Condensed matter structure and properties

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Febr.9, 2010

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1. Solid state materials - structure
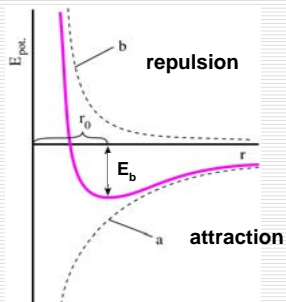
crystalline

or

(amorphous)

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1. Solid state materials - structure

Structure of crystalline materials

Ideal crystals: characterized by order

repulsion

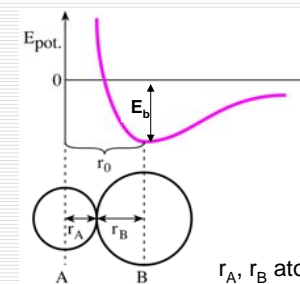$$E_{pot} = \frac{B}{r^m}$$

$$m > n$$

$$E_{pot} = -\frac{A}{r^n}$$

attraction

r_0

constituting atoms are at bond distances from each other

r= distance of two atoms forming the bond
r_o= bond distance
E_{bond}= bond energy

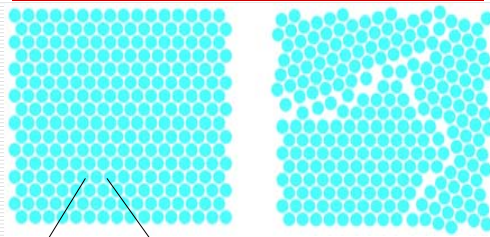### Structure of crystalline materials

$E_{pot.}$

E_b

r_0

r_A r_B

A   B

r_A, r_B atomic radii of atoms A and B

Atom	Z	van der Waals	Co-valent	Ionic	Ion
H	1	0,120	0,037	–	H⁺
C	6	0,170	0,077	0,029	C⁺
N	7	0,155	0,075	0,025	N⁺
O	8	0,152	0,073	0,140	O²⁻
F	9	0,147	0,071	0,117	F⁻
P	15	0,180	0,106	0,058	P³⁺
S	16	0,180	0,102	0,184	S²⁻

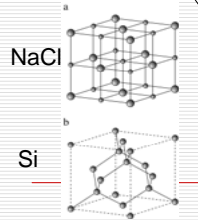*Atomic/molecular bond distances ($r_o = r_A + r_B$) and binding energies E_b depend on the type of interactions (functions a and b)*

Slide 1

Structure of crystalline materials
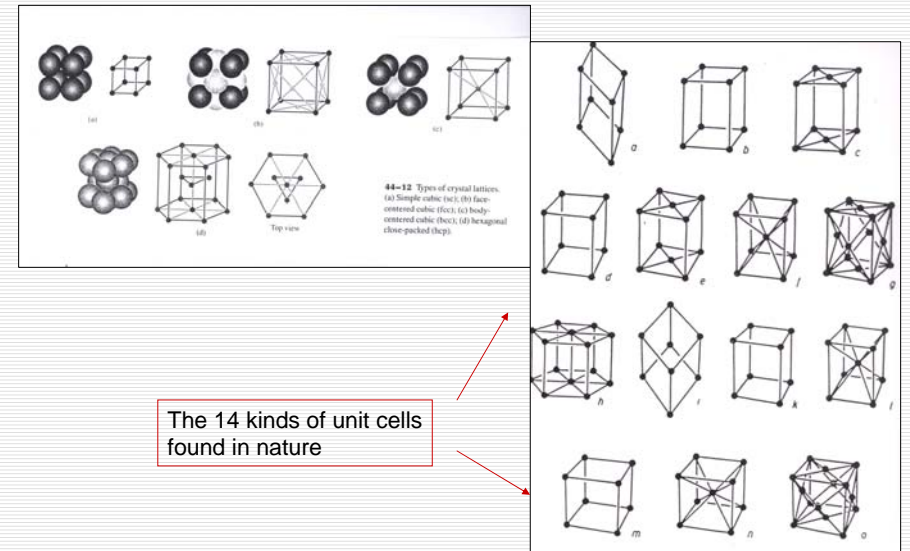
ideal crystal – single crystal
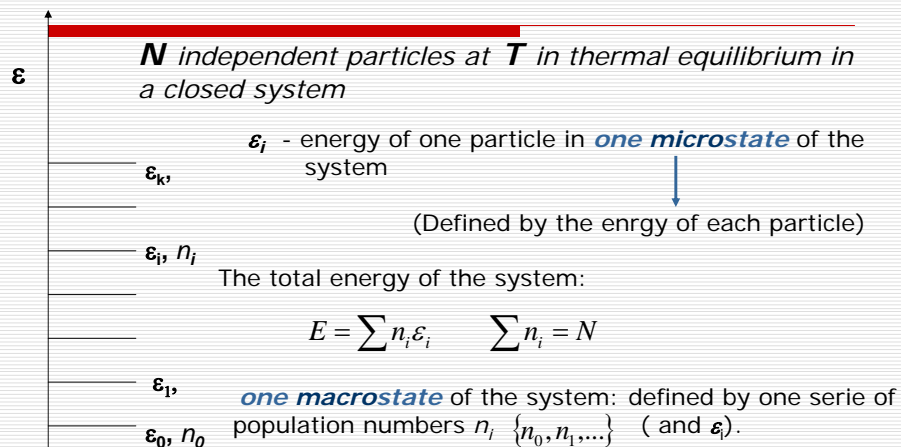

microcrystalline state (real crystals)

NaCl

unit cell
is repeated
to build up the
crystal lattice

Si

14 kinds of unit cells are found in nature

Slide 2

The 14 kinds of unit cells found in nature

Slide 3

Reminder: Boltzmann distribution

ε

N independent particles at T in thermal equilibrium in a closed system

ε_i - energy of one particle in **one microstate** of the system

ε_k,

(Defined by the enrgy of each particle)

ε_i, n_i

The total energy of the system:

$$E = \sum n_i \varepsilon_i \qquad \sum n_i = N$$

ε_1,

one macrostate of the system: defined by one serie of population numbers n_i $\{n_0, n_1, ...\}$ (and ε_i).

ε_0, n_0

Slide 4

Reminder: Boltzmann distribution

Boltzmann distribution – important formulae

$$p_i = \frac{e^{-\frac{\varepsilon_i}{kT}}}{Z}$$

probability that particles exist with ε_i energy in the system

$$Z = \sum_i^{n_i} e^{-\frac{\varepsilon_i}{kT}}$$

partition function

$$n_i = \frac{N e^{-\frac{\varepsilon_i}{kT}}}{Z}$$

$$\frac{n_i}{n_0} = e^{-\frac{\varepsilon_i - \varepsilon_0}{kT}} = e^{-\frac{\Delta\varepsilon}{kT}}$$

Boltzmann factor

The relaive population of two energy states

Structure of crystalline materials

Considering two states of bonds – intact
- broken

$$\frac{n_b}{n_i} = e^{-\frac{E_b}{kT}} \approx \frac{n}{N}$$

Boltzmann distribution

$$n_i + n_b = N$$

e.g. NaCl, E_b=6.31eV, kT(room tempr.)=0.023eV

Atomic cohesive energy

$$\frac{n_b}{n_i} = e^{-\frac{6.31}{0.023}} \approx e^{-274} \approx 10^{-110} = 0$$

E_b ~ **primary bonds** : covalent
ionic
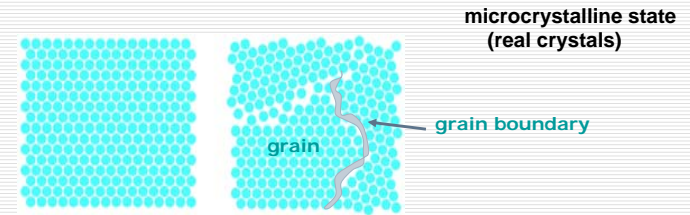metallic

1 - 13 eV $E_b >> kT$ (RoomTempr)

There would be perfect order in ideal crystals – no broken bonds

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Structure of crystalline materials

primary bonds -> **strong** bonds -> not broken thermally at **rt**

long range order in ideal crystals:large number of atoms in periodic array

Still: crystal defects in **real** crystals

**microcrystalline state
(real crystals)**

grain boundary

grain

Structure of crystalline materials

primary bonds -> **strong** bonds -> not broken thermally at **rt**

long range order in ideal crystals:large number of atoms in periodic array

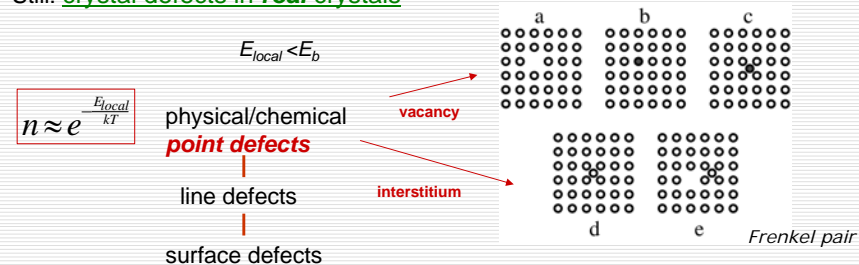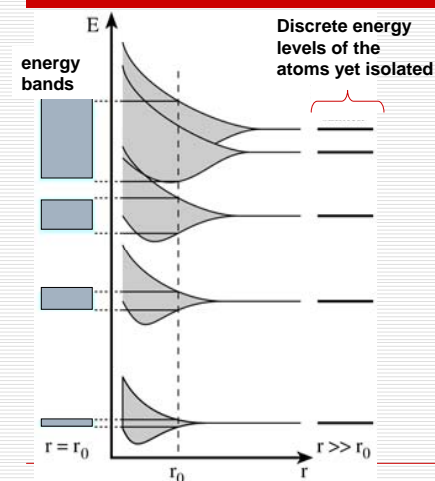Still: crystal defects in **real** crystals

$E_{local} < E_b$

$$\boxed{n \approx e^{-\frac{E_{local}}{kT}}}$$

physical/chemical
point defects

vacancy

line defects

interstitium

surface defects

Frenkel pair

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2. Solid state materials (crystals)- properties

Interaction of ordered atoms changes the electronic energy levels

energy bands
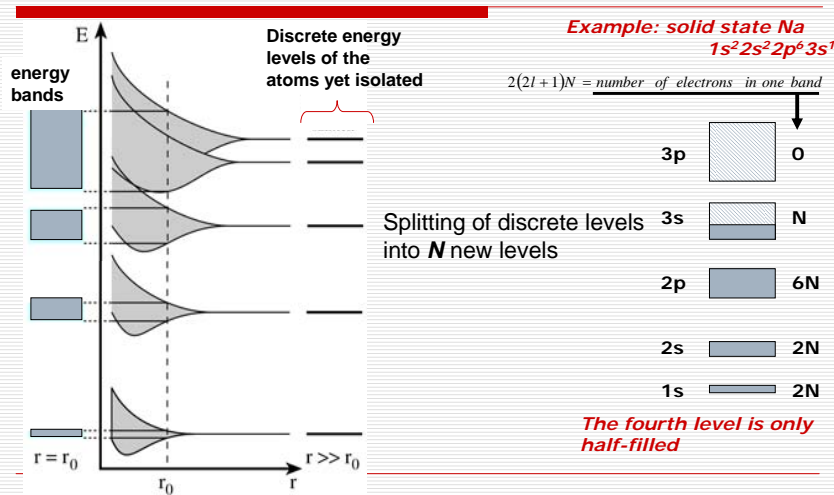
Discrete energy levels of the atoms yet isolated

N~10^{23}
N no.of isolated atoms with discrete energy levels change their electronic states when they interact to form a crystalline state with bond distance r_0.

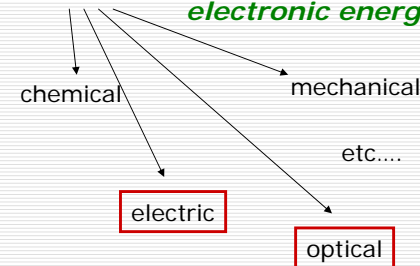Splitting of discrete levels into **N** new levels results in continuous ranges :
energy bands

2. Solid state materials (crystals)- properties
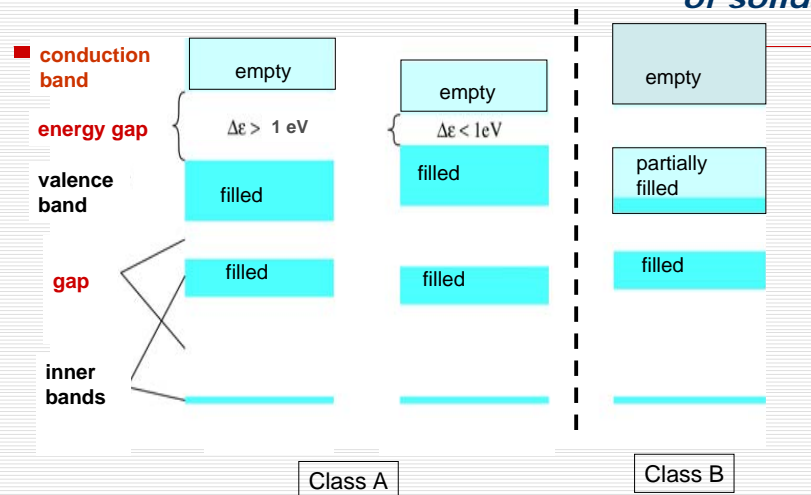
Interaction of ordered atoms changes the electronic energy levels

energy bands

Discrete energy levels of the atoms yet isolated

E

Example: solid state Na
$1s^2 2s^2 2p^6 3s^1$

$2(2l+1)N = number\ of\ electrons\ in\ one\ band$

3p		0
3s		N
2p		6N
2s		2N
1s		2N

Splitting of discrete levels into **N** new levels

The fourth level is only half-filled

$r = r_0$ r_0 $r \gg r_0$ r

Significance of electronic energy level structure

Properties of materials are the consequence of the *electronic energy levels*

chemical

mechanical

etc....

electric

optical

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4. Possible classes of electronic band features of solids

■ **conduction band**

energy gap

valence band

gap

inner bands

empty	empty	empty
$\Delta\varepsilon > 1$ eV	$\Delta\varepsilon < 1$eV	partially filled
filled	filled	
filled	filled	filled

Class A   Class B

The schematics of band structures must be completed with the effect of T>0 temperature

■ **conduction band**

energy gap

valence band

gap

inner bands

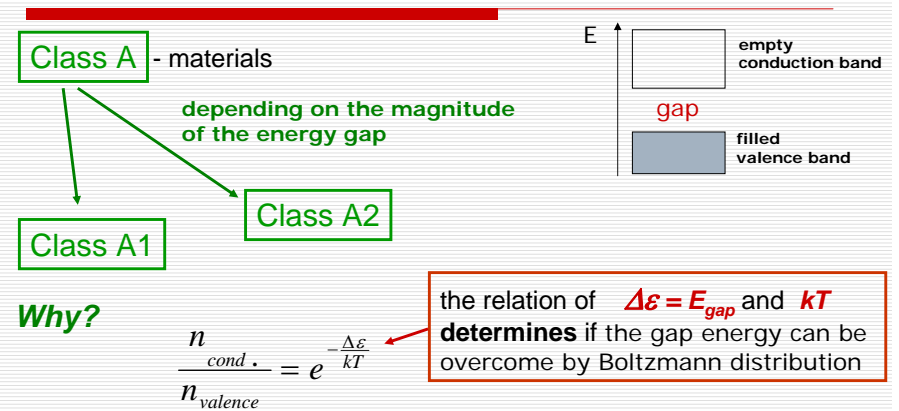| empty	empty	empty
$\Delta\varepsilon > 1$ eV	$\Delta\varepsilon < 1$eV	partially filled
filled	filled	
filled	filled	filled

Class A   Class B

The concept of Boltzmann distribution is also applicable for the population of the electronic energy levels

5. Properties related to the energy band feature in solids

conduction band	empty	empty
energy gap	$\Delta\varepsilon > 1\ eV$	$\Delta\varepsilon < 1eV$
valence band	filled	filled / partially filled
gap	filled	filled / filled
inner bands		

insulators semiconductors metals

Class A Class B

Classes of crystalline solid materials
– band features and properties

Class A - materials

depending on the magnitude of the energy gap

Class A1 **Class A2**

E

empty conduction band

gap

filled valence band

Why?

$$\frac{n_{cond.}}{n_{valence}} = e^{-\frac{\Delta\varepsilon}{kT}}$$

the relation of $\Delta\varepsilon = E_{gap}$ and kT **determines** if the gap energy can be overcome by Boltzmann distribution

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Class A1

$$E_{gap} >> 1eV \qquad \textit{insulators}$$

e.g diamond E_{gap} = 5.4 eV

$$\frac{N_{cond}}{N_{val}} = e^{-\frac{5.4}{0.023}} = e^{-235} = 0$$

-No electric conductivity (dielectric break-down: ~V/bond → 10^{10} V/m)

-No photon absorption in the **VIS range -> transparency**

- UV photons may be absorbed, IR: excitation of lattice vibrations

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Class A2

$$E_{gap} \leq 1eV \qquad \textit{intrinsic semiconductors}$$
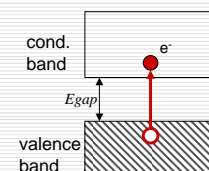
Non-transparent crystalline materials
Reasonable number of thermally excited electrons in the conduction band

0 K	$E_g\ (eV)$
Si	1.1
Ge	0.75

$$\frac{N_{cond}}{N_{val}} = e^{-\frac{0.75}{0.023}} = e^{-33} = 7*10^{-15}$$

$$N_{val} \approx 6*10^{23}\ !\Rightarrow N_{cond} \approx 4*10^{8} \qquad /cm^3$$

cond. band

$Egap$

valence band

n - type conductivity (electron conduction)

$$\sigma \approx e^{-\frac{E_{gap}}{2kT}}$$

p - type conductivity (electron-hole: + charge conduction)

Two kinds of charge carriers

Class A2 — intrinsic semiconductors

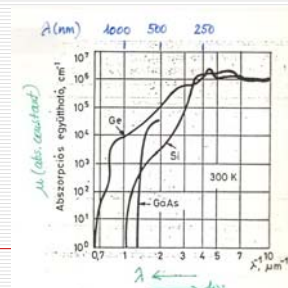$$\sigma = const * e^{-\dfrac{E_{gap}}{2kT}}$$

Slightly depends on T

Equilibrium: generation and recombination of charge carriers is of equal probability

p(recombination)~n^2, p(generation)~ Boltzmann factor

Specific conductivity is increased by temperature increase
→ **thermoresistors**

Optical properties: non-transparency in the VIS range

$$hf_{VIS} > E_{gap}$$

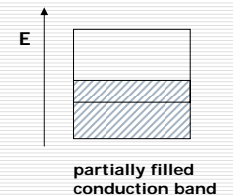Photon absorption induces conductivity
→ **photodetectors**

Class B — metals

e.g. 1-valence and 2-valence metals   Na, Mg, Cu..

	Cu	Si
n(charge)/m³	9x10²⁸	1x10¹⁶
specific resistance (Ohmxm)	2x10⁻⁸	3x10³

T=293 K

high electric conductivity

partially filled conduction band

Energy absorption is possible within the partially filled highest energy band

-Electrons conduct electricity

-Optical non-transparency

$$\sigma \approx \frac{1}{T}$$

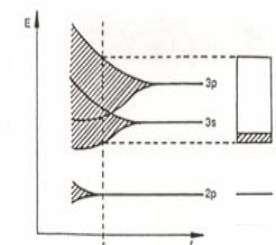Specific conductivity
decreases with T-increase

semiconductors

Class B — metals

e.g. 1-valence and 2-valence metals   Na, Mg, Cu..

	Cu	Si
n(charge)/m³	9x10²⁸	1x10¹⁶
specific resistance (Ohmxm)	2x10⁻⁸	3x10³

T=293K

high electric conductivity

The example of Na-metal
$1s^2 2s^2 2p^6 3s^1$

Energy absorption is possible within the partially filled highest energy band

Broadening → *overlap of bands 3s and 3p*
1/8-th filling of last band

Class A2** — doped semiconductors

Doping: incorporation of a second component (dopant) into the crystal lattice of an intrinsic semiconductor (host) in a small amount

$$\frac{N_{host}}{N_{dopant}} \approx 10^6 \longrightarrow \textbf{Dopant atoms are isolated in the crystal matrix}$$

Idea: properly selected **dopant may reduce E_{gap}**, thus increasing the number of thermally excited charge carriers : electrons or electron-holes

doped semiconductors

$$\frac{N_{host}}{N_{dopant}} \approx 10^6 \longrightarrow$$ **Dopants are isolated in the crystal matrix**

Dopants reduce the effective E_{gap}

Two combinations:

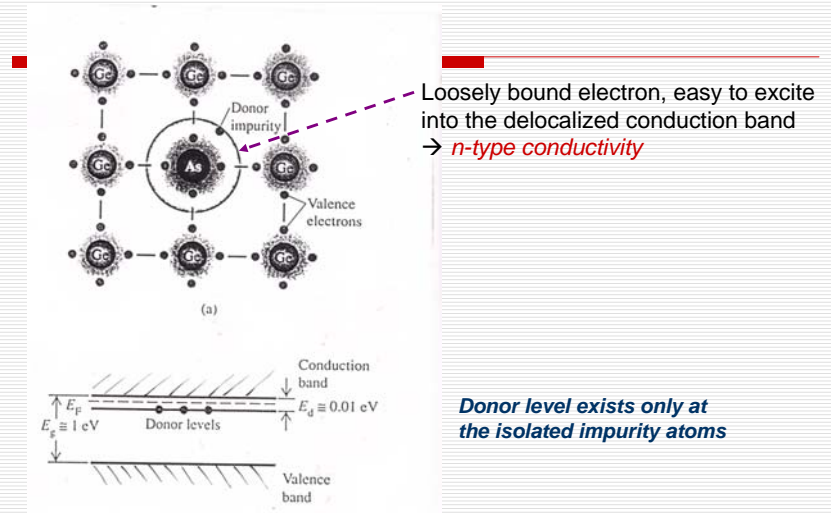-4-valent host combined with 5-valent dopant → *n-type* doped semiconductor

-4-valent host combined with 3-valent dopant → *p-type* doped semiconductor
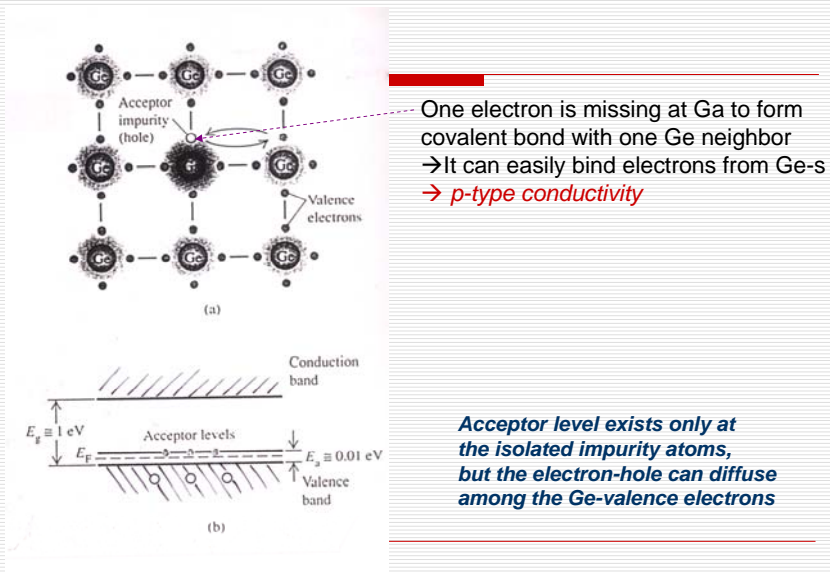
Hosts: Ge, Si   **Dopants: 5-valent : P, As, Bi**
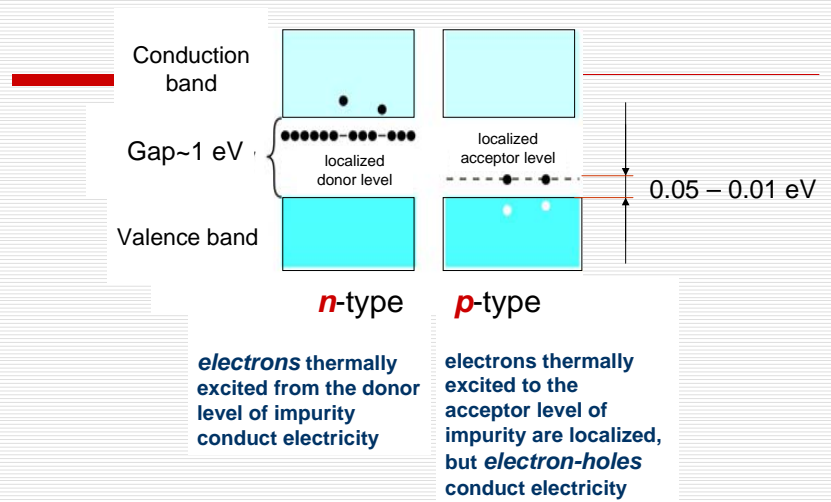   **3-valent : B, Al, Ga, In**

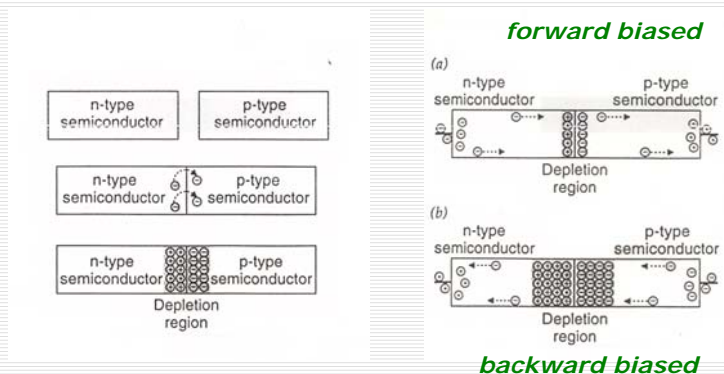*Example: Doping 4 valence Ge crystal with 5 valence As*

Loosely bound electron, easy to excite into the delocalized conduction band
→ *n-type conductivity*

Donor level exists only at the isolated impurity atoms

Example: Doping 4 valence Ge crystal with 3 valence Ga

One electron is missing at Ga to form covalent bond with one Ge neighbor
→It can easily bind electrons from Ge-s
→ *p-type conductivity*

Acceptor level exists only at the isolated impurity atoms, but the electron-hole can diffuse among the Ge-valence electrons

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Summary: n-type and p-type conduction

Conduction band

Gap~1 eV

localized donor level

localized acceptor level

Valence band

0.05 – 0.01 eV

n-type   **p-type**

electrons **thermally excited from the donor level of impurity conduct electricity**

electrons thermally excited to the acceptor level of impurity are localized, but *electron-holes* **conduct electricity**

p – n junctions $\longrightarrow$ revolution in electronics

n-type semiconductor p-type semiconductor

n-type semiconductor p-type semiconductor

n-type semiconductor p-type semiconductor Depletion region

forward biased

(a) n-type semiconductor p-type semiconductor Depletion region

(b) n-type semiconductor p-type semiconductor Depletion region

backward biased

diode and transistor:
constructed from n- and p– type doped semiconductors
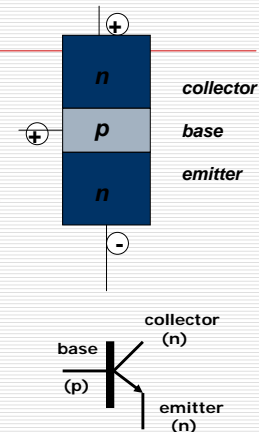
forward biased

+ p n -

diode:
- rectifier
- light source under voltage
- transducer of light into voltage

transistor:
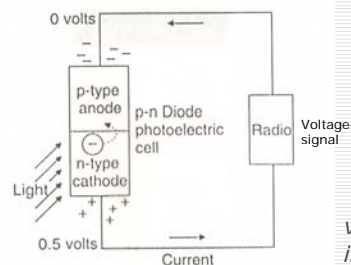- electric current amplifier
- digital unit of computers

n collector
p base
n emitter

collector (n)
base (p)
emitter (n)

Doping makes possible miniature sizes $\longrightarrow$ *microelectronics*

p – n junctions : light emitters and detectors

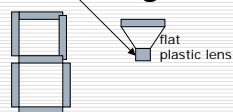**Light detector**: *excitation of valence electrons by photon absorption into the conduction band changes charge equilibrium*

$\longrightarrow$ *electric signal*
CCD camera: two dimensional diode-array

0 volts

p-type anode
p-n Diode photoelectric cell
n-type cathode
Light
0.5 volts
Current
Radio Voltage signal

LED: Light Emitting Diode

flat plastic lens

voltage brings extra charges into the conduction band – switch off leads to recombination $\rightarrow$ $E_{gap} = hf$

6. Major classes of materials
internal order (structure) and properties

- **Gases**

- **Liquids**

Mesomorphous systems:
Liquid crystals

- **Solids (crystals)**

6.1 Gases

**ideal gas:** no interaction – no bond formation – no „structure"

particle energy ~ kinetic energy

-> disorder?

two rules governing disorder

1. **average of kinetic energy** is
   determined by the temperature

$$\frac{1}{2}mv\overline{^2} = \frac{3}{2}kT$$
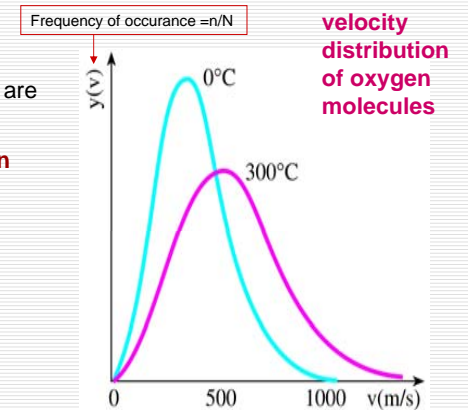
degree of freedom of
motion for point-like
partocles

6.1 Gases

two rules

Frequency of occurance =n/N

**velocity
distribution
of oxygen
molecules**

2. **deviations** from the average $\overline{v}$ are
determined by the

Maxwell – Boltzmann distribution
function

Boltzmann distribution with
$\mathcal{E}$=1/2mv²

6.2 Liquids

particles ~ molecules built up by primary bonds

interaction between particles is by _**secondary bonds**_

		E_b(eV)
	H-bond	several x 0.1
	hydrophobic	~ 0.1
van der Waals	dipole – point charge	~ 0.1-0.2
	dipole – dipole	~ 0.02
	dipole – induced dipole	~ 0.01
	temporary dipoles	~ 0.02

$\longleftrightarrow$ _**kT**_=0.025 eV

_**A large proportion of the secondary bonds are broken at room
temprature**_

6.2 Liquids

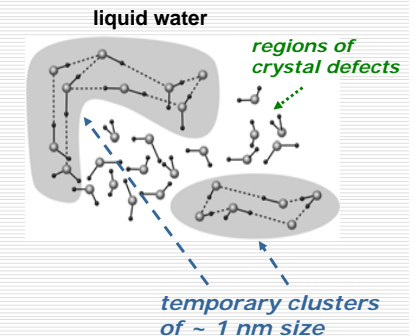interaction between particles is by _**secondary bonds**_

liquid water

e.g. H-bonds in liquid water

_regions of
crystal defects_

$$\frac{n_{broken}}{n_0} \cong 1\% \; - 0.05\% \quad at \; room \; tempr \; .$$

large number of broken bonds!

**Properties:**

short range order
deformability
isotropy

_temporary clusters
of ~ 1 nm size_

6.2 Liquids: the special properties of water

structure of ice

Loosely packed structure

Diamond

liquid water

regions of crystal defects

a

b

melting

density increases up to 4 ºC

c

short range order

temporary clusters of ~ 1 nm size

Ice crystal of snow

d

6.2 Liquids: the special properties of water

Tetrahedral symmetry of strong H-bonding
Large electric dipole

liquid water

regions of crystal defects

Outstanding
- heat of evaporation
- specific heat
- surface tension

- dielectric constant

short range order

temporary clusters of ~ 1 nm size

Hydration of biological macromolecules and biological membranes

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Live matter – what is its material class?

mitokondrium   sejtmag   citoszkelton

durva endoplazmatikus retikulum   Golgi-készülék   sima endoplazmatikus retikulum

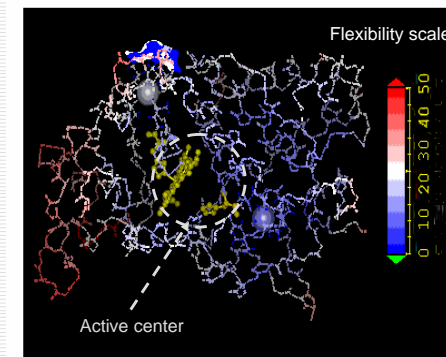**Hierarchy of strong and weaker bonds**

Primary bonds in base molecules, substrates, polimer chains – periodicity?? – quasicrystalline???,

Secondary bonds stabilize the secondary structure – sequential order, secondary order

Broad variety of bond strengths

Conformational dynamics: functional changes of the structure are made possible

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Live matter ~ mesomorphous systems– intermediate between crystals and liquids
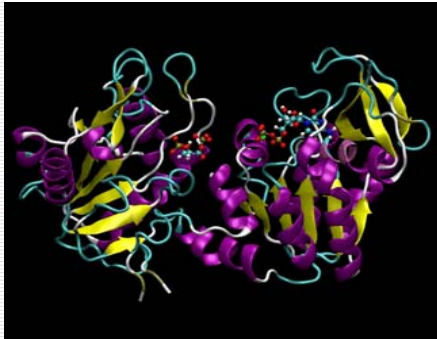
Flexibility scale

Active center

Hierarchy of strong and weaker bonds

Conformational dynamics make possible the opening of channels for substrates to reach the active center

Horseradish Peroxidase : polipeptide chain with two bound Ca ions and one prosthetic group (heme)

Live matter ~ mesomorphous systems– intermediate between crystals and liquids

Phosphoglycerate kinase

Hierarchy of strong and weaker bonds

Conformational dynamics make possible the domain closure to bring ADP and 1,3-bisphosphoglycerate into contact

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Mesomorphous systems – liquid crystals
Discussed next time – Dr. Voszka

Thank you for your attention