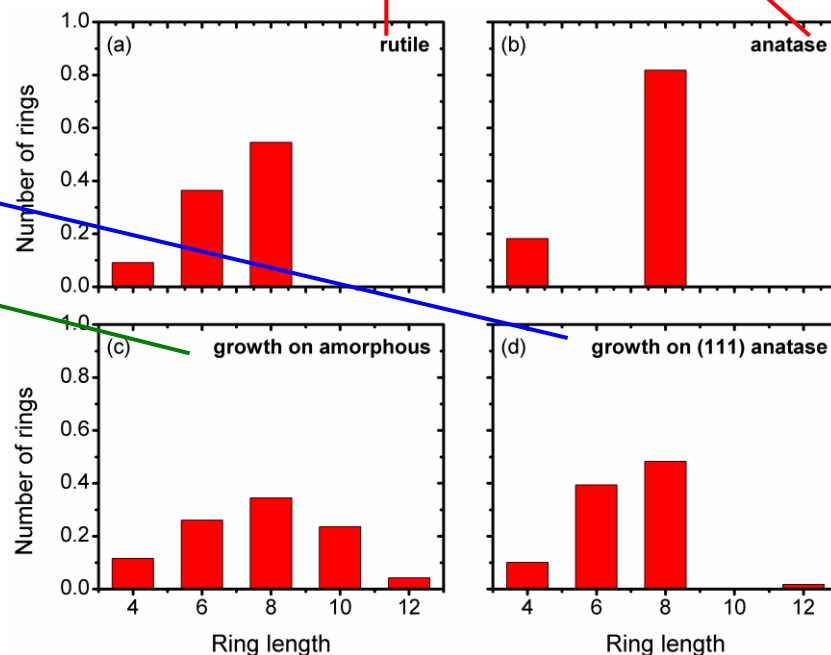
SP ring statistics - utilization

Example 1 (growth of TiO_2)

The main TiO_2 phases, rutile and anatase, have the same coordinations, bond lengths, etc., but different ring statistics.

So it is possible to identify whether the resulting structure (amorphous, deformed crystalline, etc.. ...) is closer to rutile or anatase (in this case rutile)

Amorphous structures exhibit longer SP rings than crystalline



[J. Houska et al., J. Appl. Phys. 112, 073527 (2012)]

SP ring statistics - utilization

Example 2 (a-C:H)

Change of topology because of
(i) density change and
(ii) H incorporation

TABLE II. Ring statistics.

Simulation	3	4	5	6	7	8	9
<i>a</i> -C:H (2.9 g/cm ³)	0	3	17	14	15	1	1
<i>a</i> -C:H (2.0 g/cm ³)	0	0	3	4	6	2	1
<i>a</i> -C (2.9 g/cm ³)	2	6	9	14	10	11	3

[M. Bilek et al., Phys. Rev. B 62, 3071 (2000)]

Example 3 (a-SiBCN)

Change of topology because of
Ar implantation (formation of pores
which isolated Ar sits in)

Quantity	SiBCN	SiBCNAr
Volume per atom (Å ³)	11.0	9.0
Si content	32%	32% (36%)
Si-containing bonds	75%	73% (96%)
Fraction of all B or C containing bonds which also include Si	9%	24% (66%)
Criterion 1 for segregation	43%	52%
Criterion 2 for segregation	9%	8%
Average length—all bonds (Å)	1.70	1.72
Average length—single BN (Å)	1.51	1.55
Average length—single CN (Å)	1.41	1.46
Number of rings	9.0	18.6
Average ring size	5.8	6.0

[J. Houska et al., J. Phys.: Condens. Matter 18, 2337 (2006)]

Selected quantities

which have different typical values for crys. and amorph.

(including reminder of the aforementioned ones)

Mises criterion (brittle $\times$ ductile crystalline structures) is not representative. What should be expected in this case is brittle tensile deformation and plastic compressive deformation.

Thus, hardness (resistance against plastic deformation under compression) is for a given elemental comp. usually lower. No surprise - the material is leaving a shallower energy minimum; there is not anything like healing of dislocations.

Electron states are more localized, free charge carriers have lower mobility ($\Rightarrow$ electrical and thermal conductivity)

Blurred band gap edges (Urbach tail)

Selected quantities

which have different typical values for crys. and amorph.

(continuation)

It makes no sense to distinguish direct and indirect band gap (another viewpoint: infinite primitive cell $\Leftrightarrow$ zero size of 1st BZ, i.e. electronic states order above each other), Tauc gap using the formula used for indirect band gap in the case of crystals

Isotropic $\Leftrightarrow$ only two independent components of elastic tensor ($C_{11}=C_{22}=C_{33}$, $C_{12}=C_{13}=C_{23}$, $C_{44}=C_{55}=C_{66}=[C_{11}-C_{12}]/2$)

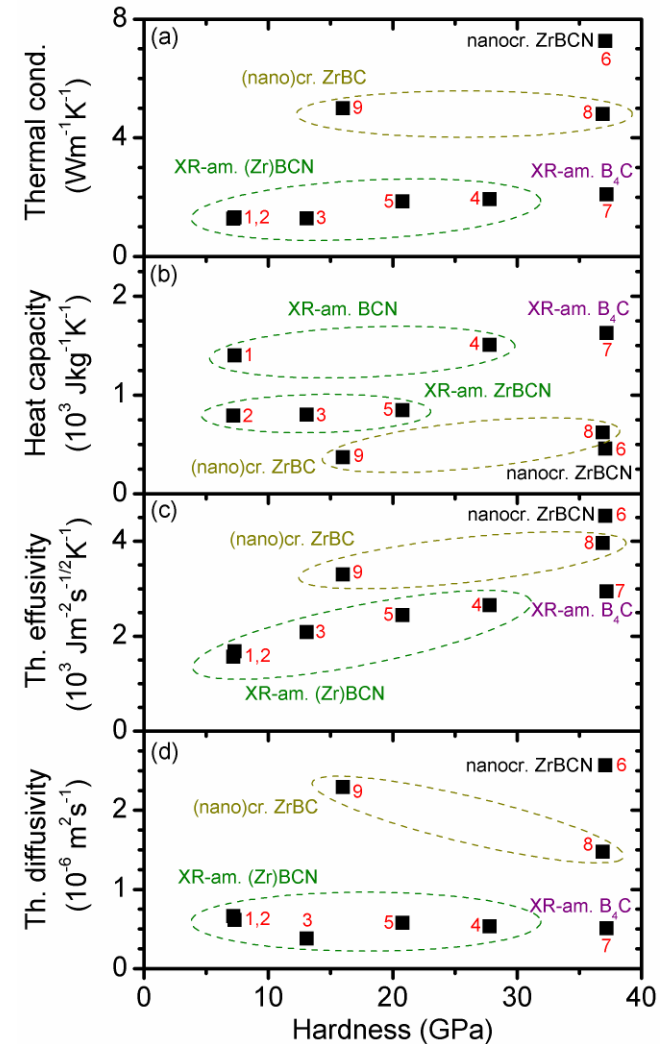
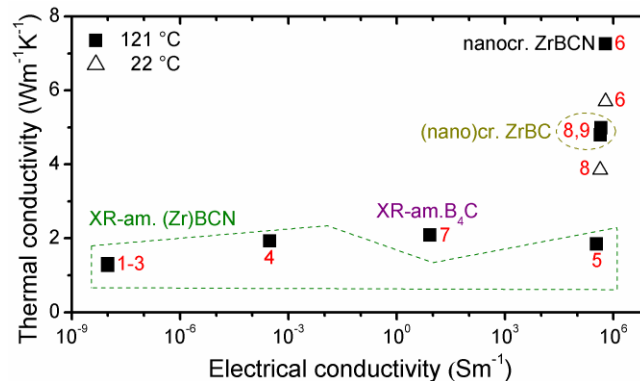
Longer network rings

Smoother dependencies $\varepsilon(\lambda)$ & $n(\lambda)$,
no sharp minima & maxima

Selected quantities

which have different typical values for crys. and amorph.

Example related to previous slide:
higher electrical and thermal conductivity (and related quantities - thermal diffusivity and effusivity) for nanocrystalline (Zr)BC(N) compared to amorphous (Zr)BC(N)



[J. Houska et al., Ceram. Int. 42, 4361 (2016)]

Selected quantities

which lead to more complex stuff in amorphous materials

Structure in itself (atomic coordinates) representing "typical" local energy minimum (role of computer simulations)

Bonding statistics showing which elements bond to which elements (as pointed out above: usually very different from statistics obtained by random distribution of atoms in cell)

Characteristics of individual bonds - length, multiplicity (single $\times$ double $\times$ triple), ionicity

Number of valence electrons which do not take part in bonding but form lonepairs (and identification of elements forming them)

Coordination numbers (owing to non-zero charges they do not result just from the number of valence el. and bond multiplicity)

Selected quantities

which lead to more complex stuff in amorphous materials

(continuation)

Segregation, if there is any (amorphicity does not necessarily mean that the material is homogeneous)

Thermal stability, temperature dependence of the segregation

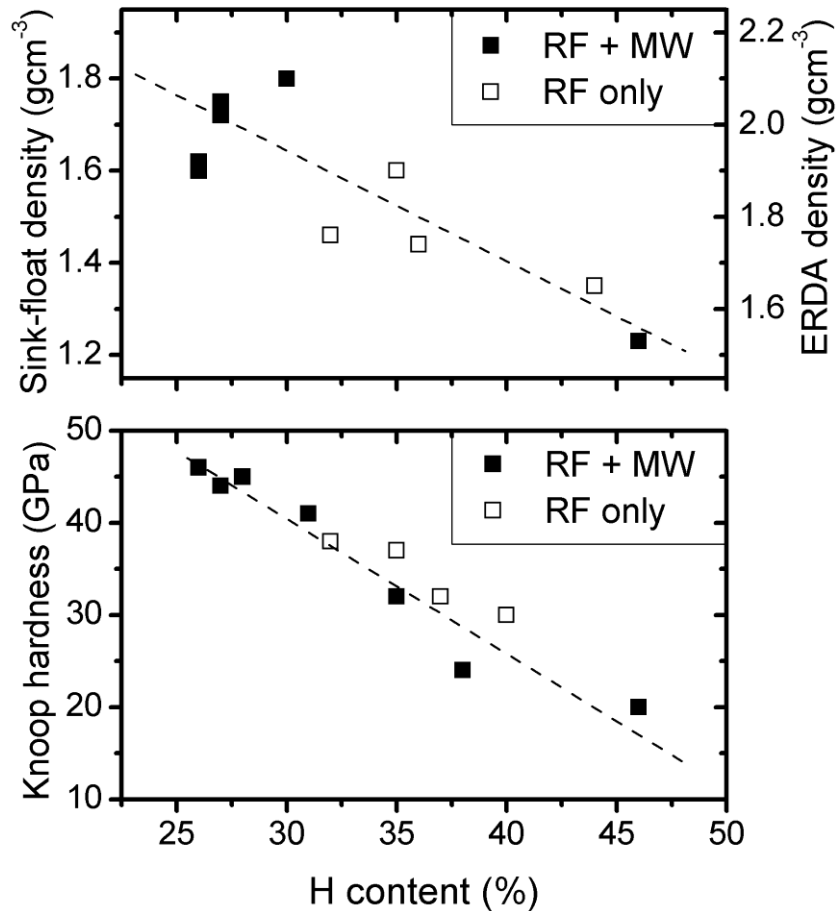
Electronic structure, specifically which atoms / atoms of which element are states localized on (this is important also in crystals, but less intuitive in the case of amorphous materials)

Electronic structure, specifically how much (on how many atoms) is the state localized (infinity in an ideal crystal)

specific examples related to atomic structure of amorphous materials follow below (see above, especially chapter 6, for examples on their electronic structure)

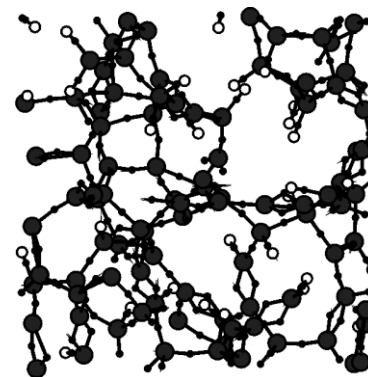
Bonding statistics - example 1 (a-C:H)

Experiment



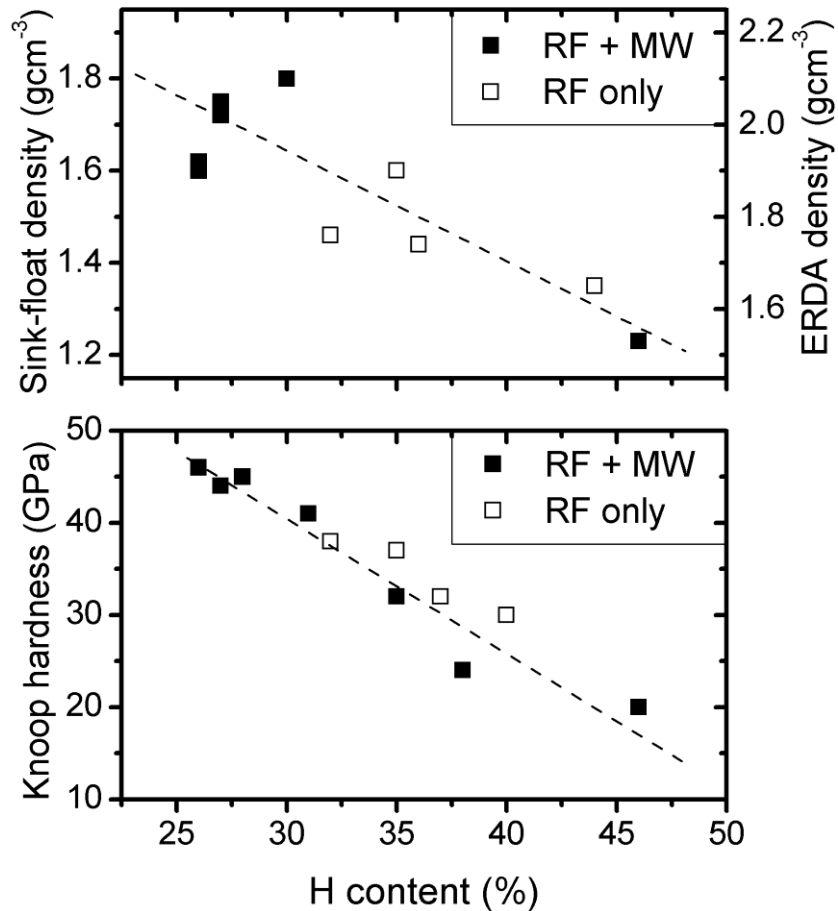
Quantities of interest

- Coordination numbers of carbon atoms
- Bond order, i.e. ratios $\text{C-C} / \text{C}=\text{C} / \text{C}\equiv\text{C}$

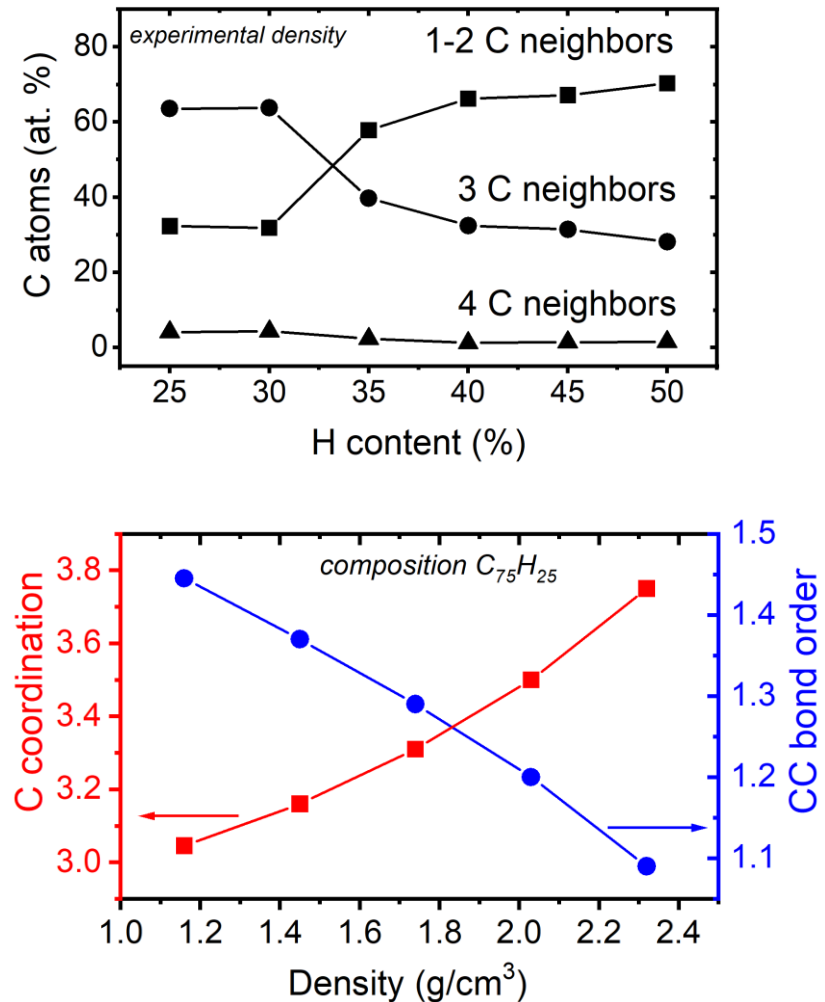


Bonding statistics - example 1 (a-C:H)

Experiment



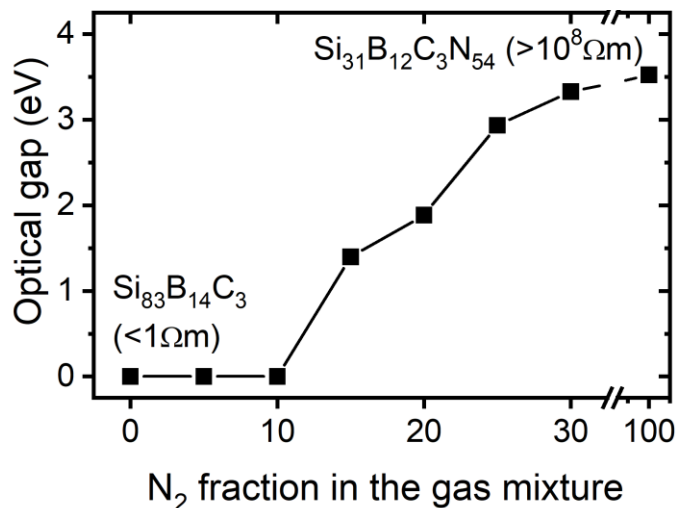
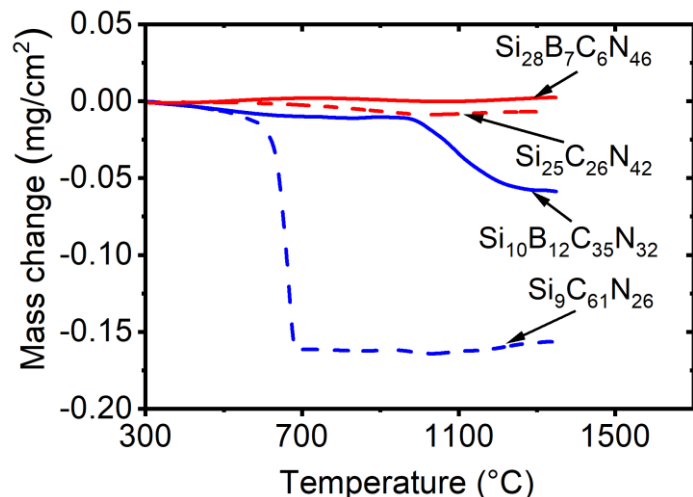
Simulation



[J. Houska et al., Surf. Coat. Technol. 203, 3770 (2009)]

Bonding statistics - example 2 (SiBCN)

Experiment



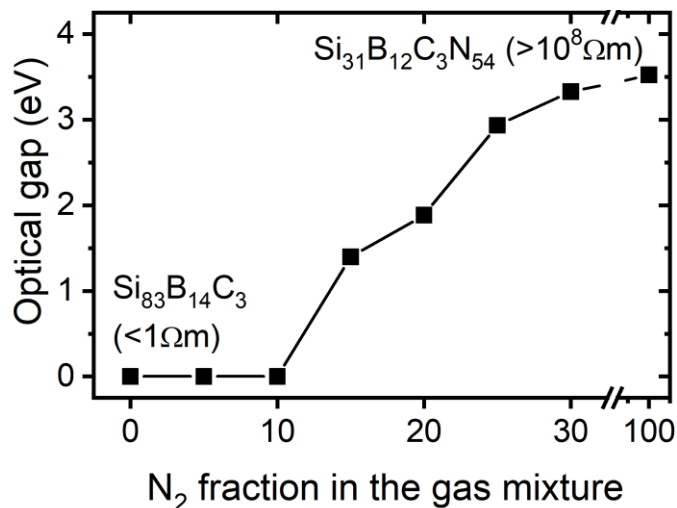
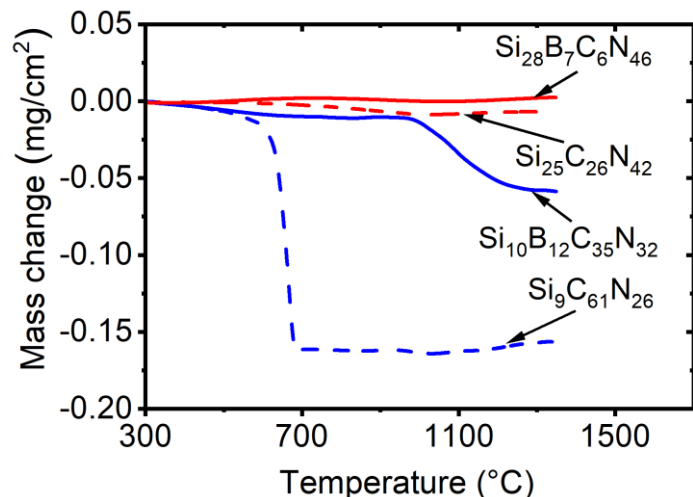
Quantities of interest

(those which are specific for multielement materials)

- Bonding preferences of individual elements
- Segregation of elements or binary/ternary components in quaternary material

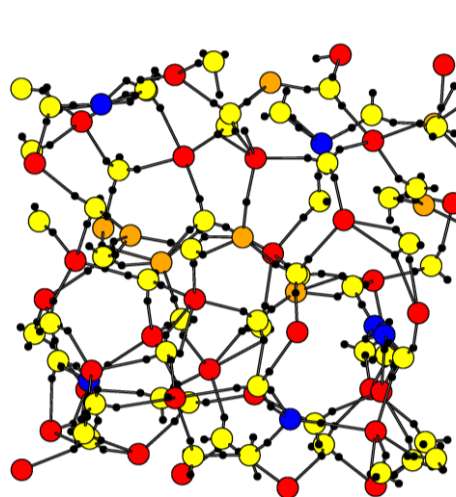
Bonding statistics - example 2 (SiBCN)

Experiment



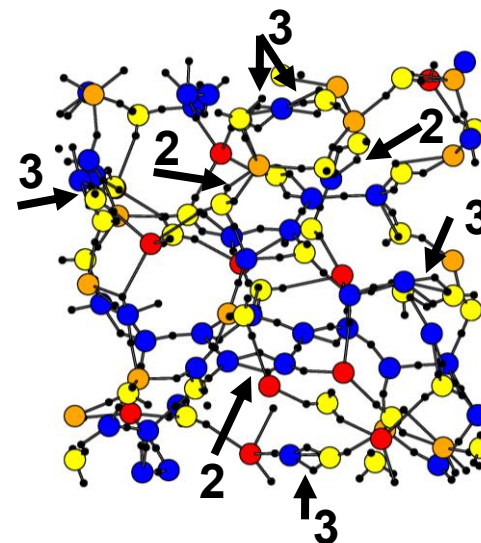
Simulation (effect of ratio Si/C)

Si: ● B: ● C: ● N: ●



Si-rich composition
single bonds Si-N
⇒ high coordination

(transparency, thermal stability, hardness)



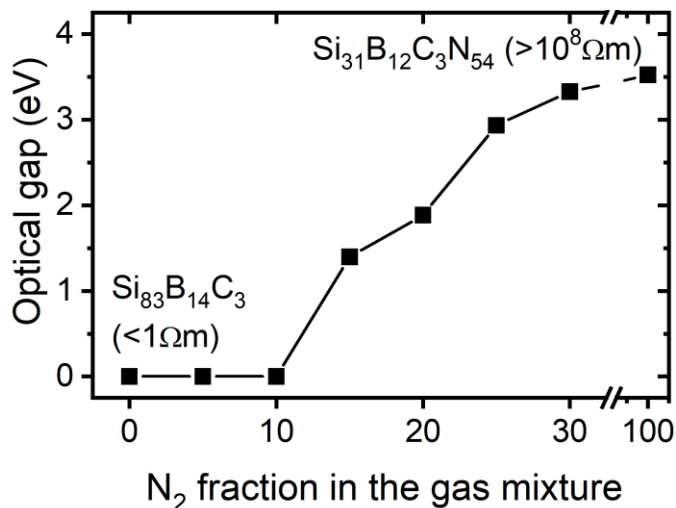
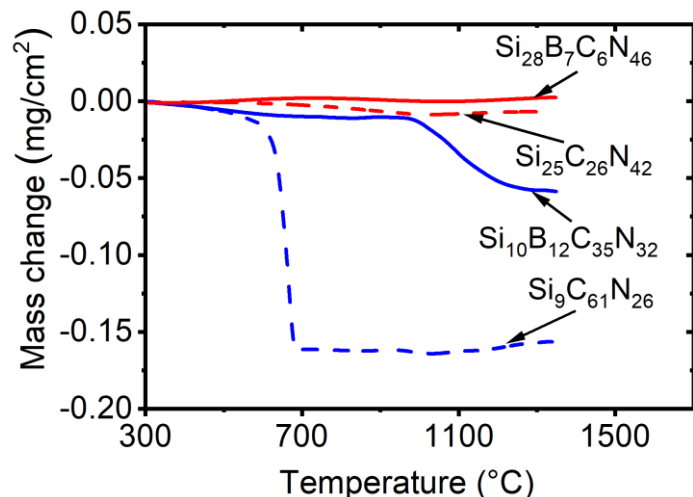
C-rich composition
double C=N, C=C and B=N, and triple C≡N
⇒ low coordination

(electrical conductivity, low friction)

[J. Houska et al., J. Vac. Sci. Technol. A. 25, 1411 (2007)]

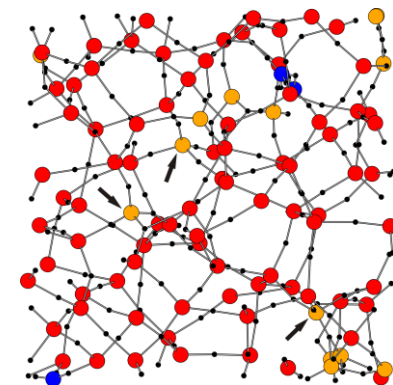
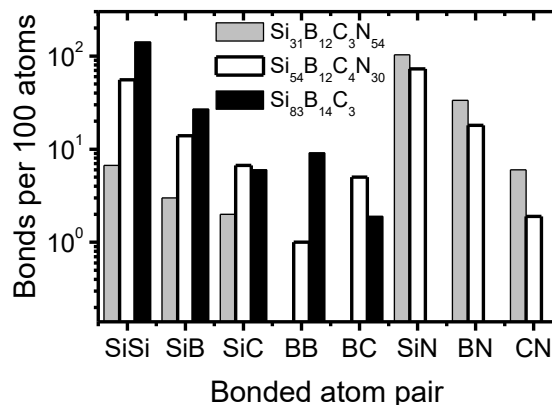
Bonding statistics - example 2 (SiBCN)

Experiment



Simulation (effect of N content)

Si: ● B: ● C: ● N: ●



N-rich composition

- homogeneous network
- high affinity of B to N
- heteropolar bonds $\Rightarrow$ wide band gap

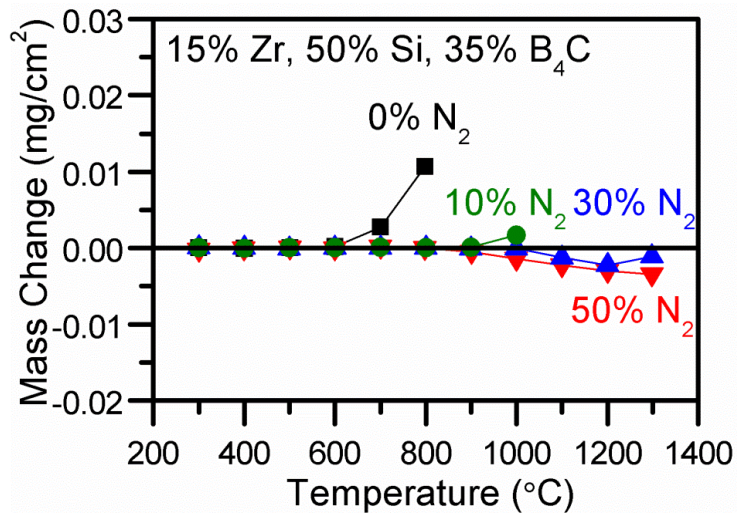
N-free (SiBC)

- segregation of B-rich zones (note BB bonds!)
- B atoms in a-Si have coord. 4 (not 3)

[V. Petrman, J. Houska et al., Acta Mater. 59, 2341 (2011)]

Bonding statistics - ex. 3 (ZrSiBCN)

Experiment



Quantities of interest

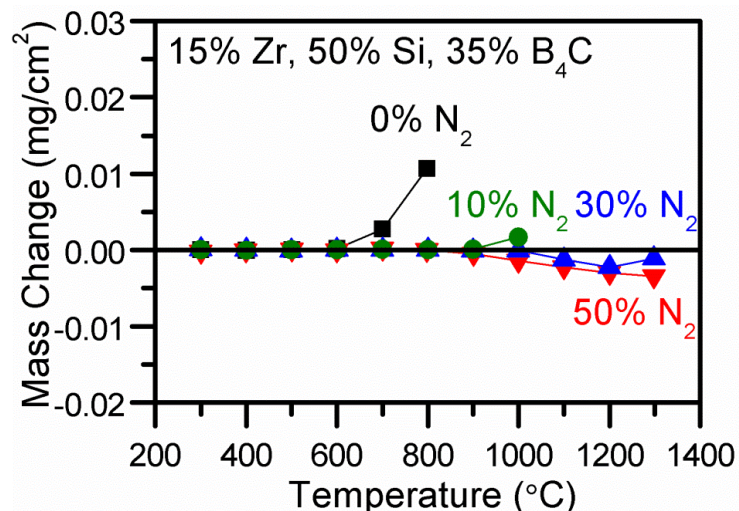
(those which are specific for transition metals)

- Contribution of metallic (not covalent) bonds

- Comparison with SiBCN:
high-temperature stability largely preserved, better electrical cond.

Bonding statistics - ex. 3 (ZrSiBCN)

Experiment



- Comparison with SiBCN:
high-temperature stability largely preserved, better electrical cond.

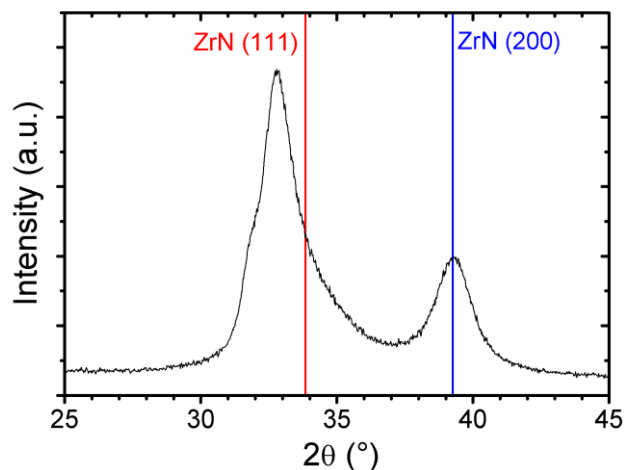
Simulation

material	metallic bonds		WFs spread (Å)	resistivity (Ωm)
	no Zr	all		
Zr ₈ B ₃₅ C ₈ N ₄₉	0	3	1.76	1.2 x 10 ⁶
Zr ₁₅ B ₅₀ C ₁₃ N ₂₂	8	28	2.11	2.9 x 10 ⁻⁶
Zr ₂₄ B ₂₁ C ₆ N ₄₉	0	15	1.97	8.5 x 10 ³
Zr ₄₀ B ₃₂ C ₈ N ₂₀	0	53	2.57	1.7 x 10 ⁻⁶

- Metallic bonds**
 - usually include Zr
 - but their number depends on N content rather than Zr content
- Measure of electronic mobility:** space volume occupied (high probability of occurrence) by them: WFs spread

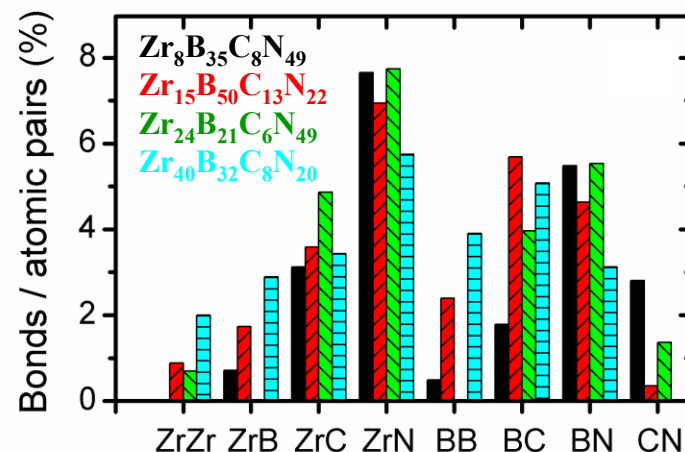
Bonding statistics - ex. 3 (ZrSiBCN)

Experiment



- Comparison with SiBCN:
high-temperature stability largely preserved, better electrical cond.
- Hardness
 - at low Zr content: up to 27 GPa
 - at high Zr content: 37 GPa

Simulation



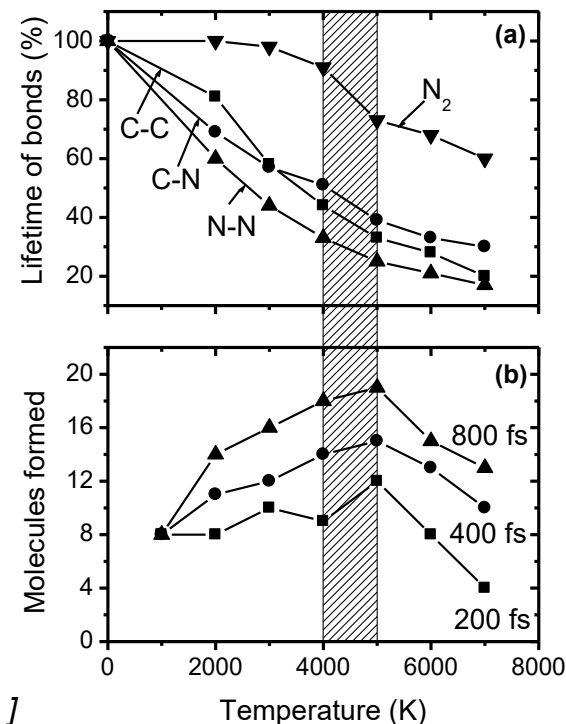
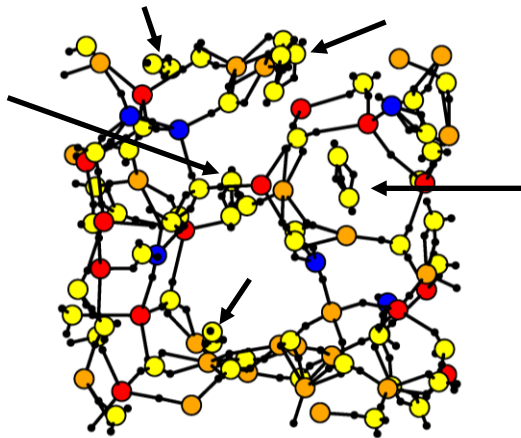
- Useful criterion: ratio of the actual and the maximum number of bonds (pairs of atoms)
- Strong preference to form Zr-N
 - ↓
 - At high Zr content (40%):
hard nanocomposite containing (200) ZrN and (111) ZrBN

Special case 1: N₂ molecules

Formation of N₂ molecules during the thermal spike cooling after an energetic particle impact is supported by the stability of triple N≡N bonds at T when the rest of the material is still molten

Experimentally N₂ were not observed - leave to the atmosphere, but they cannot do that during simul. (periodical boundaries)

When this effect is quantitatively important (high N content, low density) it is necessary to start simulation with N excess, and remove N₂ manually

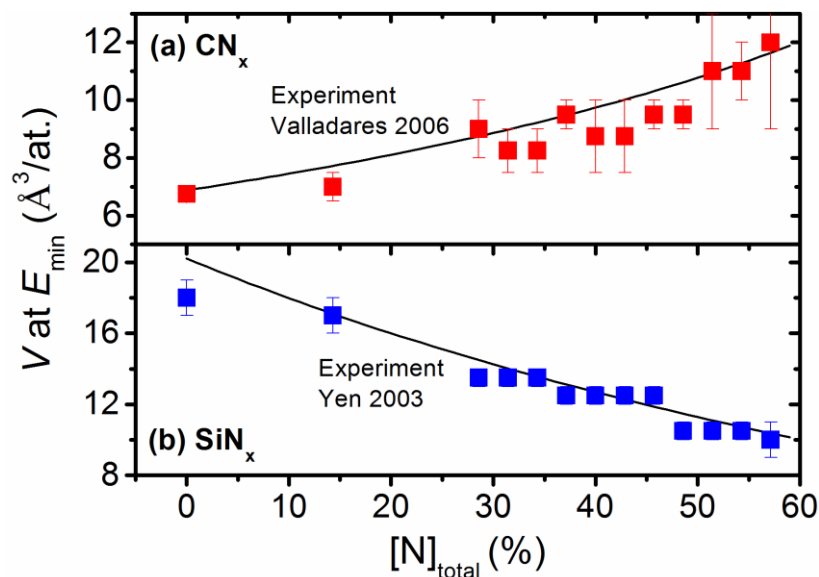


[J. Houska et al., Phys. Rev. B 72, 054204 (2005)]

Special case 1: N₂ molecules

Formation of N₂ molecules during the thermal spike cooling after an energetic particle impact is supported by the stability of triple N≡N bonds at T when the rest of the material is still molten

Thus, there is a maximum achievable nitrogen content (threshold for intensive formation of N₂ molecules) during an atom-by-atom growth of materials. Depends on the composition of course.



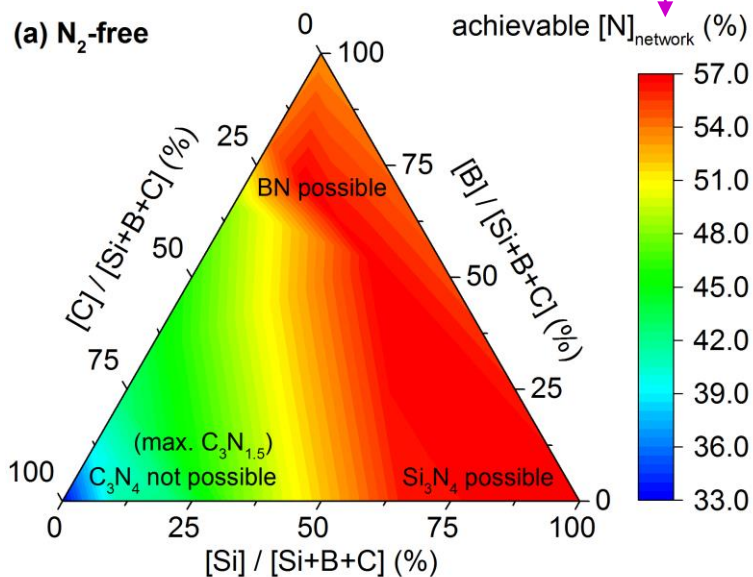
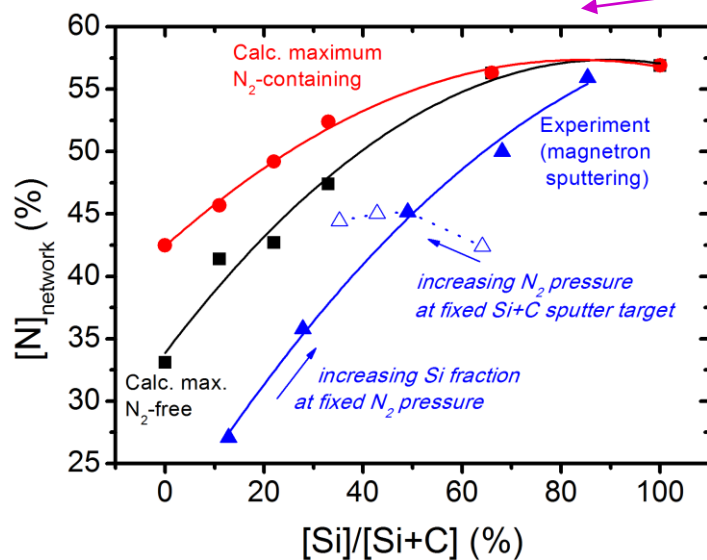
CN_x : intensive N₂ formation
large V of pores for N₂

SiN_x : up to $[N]_{\text{total}} = 57\%$ no N₂
zero V of pores for N₂

Special case 1: N₂ molecules

Formation of N₂ molecules during the thermal spike cooling after an energetic particle impact is supported by the stability of triple N≡N bonds at T when the rest of the material is still molten

Thus, there is a maximum achievable nitrogen content (threshold for intensive formation of N₂ molecules) during an atom-by-atom growth of materials. Role of composition of SiCN, SiBCN, etc.

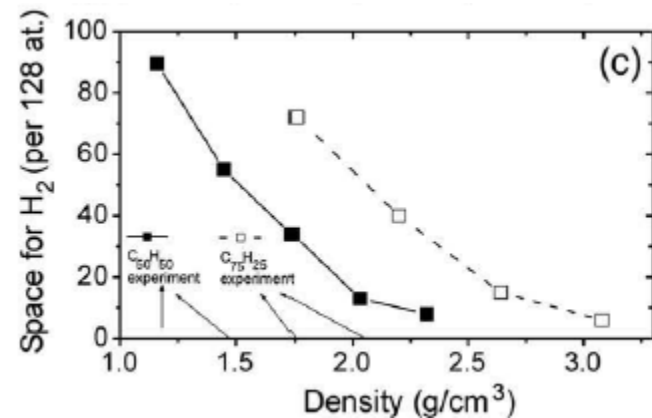
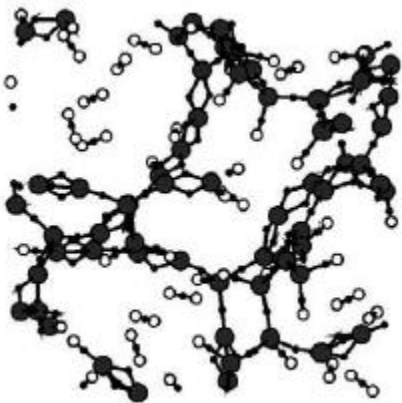


Special case 2: H₂ molecules

Formation of H₂ molecules during cooling is not very intensive (contrary to N₂)

However, H₂ molecules can arrive from plasma and stay in the material ("unbonded hydrogen") - there are (in a wide range of densities) enough pores which are sufficiently large for H₂

- Possibility to include them in simulation (present since start of cooling)
- Possibility to analyze (after end of simulation) the volume of pores which they can sit in



[J. Houska et al., Surf. Coat. Technol. 203, 3770 (2009)]

Special case 3: inert Ar

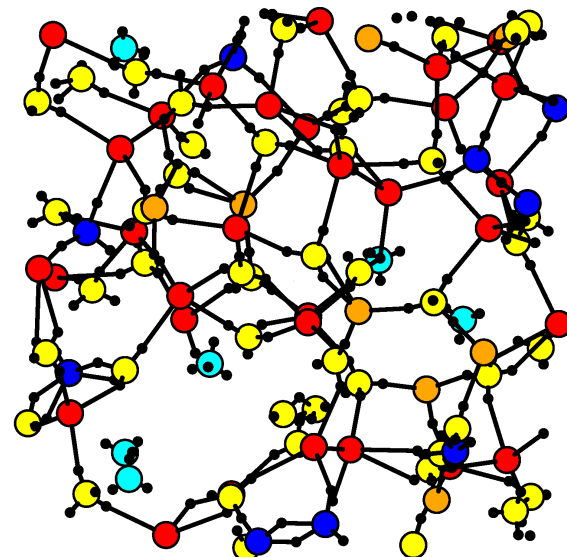
H_2 (or He) can sit in small pores which are in the material anyway, so they do not affect the rest of material very much.

Big implanted Ar atoms sit in large pores, existing because of them. Therefore they can affect the rest of structure.

High Ar content $\Rightarrow$ homogeneous structure

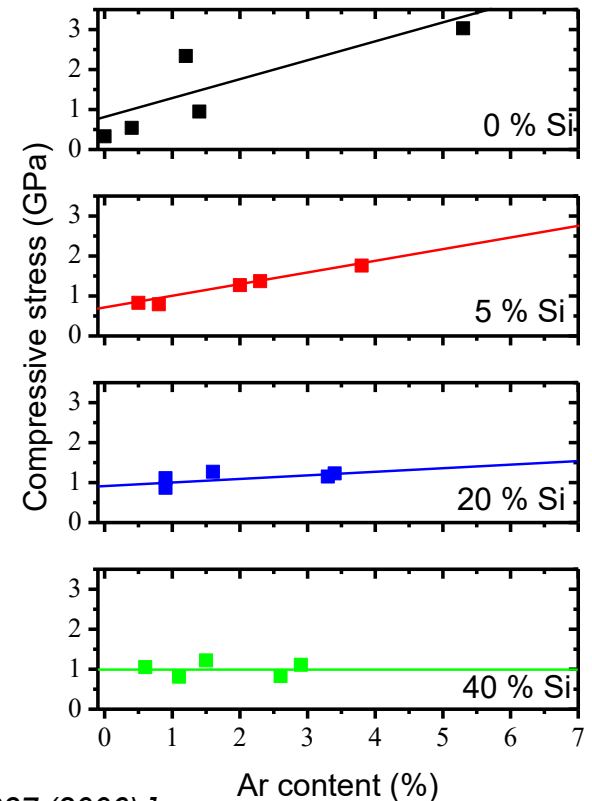
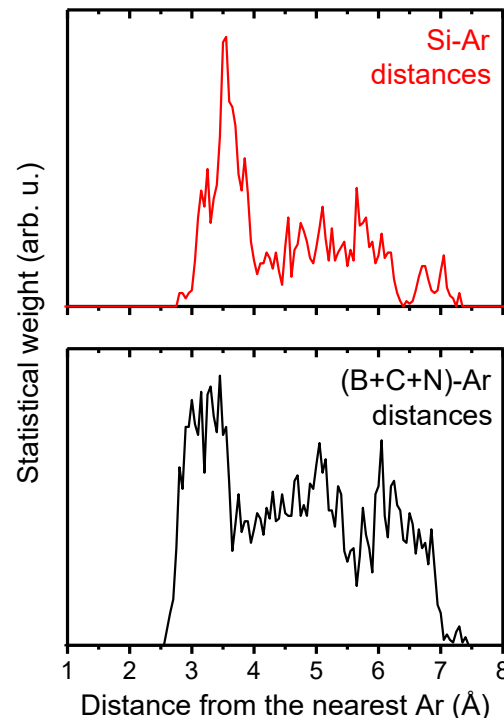
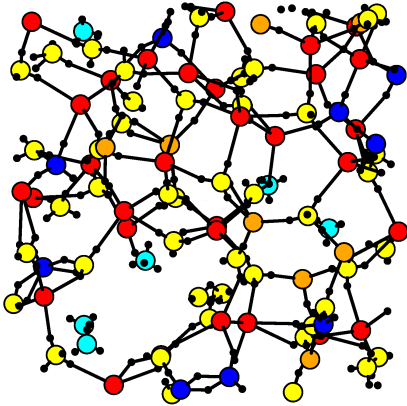
Low Ar content $\Rightarrow$ zones close to / far from Ar $\Rightarrow$ stronger effect

Example for SiBCN: formation of Si-rich zones around Ar (surrounding of large pores by longer and more flexible bonds is easier $\Rightarrow$ relieving of that part of stress which would be otherwise caused by Ar)



Special case 3: inert Ar

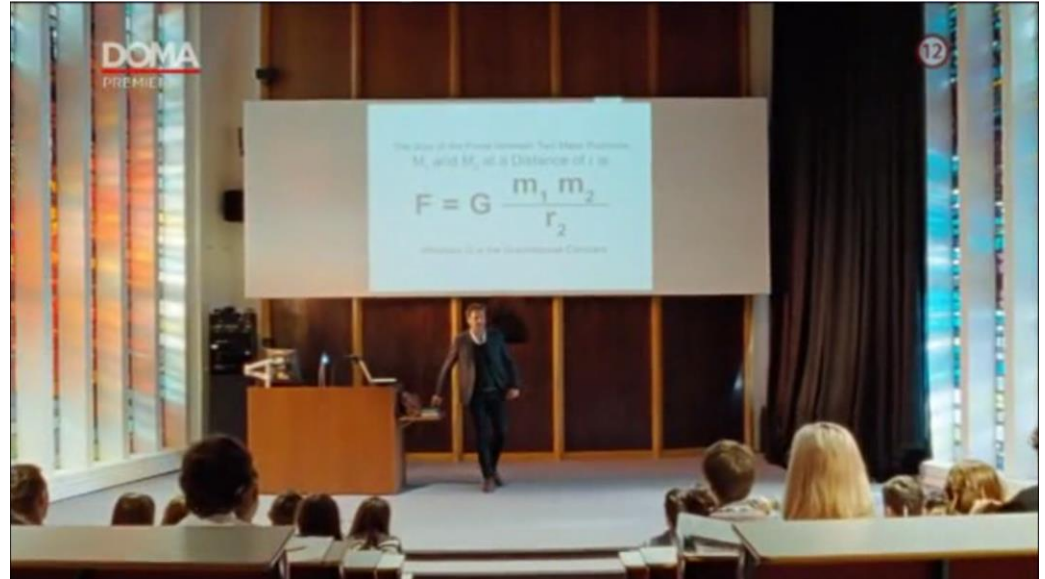
Example for SiBCN: formation of Si-rich zones around Ar (surrounding of large pores by longer and more flexible bonds is easier $\Rightarrow$ relieving of that part of stress which would be otherwise caused by Ar)



[J. Houska et al., J. Phys.: Condens. Matter 18, 2337 (2006)]

The End

Hopefully there were not too many typos like this one ...



screenshot from a romantic movie Rosamunde Pilcher: The Power of Love: the main hero (professor of physics) presents a new version of the gravity law

Acknowledgment (especially sources of some images)

- lecture notes of colleagues, especially B. Buckely, B. Gonul, P. Hofmann, J. Hu, P. Martin, B.K. Nikolic, P. Novak, J. Slavik
- for brevity, sources of (other) completely routine images (common knowledge available at many internet sites) are not cited, often wikipedia
- sources of images which are not commonly known (original results from scientific papers) are cited at the corresponding slides

Exam



Exam

(translation of slide which is primarily for MSc students:
PhD students have the .doc list of questions)

Many short questions, e.g.:

- How do the primitive unit cells of graphite and h-BN differ and why?
- Why we do not observe an interference on thick layers (e.g. glass substrate)?
- What is the difference between spinodal and binodal decomposition?
- Why are some carbon nanotubes conductive and some semiconductive?

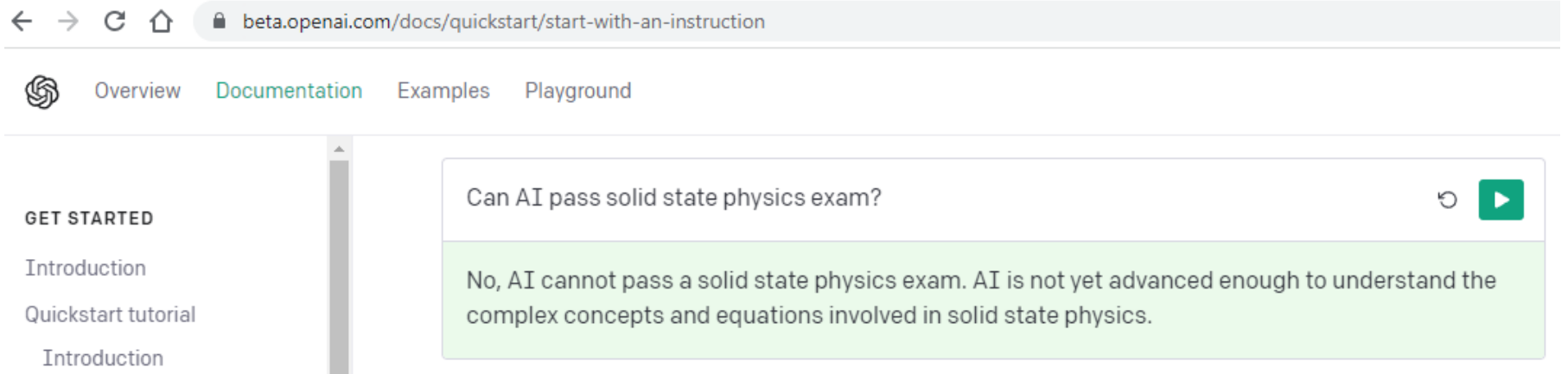
There is no need to memorize long non-intuitive equations
(e.g. learn that there are dispersion relations which can be used for materials with a band gap - Tauc-Lorentz and Cody-Lorentz, but it is not necessary to write them)

There will not be many questions from the field of simulations
(chapters 4 and 8) - they can wait for the MPPL exam

In a case of modifications of this presentation, the version valid
at the start of semester is sufficient to pass the exam

Exam

Is the exam difficult? Ask the artificial intelligence!



The screenshot shows the OpenAI Playground interface. The browser address bar displays the URL `beta.openai.com/docs/quickstart/start-with-an-instruction`. The navigation menu includes "Overview", "Documentation" (highlighted), "Examples", and "Playground". On the left sidebar, under "GET STARTED", the "Introduction" link is selected. The main content area shows a text input field with the query "Can AI pass solid state physics exam?". To the right of the input is a refresh icon and a green play button. Below the input, a green response box contains the text: "No, AI cannot pass a solid state physics exam. AI is not yet advanced enough to understand the complex concepts and equations involved in solid state physics."

← → ↺ 🏠 beta.openai.com/docs/quickstart/start-with-an-instruction

 Overview Documentation Examples Playground

GET STARTED

- Introduction
- Quickstart tutorial
- Introduction

Can AI pass solid state physics exam?

No, AI cannot pass a solid state physics exam. AI is not yet advanced enough to understand the complex concepts and equations involved in solid state physics.