Lecture: Solid State Chemistry - WP I/II

Chapter 2: Structure and bonding in solids

2.1 Bond valence, Radius ratio and Pauling rules

2.2 Lattice enthalpy of ionic solids

2.3 Chemical bonding in metals, alloys and semiconductors (insulators)

2.4 Hydrogen bonding

2.5 Molecular interactions and packing of molecules

2.6 Models, rules and principles of bonding/building

Chapter 2. Chemical bonding in solids

Bonding models and theories of solids must account for basic properties as:

- type, stability and distribution of crystal structures

- mechanism and temperature dependence of the electrical conductivity of insulators, semiconductors, metals and alloys

- lustre of metals, thermal conductivity and color of solids, ductility and malleability of metals ...

Useful models and theories are e.g.:
   - radius ratio and Pauling rules (ionic solids)
   - concept of lattice enthalpy (ionic solids)
   - band model (various types of solids)
   - Kitaigorodskii's packing theory (molecular solids)

2.1 Bond valence, Radius ratio and Pauling rules

- ionic structures consist of charged, elastic and polarizable speres

- they are arranged so that cations are surrounded by anions and vice versa, and are held together by electrostatic forces

- to maximize the electrostatic attraction (the lattice energy), coordination numbers are as high as possible, provided that neighbouring ions of opposite charge are in contact

- next nearest anion-anion and cation-cation interactions are repulsive, leading to structures of high symmetry with maximized volumes → attraction vs repulsion!

- the valence of an ion is equal to the sum of the electrostatic bond strengths between it and adjacent ions of opposite charge (see Pauling rule no 2)

2.1 Bond valence, Radius ratio and Pauling rules

(1) A coordination polyhedron of anions is formed around each cation. The cation-anion distance is determined by the radius sum and the coordination number CN of the cation by the radius ratio.

(2) The (bond) valence (s) of a cation M^{m+} surrounded by n anions (A) is

$$s = m/n$$

$\sum s_{ij}$ **should be equal to the charge of A** (originally for oxides only)

Example 1 - TiO_2 (Rutile) :

$CN(Ti^{4+}) = 6$ $s(Ti-O) = 4/6 = 2/3$

$CN(O^{2-}) = 3$, $\sum s_{ij} = 3 \times 2/3 = 2$

Example 2 – CaO (rocksalt)

$CN(Ca^{2+}) = 6$, $s(Ca-O) = 2/6 = 1/3$

$CN(O^{2-}) = 6$, $\sum s_{ij} = 6 \times 1/3 = 2$

Example 3 - TiO_2 (Fluorite-hypothetic) :

$CN(Ti^{4+}) = 8$ $s(Ti-O) = 4/8 = 1/2$

$CN(O^{2-}) = 4$, $\sum s_{ij} = 4 \times 1/2 = 2$ (!)

Example 4 – $MgAl_2O_4$ (spinell)

$CN(Mg^{2+}) = 4$, $s(Mg-O) = \frac{1}{2}$

$CN(Al^{3+}) = 6$, $s(Al-O) = \frac{1}{2}$

$CN(O^{2-}) = 1Mg + 3Al = 1/2 + 3/2 = 2$

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2.1 Bond valence, Radius ratio and Pauling rules

(3) The presence of shared edges, and particularly shared faces decreases the stability of a structure. This is particularly true for cations with large valences and small CN.

Repulsion effect!

(4) In a crystal containing different cations those with large valence and small CN do not tend to share polyhedron elements (corners, edges, faces) with each other.

(5) The number of chemically different coordination environments for a given ion in a crystal tends to be small (e.g. tetrahedra or octahedra only). (exceptions e.g.$CdSO_3$)

2.2 Lattice enthalpy of ionic solids

The <u>lattice enthalpy</u> is the standard molar enthalpy change for the following process:

$$M^+_{(gas)} + X^-_{(gas)} \rightarrow MX_{(solid)} \quad \Delta H_L: \text{lattice enthalpy}$$

Because the formation of a solid from a „gas of ions" is always <u>exothermic</u> lattice enthalpies (defined in this way !!) are usually negative numbers.

If entropy considerations are neglected the <u>most stable crystal structure</u> of a given compound is the one with the <u>highest lattice enthalpy.</u>

ΔH_L can be derived from a simple **electrostatic model** or the **Born-Haber cycle**

2.2 Lattice enthalpies can be determined by a thermodynamic cycle → <u>Born-Haber cycle</u>

After Hess (and the 1. set of thermodynamics) reaction enthalpy is independent of the reaction path. For the formation of an ionic solid MX this means:
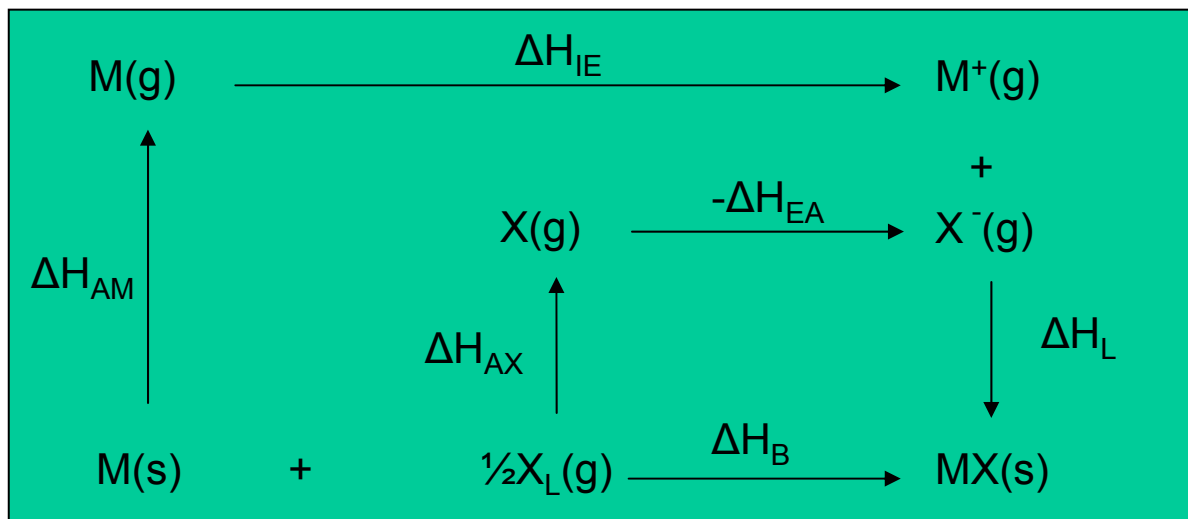
with: $\Delta H_B = \Delta H_{AM} + \Delta H_{AX} + \Delta H_{IE} - \Delta H_{EA} + \Delta H_L$

ΔH_{AM} and ΔH_{AX}: enthalpy of atomisation to gas of M and X (~ enthalpy of sublimation for M and $\frac{1}{2}$ of the enthalpy of dissoziation) for X_2)
ΔH_{IE} and ΔH_{EA}: enthalpy of ionisation of M and electron affinity of X
ΔH_B: enthalpy of formation, ΔHL: lattice enthalpy

2.2 Lattice enthalpies can be determined by a thermodynamic cycle → __Born-Haber cycle__
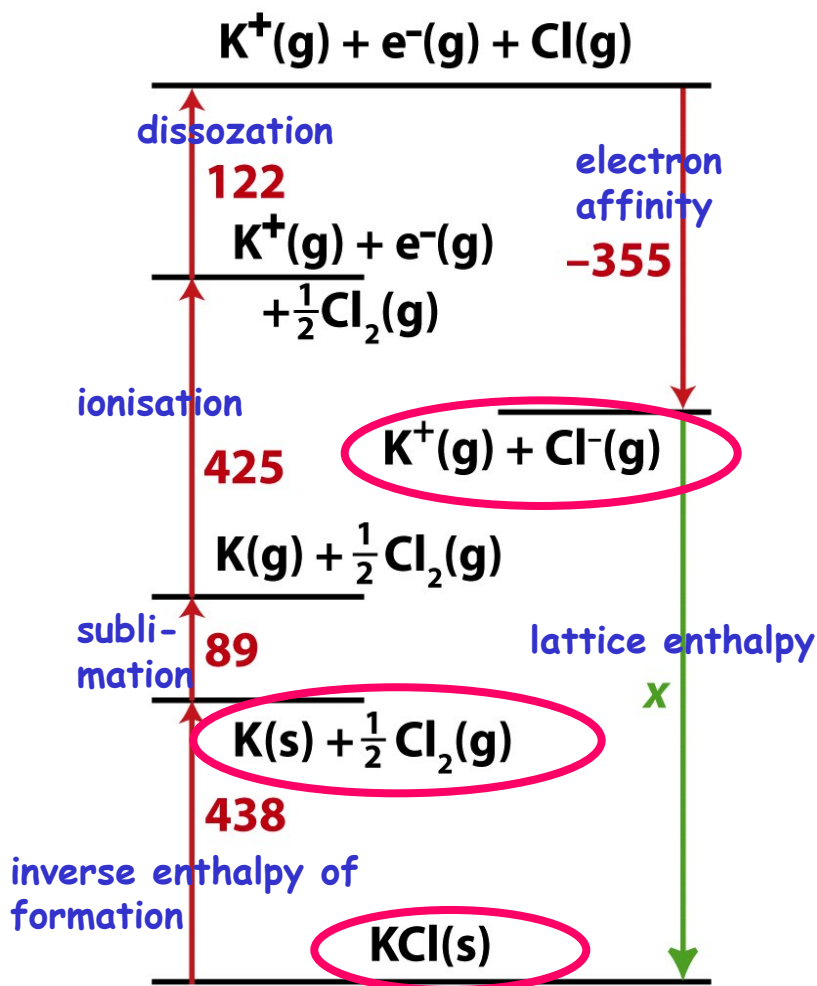

$K^+(g) + e^-(g) + Cl(g)$

dissozation
122

electron affinity
−355

$K^+(g) + e^-(g) + \frac{1}{2}Cl_2(g)$

ionisation
425

$K^+(g) + Cl^-(g)$

$K(g) + \frac{1}{2}Cl_2(g)$

subli-mation
89

lattice enthalpy
x

$K(s) + \frac{1}{2}Cl_2(g)$

438

inverse enthalpy of formation

KCl(s)

Figure 3-44
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A Born-Haber diagram for KCl

(all enthalpies: kJ mol^{-1} for __normal conditions__ → standard enthalpies)

standard enthalpies of
- sublimation, ΔH_{Ax}: +89 (K)
- ionization, ΔH_{IE}: +425 (K)
- dissoziation, ΔH_{AM}: +244 (Cl_2)
- electron affinity, ΔH_{EA}: -355 (Cl)
- lattice enthalpy, ΔH_L: x = 719
- enthalpy of formation, ΔH_B: -438 (for KCl)

the harder the ions, the higher ΔH_B

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2.2 Calculation of lattice enthalpies

$$\Delta \mathrm{H}_L^0 = V_{AB} + V_{Born}$$

V_{AB} = Coulomb (electrostatic) interaction between <u>all</u> cations and anions treated as <u>point charges</u> (Madelung part of lattice enthalpy („MAPLE")

V_{Born} = Repulsion due to the overlap of electron clouds (Born repulsion)

2.2 Calculation of lattice enthalpies

1. MAPLE (V_{AB})
(Coulombic contributions to lattice enthalpies, MADELUNG Part of Lattice Enthalpy, atoms treated as <u>point charges</u>)

$$V_{AB} = -A \ N_A \left(\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_{AB}} \right)$$

Coulomb potential of an ion pair

V_{AB}: Coulomb potential (electrostatic potential)
A: <u>Madelung constant</u> (depends on structure type)
N_A: Avogadro constant
z: charge number
e: elementary charge
ε_0:   dielectric constant (vacuum permittivity)
r_{AB}: shortest distance between cation and anion
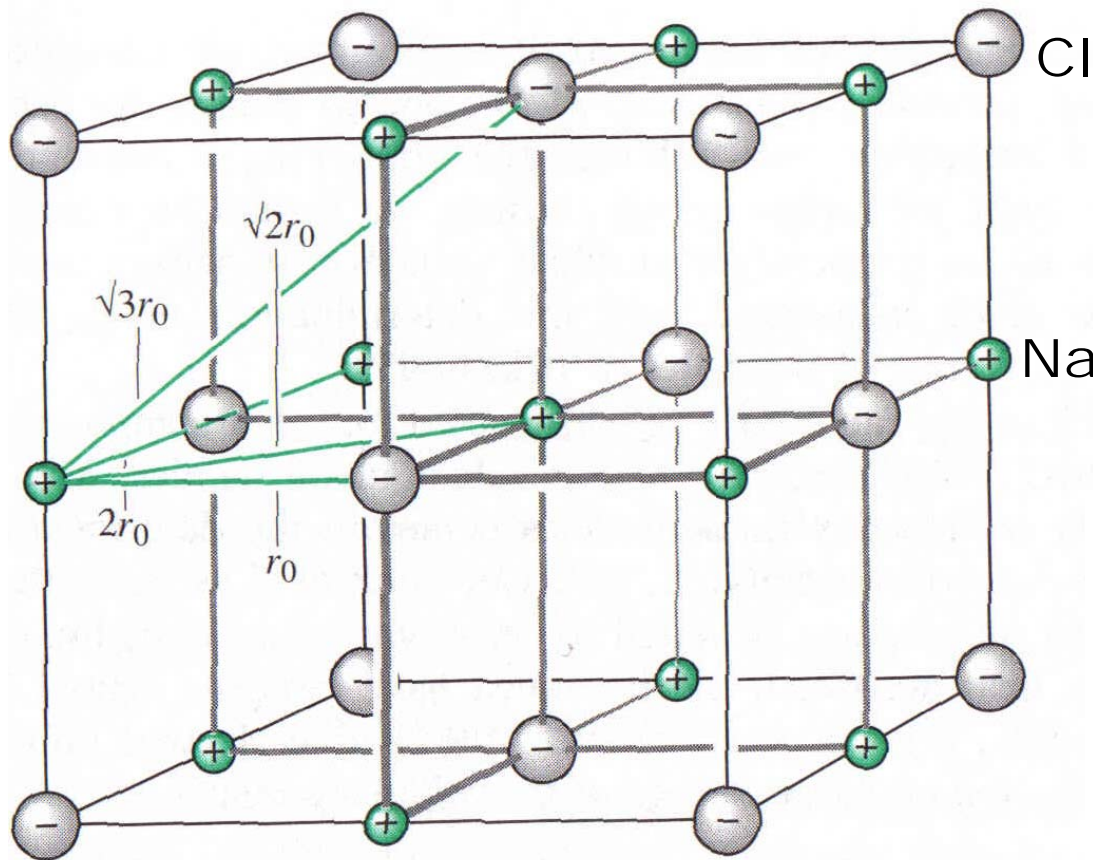
typical for 3D ionic solids:
Coulomb attraction and repulsion

Madelung constants:
CsCl: 1.763
NaCl: 1.748
ZnS: 1.641 (wurtzite)
ZnS: 1.638 (sphalerite)
ion pair: 1.0000 (!)

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}}...$$

= 1.748... (NaCl)
(infinite summation)

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2.2 Born repulsion (V_{Born})
**(Repulsion arising from overlap of electron clouds, atoms do not behave as point charges)**
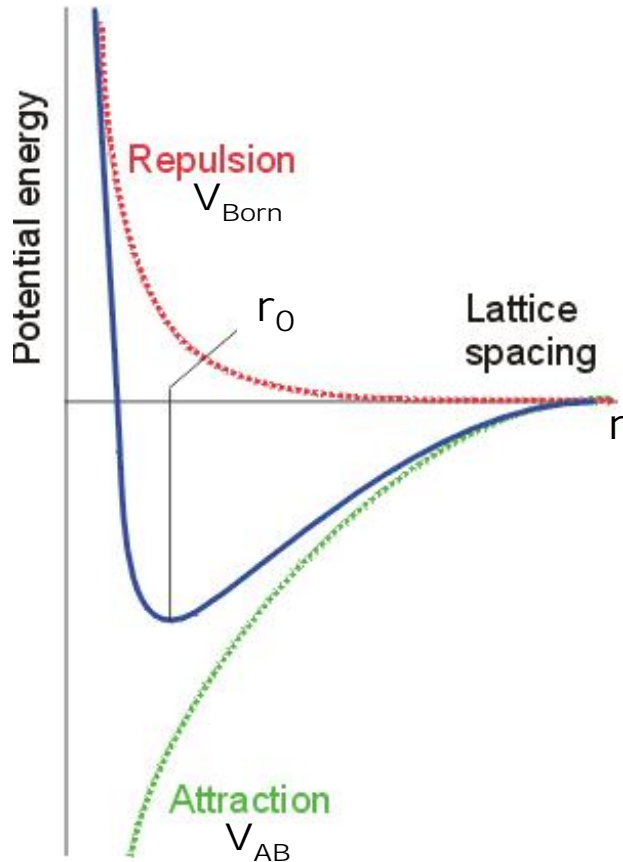
Because the electron density of atoms decreases exponentially towards zero at large distances from the nucleus the Born repulsion shows the same behaviour

approximation:

$$V_{Born} = \frac{B}{r_{AB}^{\,n}} N_A$$

B and n are constants for a given atom type; n can be derived from compressibility measurements (~8)

2.2 Total lattice enthalpy from Coulomb interaction **and** Born repulsion
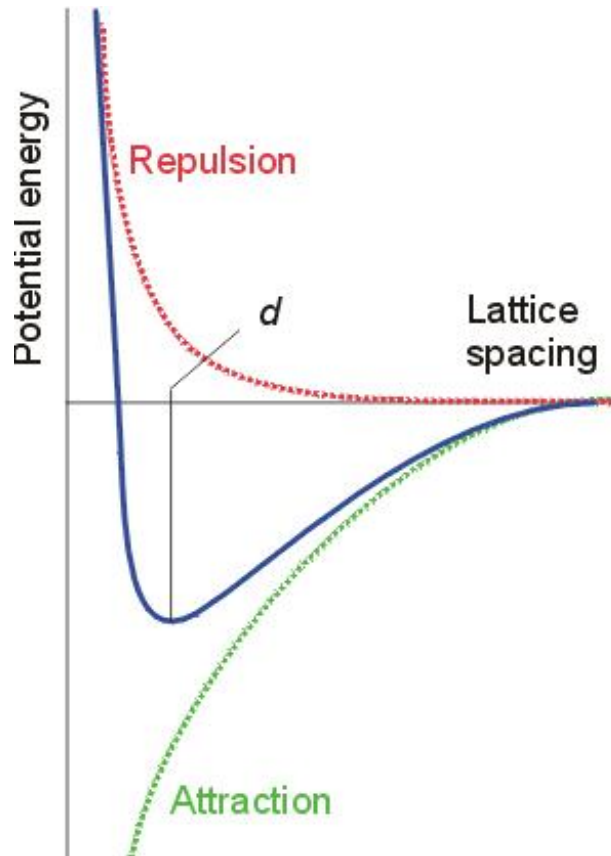
$$\Delta H_L^0 = V_{AB} + V_{Born}$$

$$V_{AB} = -A\,N_A\,\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_{AB}}$$

$$V_{Born} = \frac{B}{r_{AB}^{\,n}}\,N_A$$

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2.2 Total lattice enthalpy from Coulomb interaction and Born repulsion

$$\Delta H_L^0 = V_{AB} + V_{Born}$$

$$V_{AB} = -A\,N_A\,\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_{AB}}$$

$$V_{Born} = \frac{B}{r_{AB}^{\,n}}\,N_A$$

$$\Delta H_L^0 \Rightarrow Min.\,(V_{AB} + V_{Born})$$

(set first derivative of the sum to zero)

$$\Delta H_L^0 = -A\,\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0}\,N_A\left(1 - \frac{1}{n}\right)$$

2.2 Total lattice enthalpy from Coulomb interaction <u>and</u> Born repulsion

$$\Delta H_L^0 = Min. \; (V_{AB} + V_{Born})$$

$$\Delta H_L^0 = -A \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0} N_A (1 - \frac{1}{n})$$

Lattice enthalpies (kJ mol^{-1}) by Born-Haber cyle and (calculated)
NaCl: –772 (-757); CsCl: -652 (-623) ...

Applications of lattice enthalpy calculations:
→ lattice enthalpies and stabilities of „non existent"
   compounds and calculations of electron affinity
   data (see next transparencies)
→ Solubility of salts in water (see Shriver-Atkins)

2.2 Calculation of the lattice enthalpy for NaCl

$$\Delta H^0_L = -A \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0} N_A (1 - \frac{1}{n})$$

$\varepsilon_0 = 8.854\times10^{-12}$ C^2/Jm; $e = 1.602\times10^{-19}$ C; $N_A = 6.023\times10^{23}$ mol^{-1}

$A = 1.748$; $r_0 = 2.8\times10^{-10}$ m; $n = 8$ (Born exponent)

$1/4\pi\varepsilon_0 = 8.99\times10^9$ Jm/C^2 $e^2 N_A = 1.542\times10^{-14}$ C^2/mol

$\Delta H_L = -1.386\times10^{-5}\times A/r_0\times(1-1/n)$ $Jmol^{-1}$ (for univalent ions !)

Dimensions: $\dfrac{C^2 \ Jm}{C^2 \ m \ mol} = J/mol$

NaCl: $\Delta H_L' = -865$ kJ mol^{-1} (only MAPLE)
      $\Delta H_L = -757$ kJ mol^{-1} (including Born repulsion)

Can MgCl (Mg^+Cl^-) be a stable solid when crystallizing in the rocksalt structure?

The energy of formation of MgCl can be calculated from Born Haber cycle based on similar r_{AB} as for NaCl !! to be H_{Form} ~ -126 kJ mol^{-1}

This means that MgCl should/can be a stable compound !!!!!

However: Chemical intuition should warn you that $MgCl_2$ is more stable and that there is a risk of disproportionation:

   $2 MgCl_{2(s)} \rightarrow Mg_{(s)} + MgCl_{2(s)}$ H_{Dispro} = ??????

   $2 MgCl \rightarrow 2 Mg + Cl_2$ H_F = +252 kJ (twice the enthalpy of formation)
   $Mg + Cl_2 \rightarrow MgCl_2$ H_F = -640 kJ (from calorimetric measurement)

Σ $2 MgCl \rightarrow Mg + MgCl_2$ H_{Dispro} = -388 kJ

(thus disproportionation reaction is favored)

Calculation of the electron affinity H_{EA} of Cl from the Born-Haber cycle for CsCl

Standard enthalpy of	formation	H_B	= - 433.0 kJ/mol
	sublimation	H_{AX}	= 70.3
½	atomization/dissociation	H_{AM}	= 121.3
	ionization	H_{IE}	= 373.6
Lattice enthalpy		H_L	= - 640.6

$$H_{Form} = H_{Subl} + \tfrac{1}{2} H_{Diss} + H_{Ion} + H_{EA} + H_{Lattice}$$

$$H_{EA} = H_B - (H_{AX} + \tfrac{1}{2} H_{AM} + H_{IE} + H_L)$$

$$H_{EA} = - 433 - (70.3 + 121.3 + 373.6 - 640.6) = \underline{-357.6 \ kJ/mol}$$

Not bad compared to the real value of ΔH_{EA} : -355 kJmol^{-1}

2.2 Comparison of theoretical and experimental (Born-Haber cycle) lattice enthalpies for some rocksalt structures

	ΔH_L^{calc} / $(kJ\ mol^{-1})$	ΔH_L^{exp} / $(kJ\ mol^{-1})$	$(\Delta H_L^{exp} - \Delta H_L^{calc})$ / $(kJ\ mol^{-1})$
LiF	1029	1030	6
LiCl	834	853	19
LiBr	788	807	19
LiI	730	757	27
AgF	920	953	33
AgCl	832	903	71
AgBr	815	895	80
AgI	777	882	105

Table 3-9
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the harder the ions the higher ΔH_L and the lower the difference

2.3 Chemical bonding in metals, alloys and semiconductors (insulators)

Metallic compounds are characterized by delocalized valence electrons, i.e. by electrons being free to migrate through the structure. (In covalent and ionic compounds the valence electrons are localized.)

These delocalized, migrating electrons are responsible for the high electrical conductivity of metals.

The bonding theory used to account for delocalized electrons is the **band theory** or the **band model** of solids.
It can be described as an extension of the MO theory of small, finite molecules to infinite 3D structures leading to **valence bands** instead of MO's.

The band model must reflect the physical properties like electrical conductivity of metals, alloys and semiconductors.

2.3 Band model: temperature dependence of the electrical conductivity of metals and semiconductors (insulators)

key to understanding: „band model"

conductivity S cm^{-1}

Metal and Alloy → decreasing conductivity

Superconductor → conductivity below T$_c$: ∞ !!

Semiconductor and Insulator → Increasing conductivity
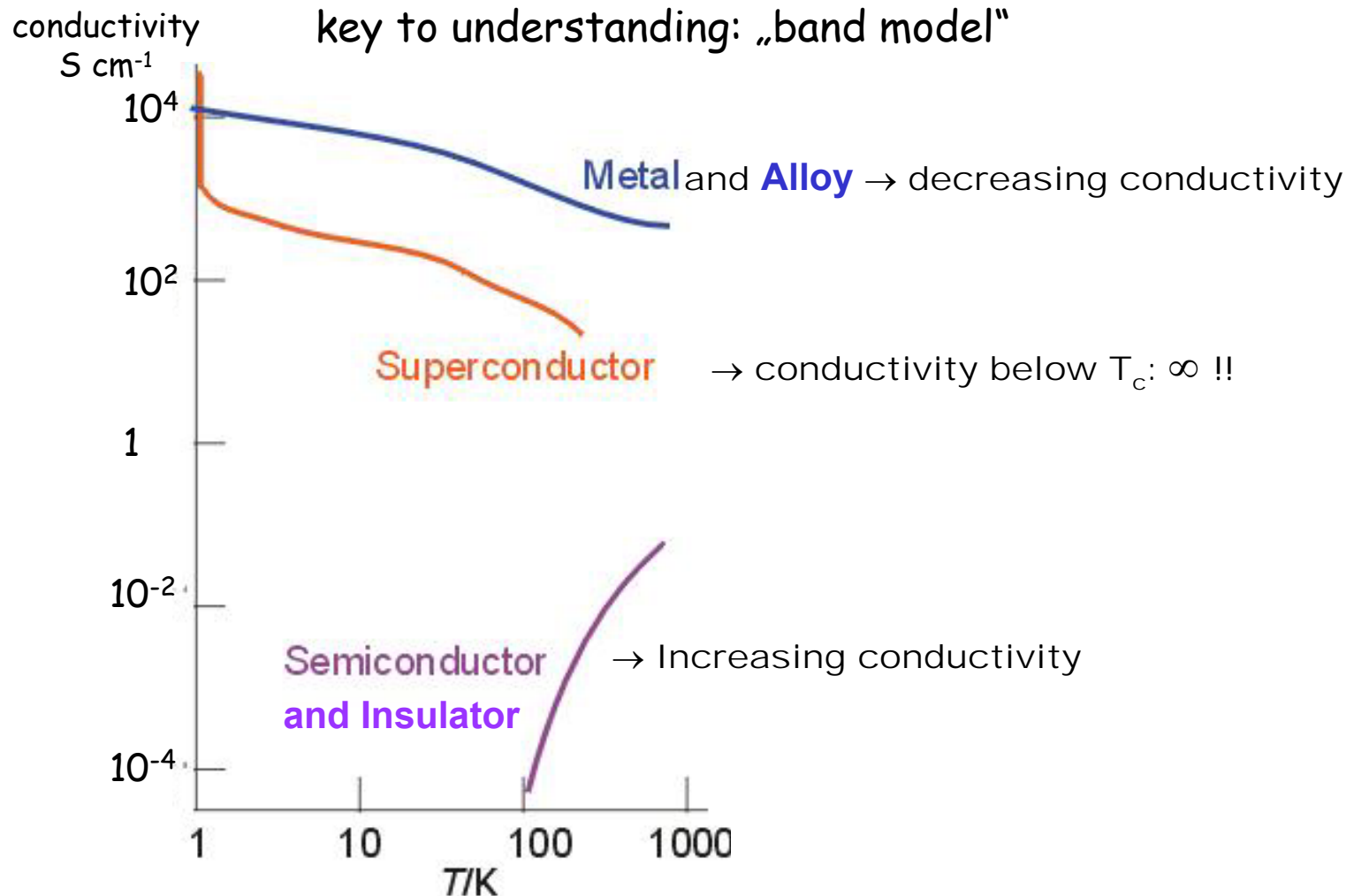
Orders of magnitude of electrical conductivity values
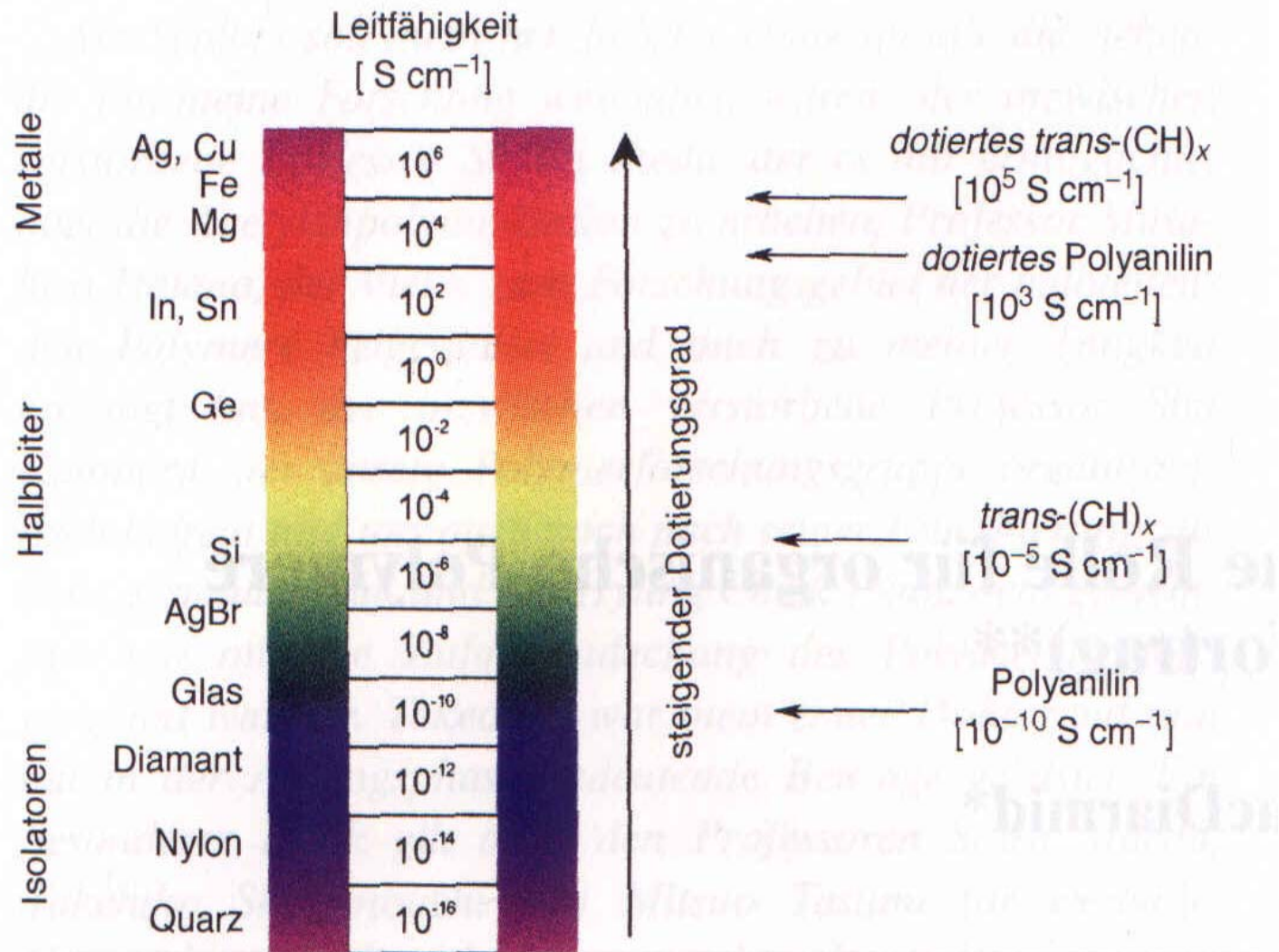
2.3 The origin of the simple band model for solids: band formation by overlap of atomic orbital (basically a continuation of the Molecular Orbital model)

Most antibonding

Non-bonding

Most bonding

Energy

1 2 3 4 5 6 7 8 9 10 11 12 ... 20 ... ∞

N

Band

Band gap

Band

Band gap

Band

Energy

$\delta E << kT_c$ of ~ 0.025 eV
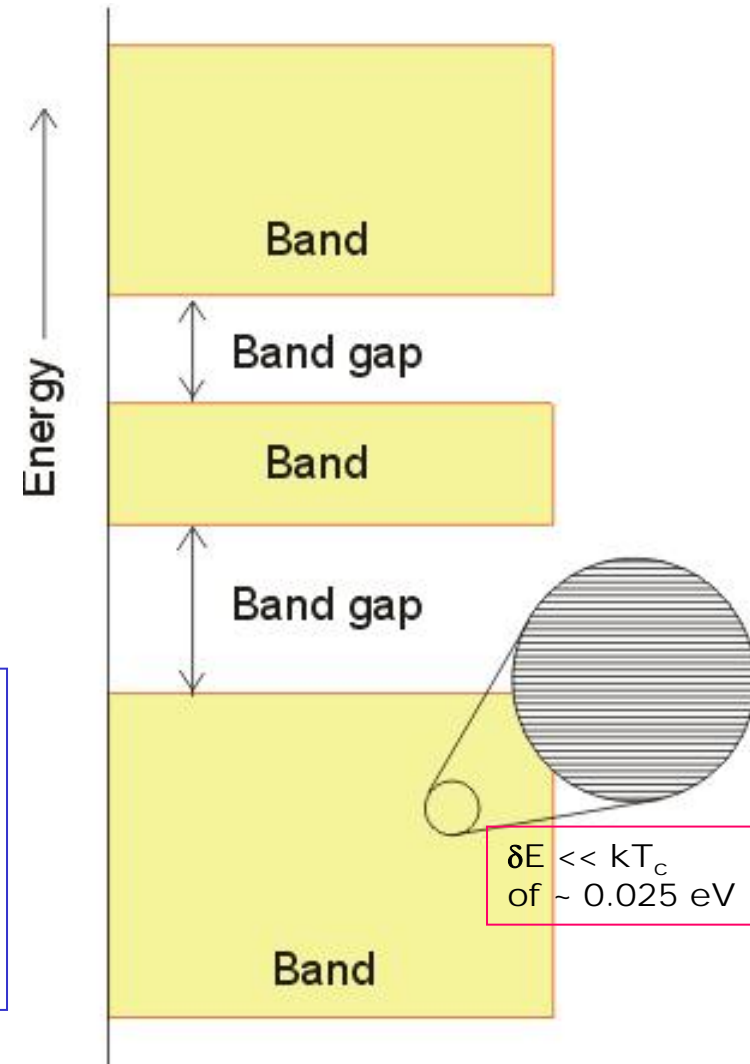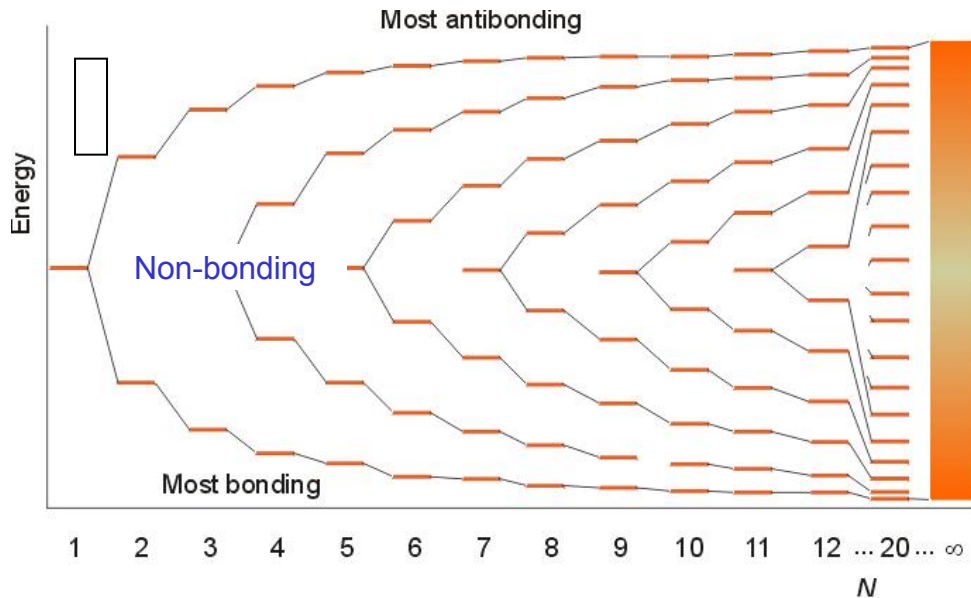
The overlap of atomic orbitals in a solid gives rise to the formation of <u>bands</u> separated by energy <u>gaps</u>
(the band width is a rough measure of interaction between neighbouring atoms)

2.3 s and p bands in a one-dimensional solid

Energy
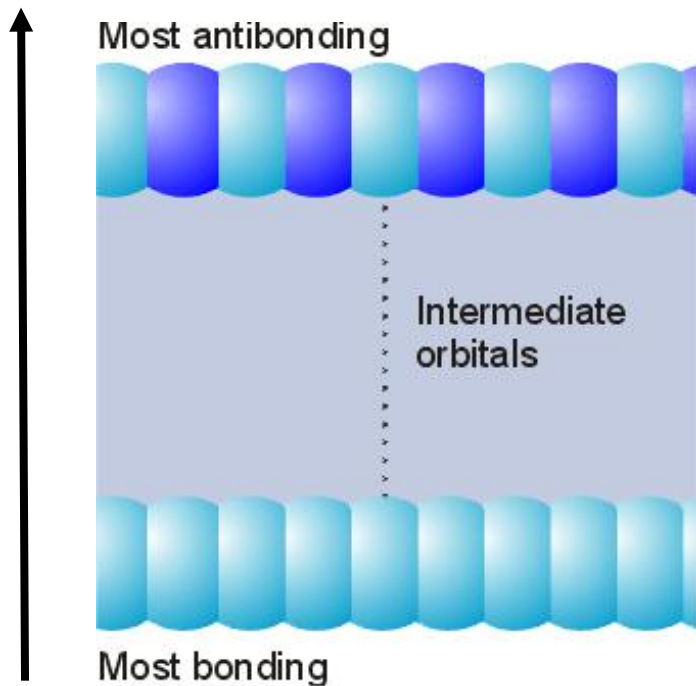
Most antibonding

max number of nodes

Intermediate orbitals

min number of nodes

Most bonding

s-band

Most antibonding

Intermediate orbitals

Most bonding
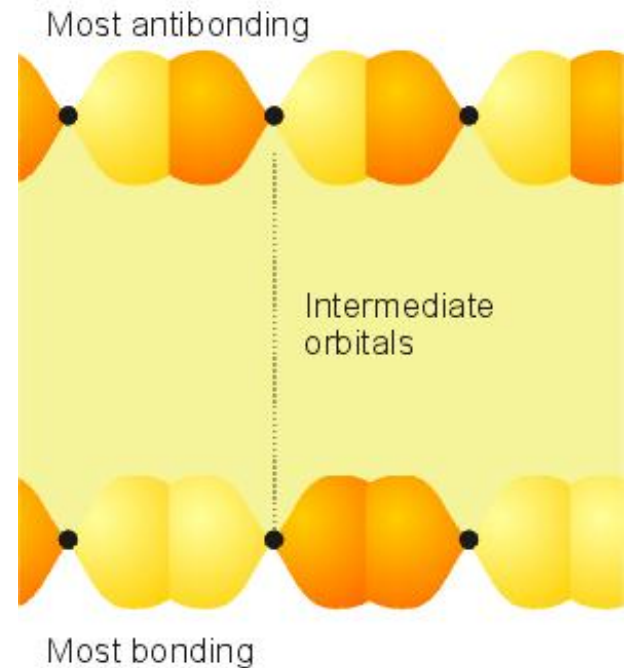
p-band

N AO's give N MO's

- Whether there is in fact a gap between bands (e.g. s and p)
  depends on the energetic <u>separation of the respective orbitals</u>
  of the atoms and <u>the strength of interaction</u> between them.
- If the interaction is strong, the bands are wide and may overlap.
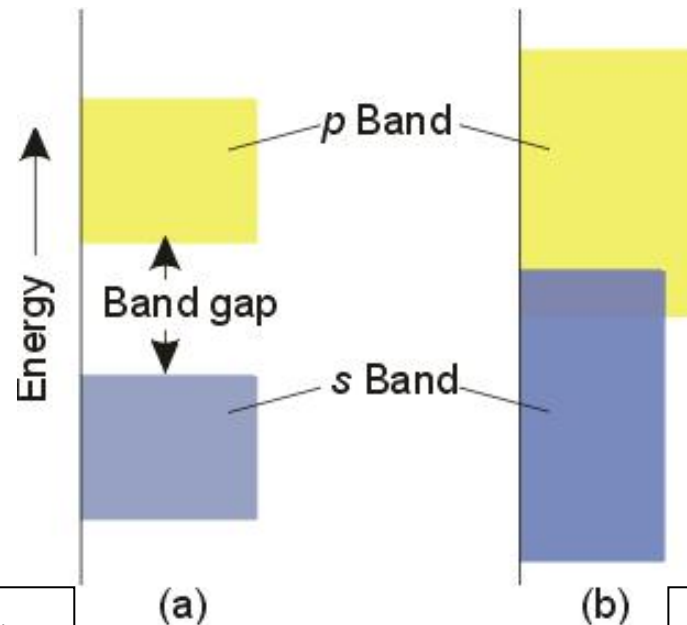
weak interaction
weak overlap
small bands

strong interaction
strong overlap
wide bands

2.3 Insulator, Semiconductor, Metal (T = 0 K)

Energy

electrical conductivity requires easy accessible free energy levels above E_F

conduction band (empty)

e⁻

E_F

hole:+

o

valence band (filled with e⁻)

band overlap

Insulator (> 1.5 eV)

Semiconductor (< 1.5 eV)

Metal (no gap)

(at T = 0 K <u>no</u> conductivity)
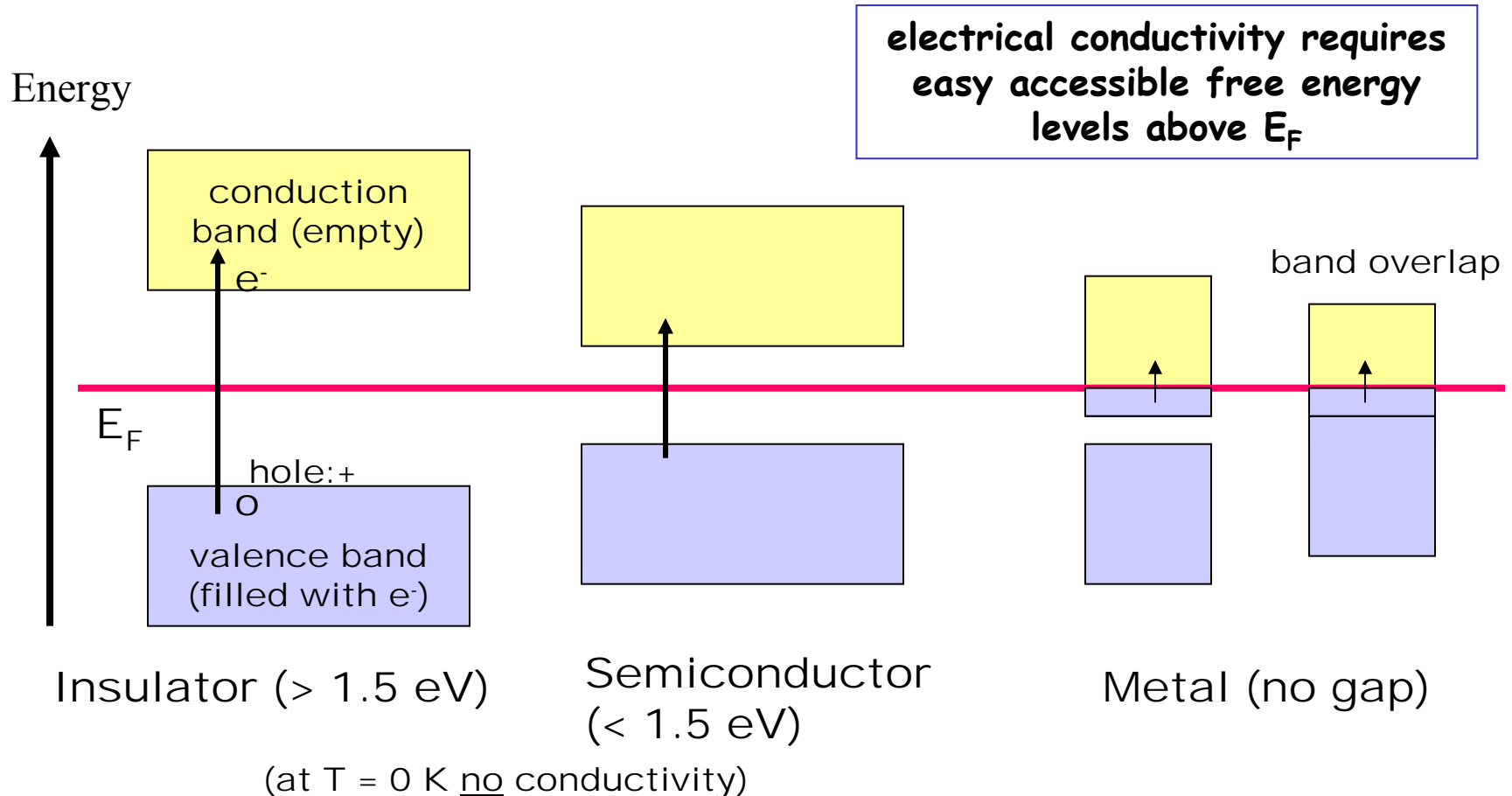
E_F = Fermi level - energy of <u>highest occupied</u> electronic state
- states above E_F are <u>empty at T = 0 K</u>

2.3 Densities of states (DOS)

δE << kT_c of ~ 0.025 eV
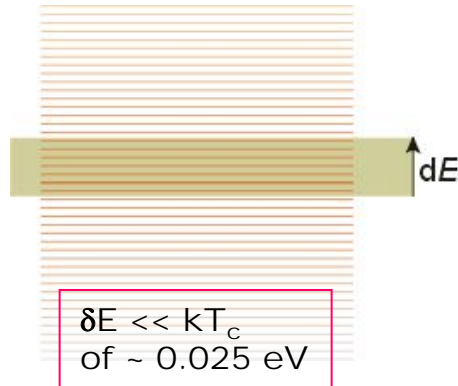
The number of electronic states in a range dE of E divided by the width of the range is called the <u>density of states</u> (DOS).

simplified, symbolic shapes for DOS representations !!
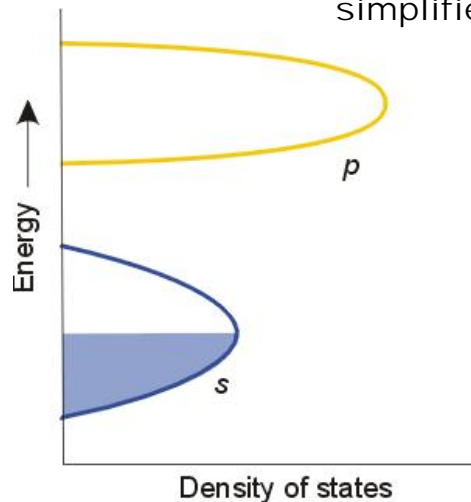
electrons

Typical DOS representation for a metal
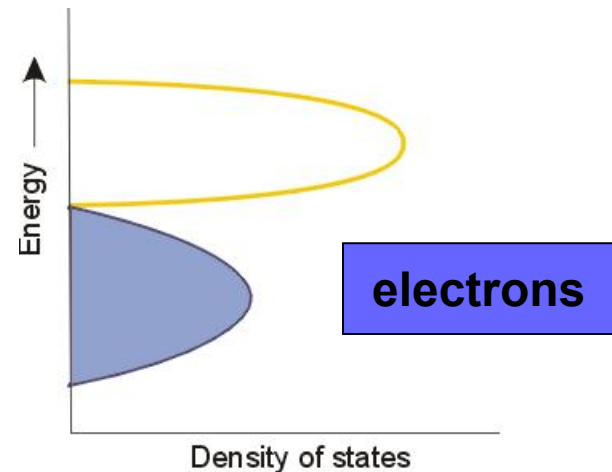
Typical DOS representation for a semimetal

conduction band

p

band gap

valence band

s

Density of states

T = 0 K

thermal excitation of electrons

p

s

Density of states
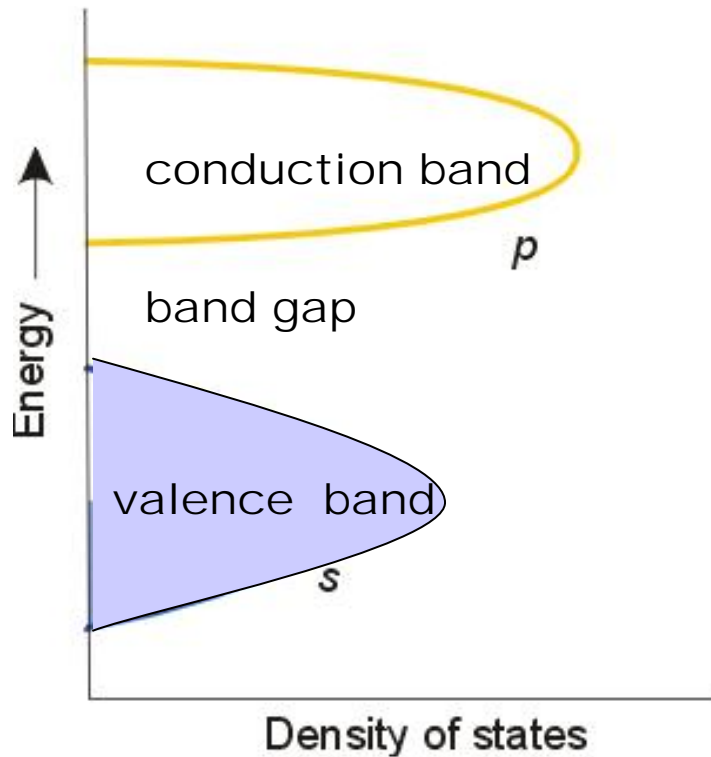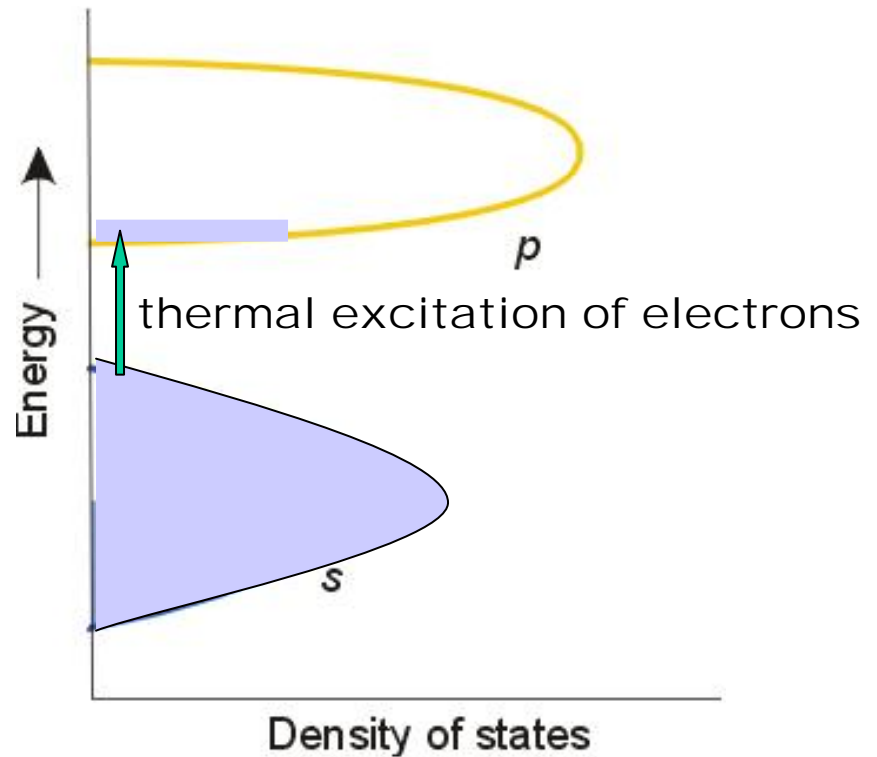
T > 0 K

2.3 Semiconductors

The electrical (electronic) conductivity σ of a semiconductor:

$$\sigma = qcu \quad [\Omega^{-1}cm^{-1}] = [S\ cm^{-1}]$$

(S: Siemens)

q: elementary charge (C = A s)
c: concentration of charge carriers (cm^{-3})
u: electrical mobility of charge carriers [cm^2/Vsec]

- charge carriers can be <u>electrons or holes</u> (!)

<u>example for Ge:</u> $u(n) = 3.8 \times 10^3\ cm^2V^{-1}s^{-1}$
                        $u(p) = 1.8 \times 10^3\ cm^2V^{-1}s^{-1}$

Diffusion coefficients $D(n) = 9.5 \times 10^1\ cm^2s^{-1}$
                          $D(p) = 4.5 \times 10^1\ cm^2s^{-1}$
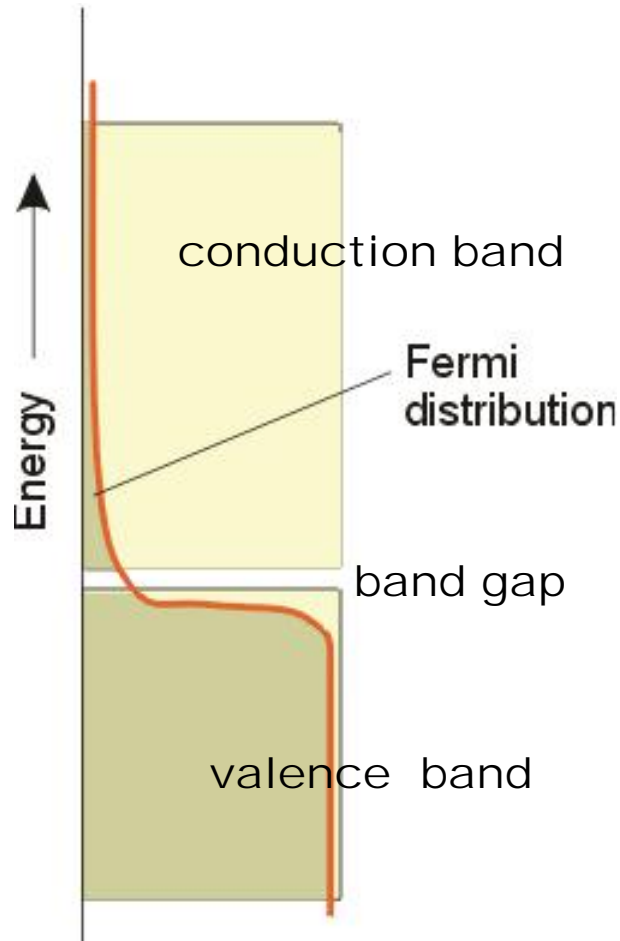
Arrhenius type behaviour:

conduction band

Fermi distribution

band gap

valence band

Energy

$$\sigma = \sigma_0 \cdot e^{\frac{-E_a}{kT}}$$

$$\ln \sigma = -\frac{E_a}{kT} + \ln \sigma_0$$

$\rightarrow$ **ln σ = f(1/T) $\rightarrow$ linear**

Typical band gaps (eV): C(diamond) 5.47, Si 1.12, GaAs 1.42

Electrical conductivity σ as a function of the reciprocal absolute temperature for <u>intrinsic</u> semiconduction of silicon.

T,K

$\sigma/(\Omega^{-1}m^{-1})$

1200   800   500   300

10^4

$\sigma, (\Omega \cdot m)^{-1}$

10^2

1

0.001   0.002   0.003

1/T,K^{-1}
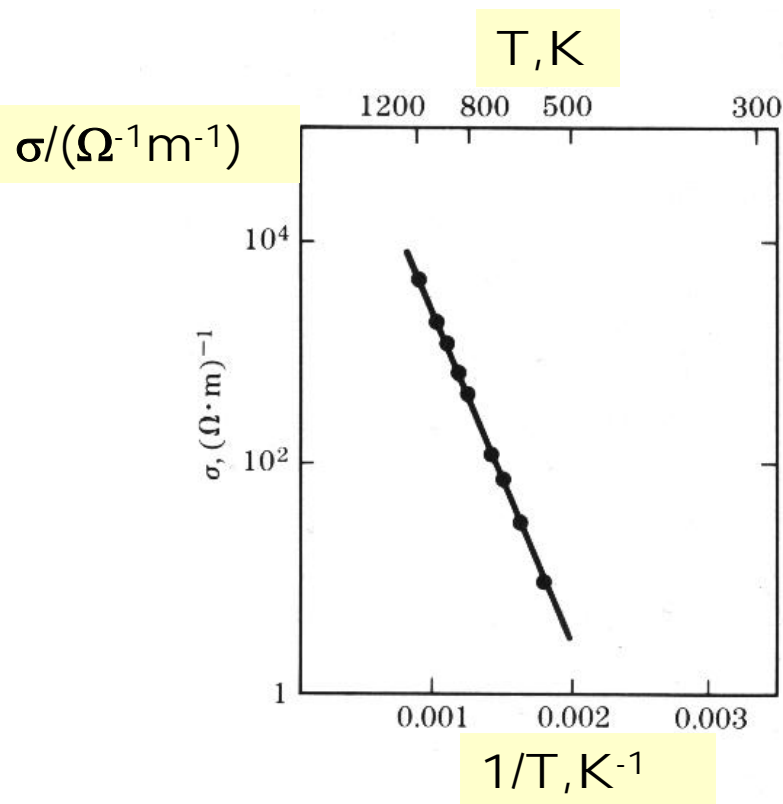
A semiconductor at room temperature usually has a much lower conductivity than a metallic conductor because only few electrons and/or holes can act as charge carriers

$$\ln \sigma = -\frac{E_a}{kT} + \ln \sigma_0$$

$\rightarrow$ **slope gives E$_a$**

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2.3 A more detailed view of semiconductors:
Intrinsic and extrinsic semiconduction

thermal excitation of electrons

T > 0 K
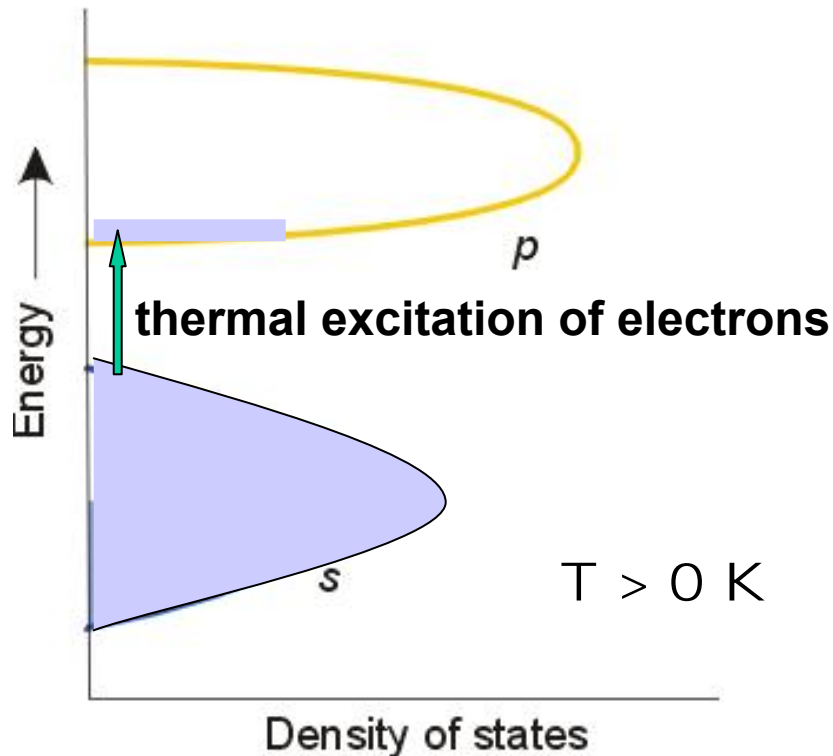
Intrinsic semiconduction appears, when charge carriers are based on electrons excited from the valence into the conduction band (e.g. very pure silicon).

2.3 A more detailed view of semiconductors:
Intrinsic and extrinsic semiconduction

Energy →

conduction band

Donor band

Acceptor band

band gap

valence band

(a)   (b)
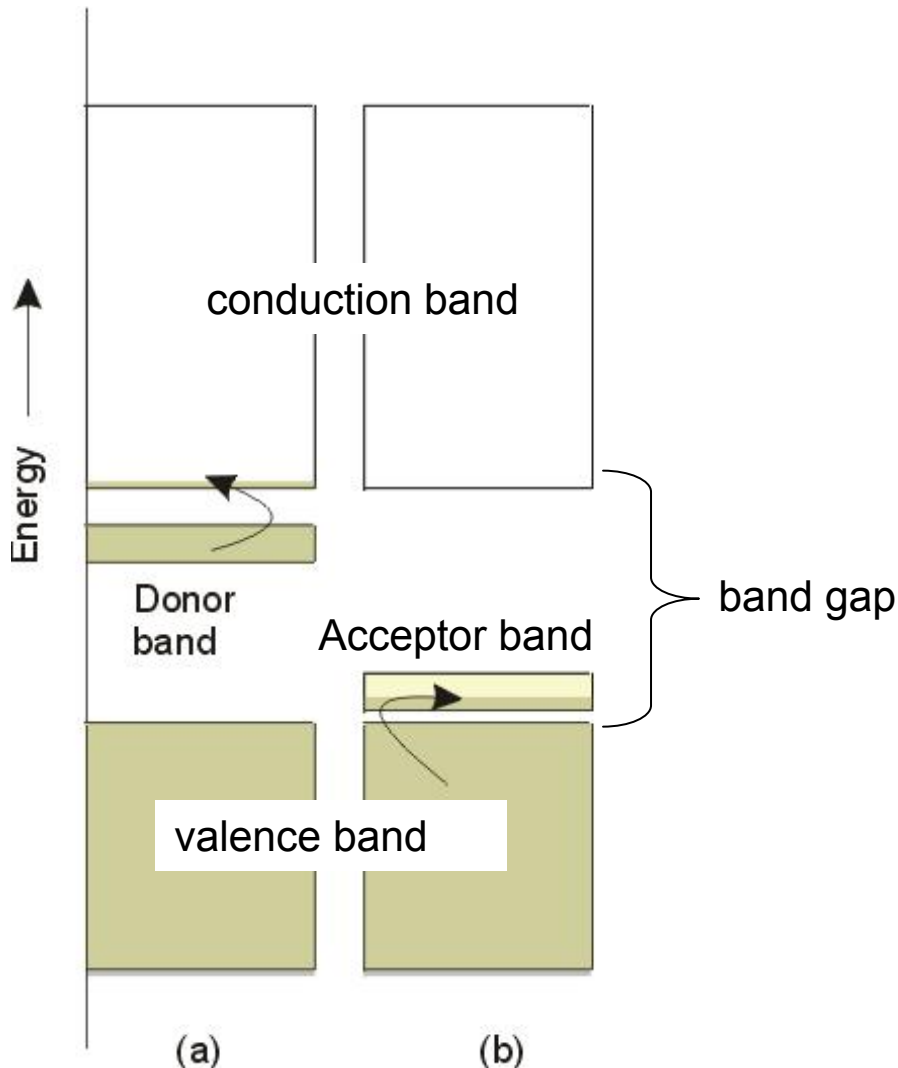
Extrinsic semiconduction appears if the semiconductor is not a pure element but „doped" by atoms of an element with either more or less electrons e.g. Si doped by traces of
(a) phosphorous [n-type doping] with an additional donoror band
or
(b) boron [p-type doping] with an additional acceptor band

2.3 A more detailed view of semiconductors:
Intrinsic and extrinsic semiconduction

MO ZnO_{1-x} $Mn_{1-x}O$

(a)   (b)   (c)
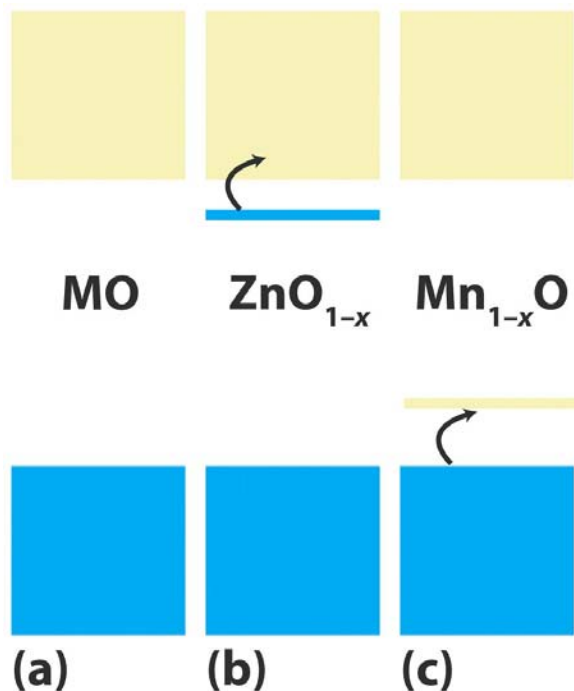
Figure 3-61
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Extrinsic semiconduction can appear also for non-stoichiometric compounds like oxides MO

(a) stoichiometric oxide MO [insulator]
(b) anion-deficient [n-type conductor] with an additional donoror band or
(c) cation-deficient [p-type conductor] with an additional acceptor band

2.3 A more detailed view of semiconductors:
Intrinsic and extrinsic semiconduction

intrinsic range

slope: $-E_{A2}/kT$

$$\ln \sigma = -\frac{E_a}{kT} + \ln \sigma_0$$

Exhaustion range

extrinsic range

slope: $-E_{A1}/kT$

High temp

$1/(293\ K)$

Low temp

$1/T, K^{-1}$
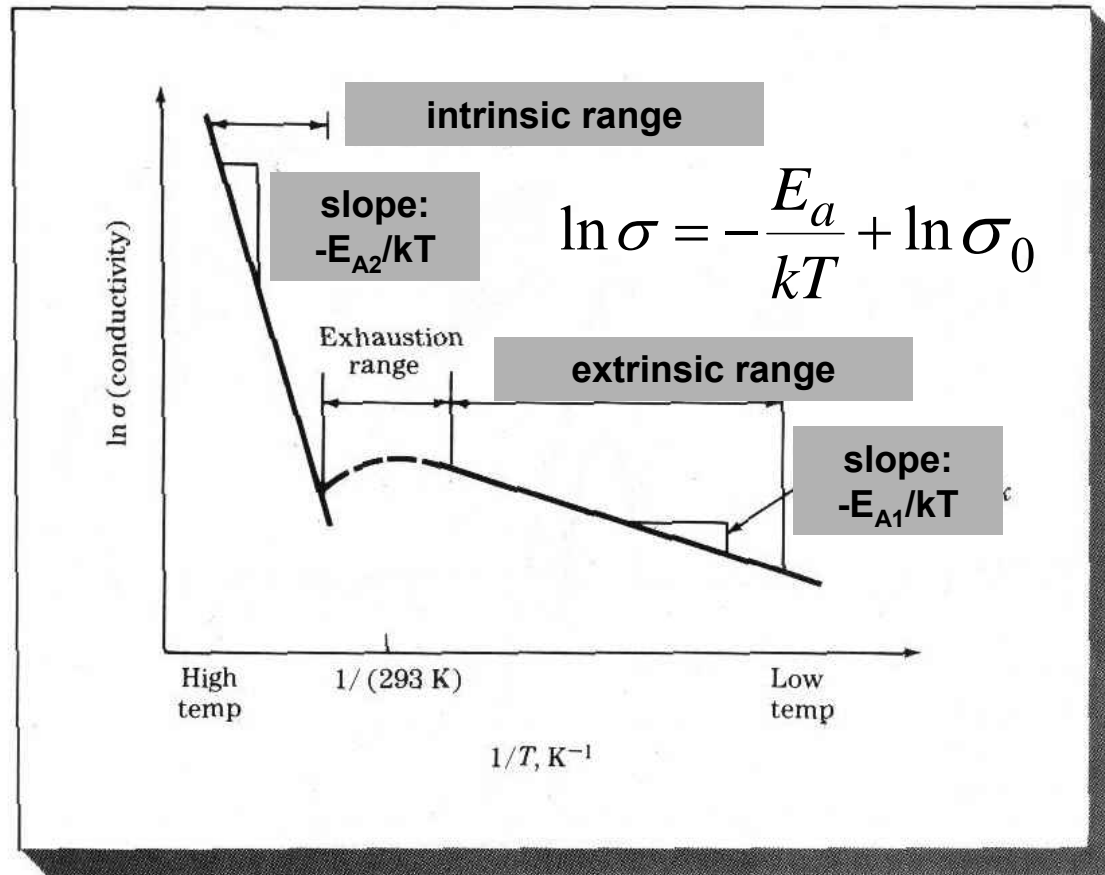
Temperature dependance of conductivity is different for intrinsic and extrinsic semicondurs

2.4 Hydrogen bonding
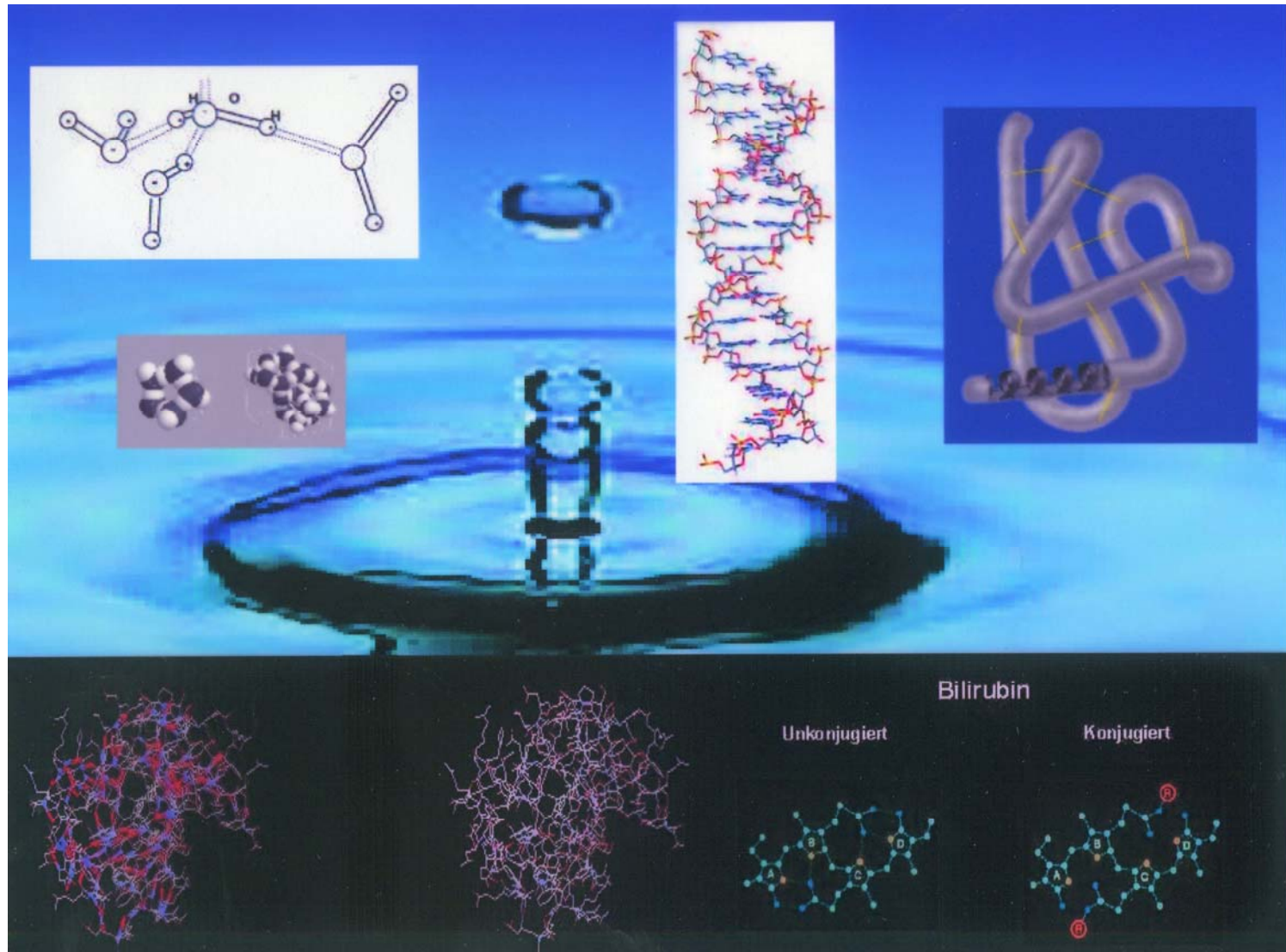
Where to find hydrogen bonds?

2.4 Hydrogen bonding

WHAT IS A HYDROGEN BOND?

A *hydrogen bond* exists when a hydrogen atom is bonded to two or more other atoms, a donor atom X and an acceptor atom Y.

Since the hydrogen atom has only one orbital (1s) at sufficiently low energy, hydrogen bonds are mainly electrostatic in nature but covalent and repulsive orbital-orbital interactions are also present.

Depending on the type of X and Y, there are strong and weak hydrogen bonds.

In the case of *weak and very weak hydrogen bonds*, hydrogen bonding is mainly electrostatic in nature.

In the case of *strong and very strong hydrogen bonds*, covalent bonding phenomena are also of some importance.

This means that hydrogen bonds are something special.

2.4 Hydrogen bonding

The structure of ice. The large spheres represent the O atoms; the H atoms lie on the lines joining O atoms.
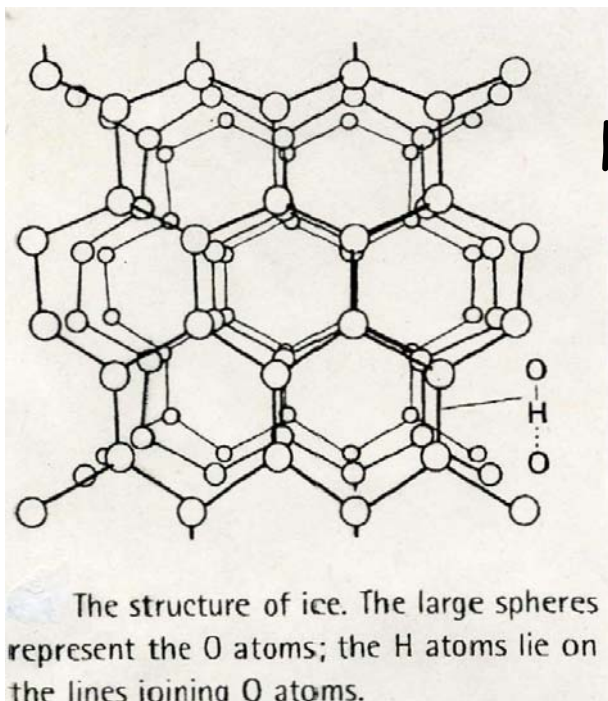
Hydrogen bonds
in
solid H_2O (weak)
and HF (strong)
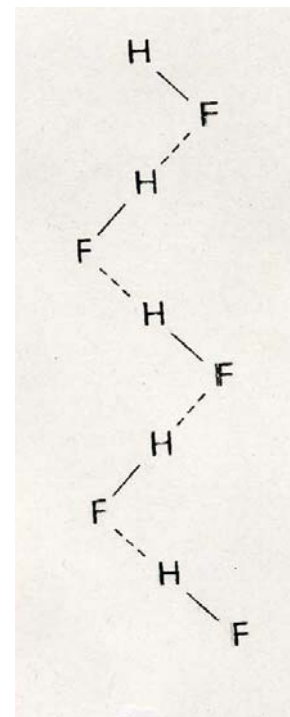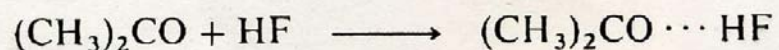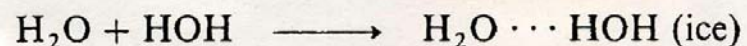
$$F^- + HF \longrightarrow FHF^- \qquad \Delta H = -155^{18} \text{ kJ mol}^{-1}$$
$$(CH_3)_2CO + HF \longrightarrow (CH_3)_2CO \cdots HF \qquad \Delta H = -46 \text{ kJ mol}^{-1}$$
$$H_2O + HOH \longrightarrow H_2O \cdots HOH \text{ (ice)} \qquad \Delta H = -25 \text{ kJ mol}^{-1}$$

The strongest hydrogen bonds are formed to the most electronegative elements

2.4 Hydrogen bonding

Table 2.4 Comparison of hydrogen bond enthalpies with the corresponding E—H covalent bond enthalpies (kJ mol^{-1})

Hydrogen bond ($\cdots$)		Covalent bond (—)	
$HS{-}H\cdots SH_2$	7	S—H	363
$H_2N{-}H\cdots NH_3$	17	N—H	386
$HO{-}H\cdots OH_2$	22	O—H	464
$F{-}H\cdots F{-}H$	29	F—H	565
$HO{-}H\cdots Cl^-$	55	Cl—H	428
$F\cdots H\cdots F^-$	165	F—H	565

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H^\circ_{fus} = 6.02 \text{ kJ/mol}$$
$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H^\circ_{vap} = 40.7 \text{ kJ/mol}$$

$$F^- + HF \longrightarrow FHF^- \qquad\qquad \Delta H = -155^{18} \text{ kJ mol}^{-1}$$
$$(CH_3)_2CO + HF \longrightarrow (CH_3)_2CO\cdots HF \qquad \Delta H = -46 \text{ kJ mol}^{-1}$$
$$H_2O + HOH \longrightarrow H_2O\cdots HOH \text{ (ice)} \qquad \Delta H = -25 \text{ kJ mol}^{-1}$$
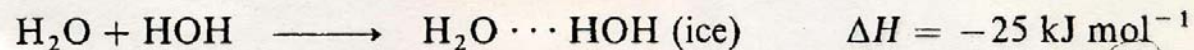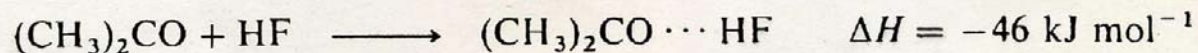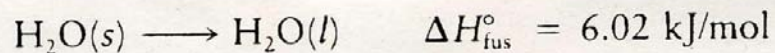
Enthalpies of some hydrogen bonded systems and transitions

2.4 Hydrogen bonding
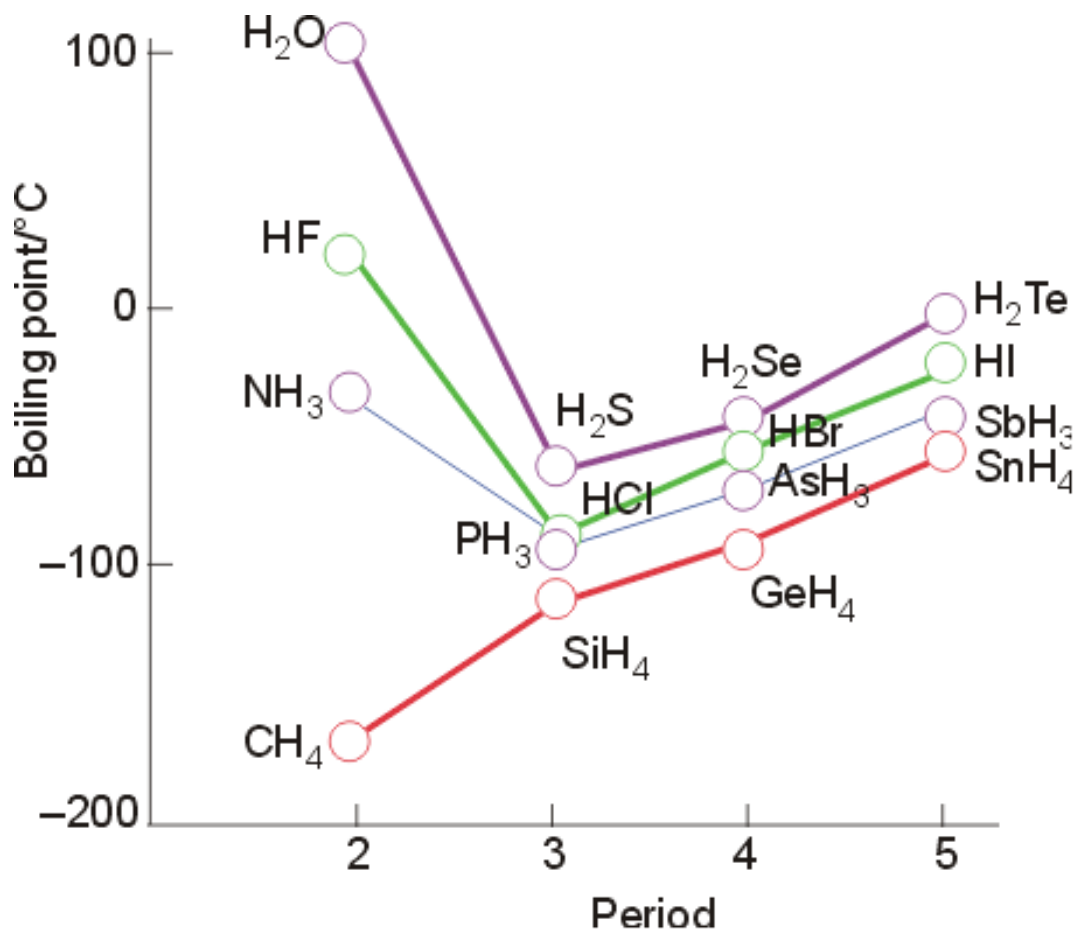
Normal boiling points of p-block binary hydrogen compounds

2.4 Hydrogen bonding
is directed by the lone pairs of the acceptor atom(s) Y
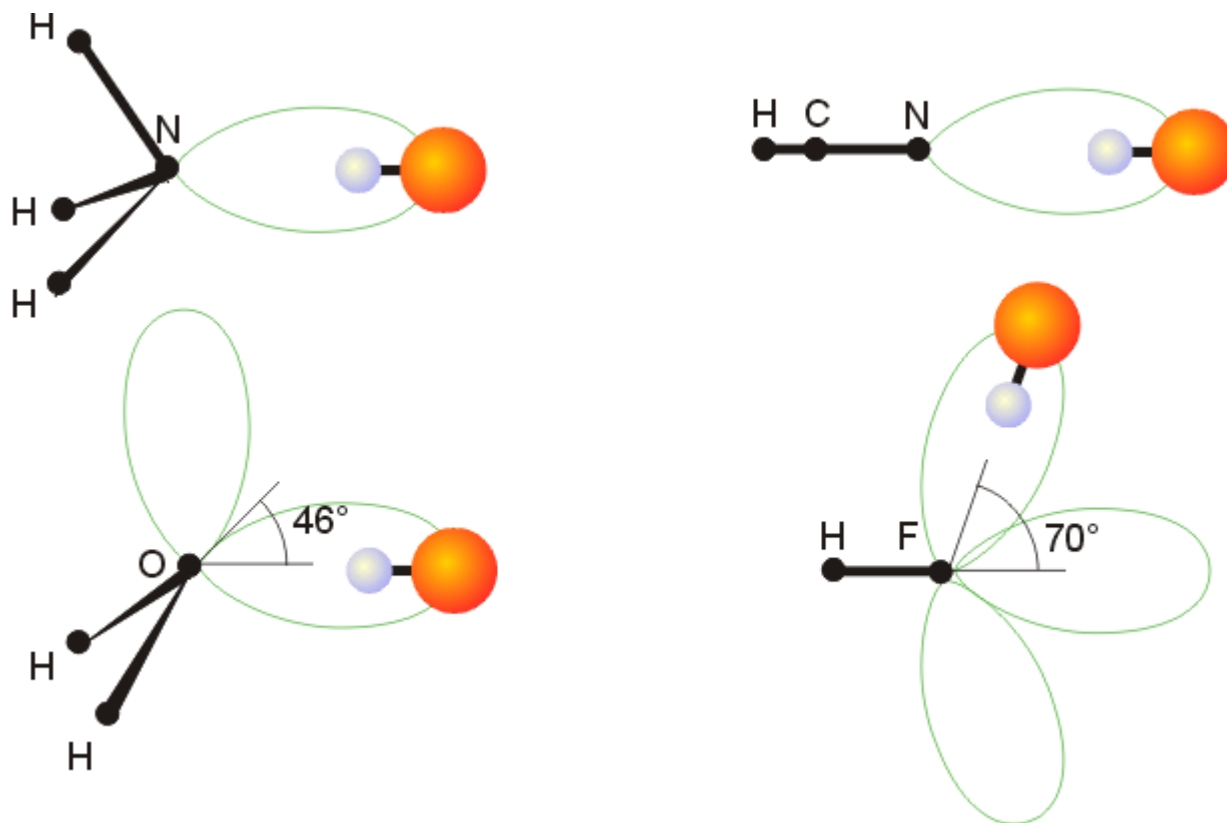
Gas-phase hydrogen-bonded complexes formed with HF and lone pair orientation as indicated by VSEPR theory
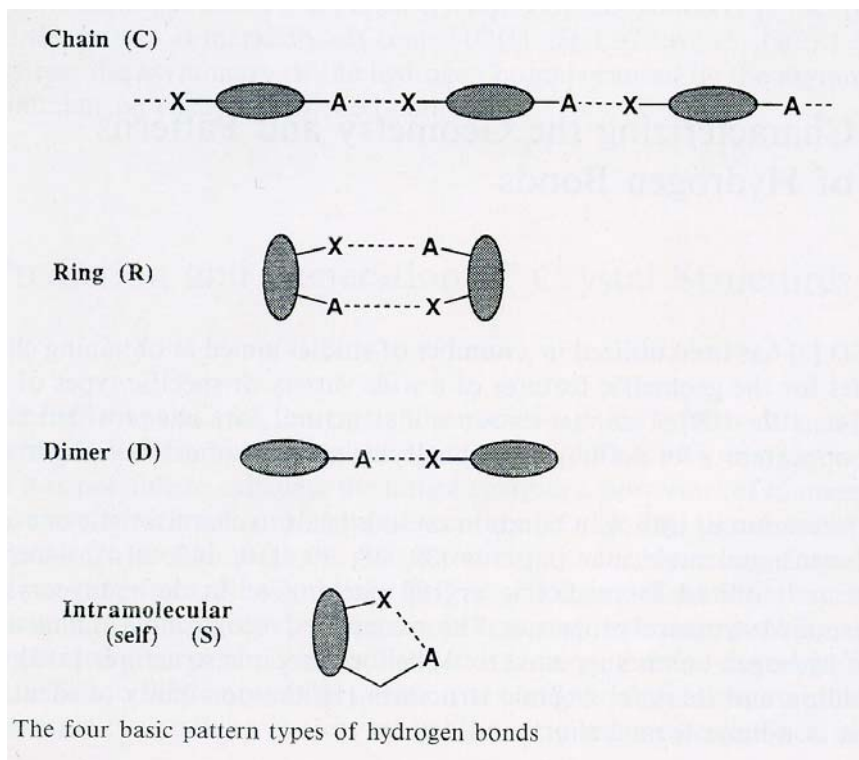
2.4 Hydrogen bonding

for Y = O this leads to

O–H
 O
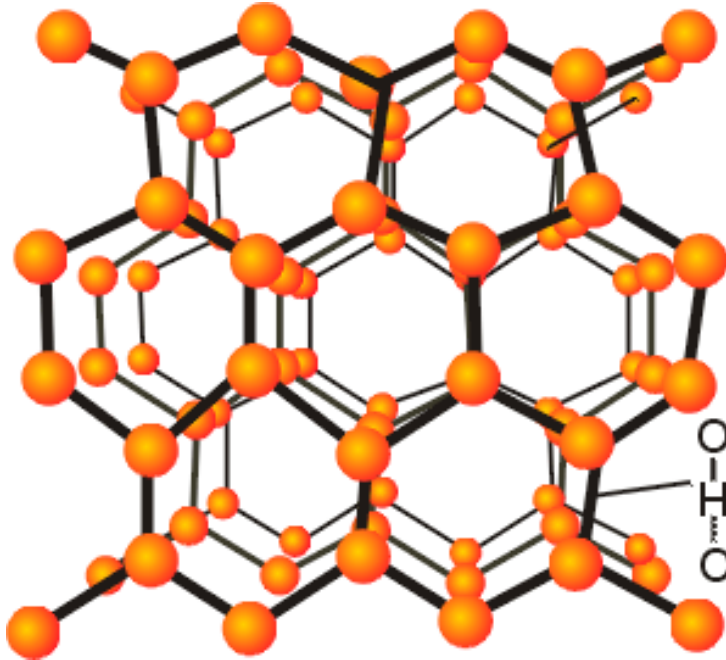
The crystal structure of ice. The large cycles represent O atoms. The H atoms are placed between the O atoms.
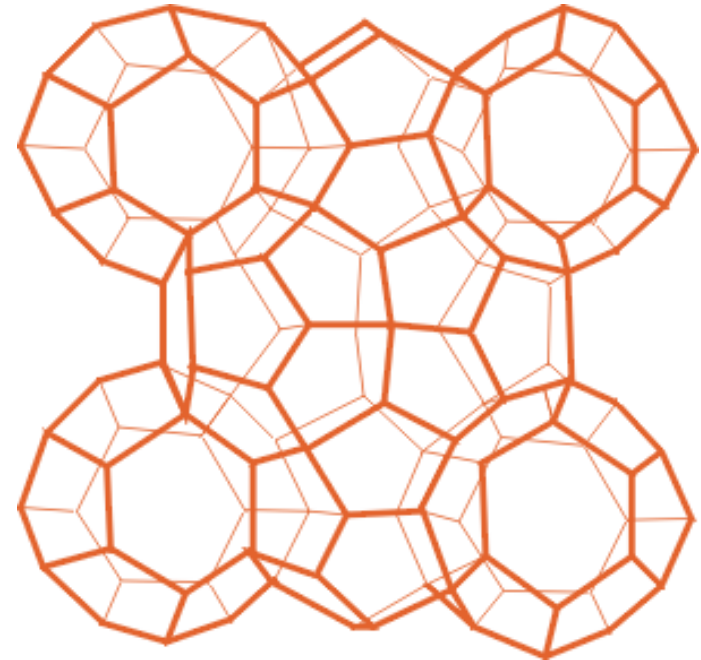
H_2O cages in the clathrate hydrate $Cl_2.(H_2O)_{7.25}$. O atoms occupy intersections H atoms the lines.

Structure building of hydrogen bonds
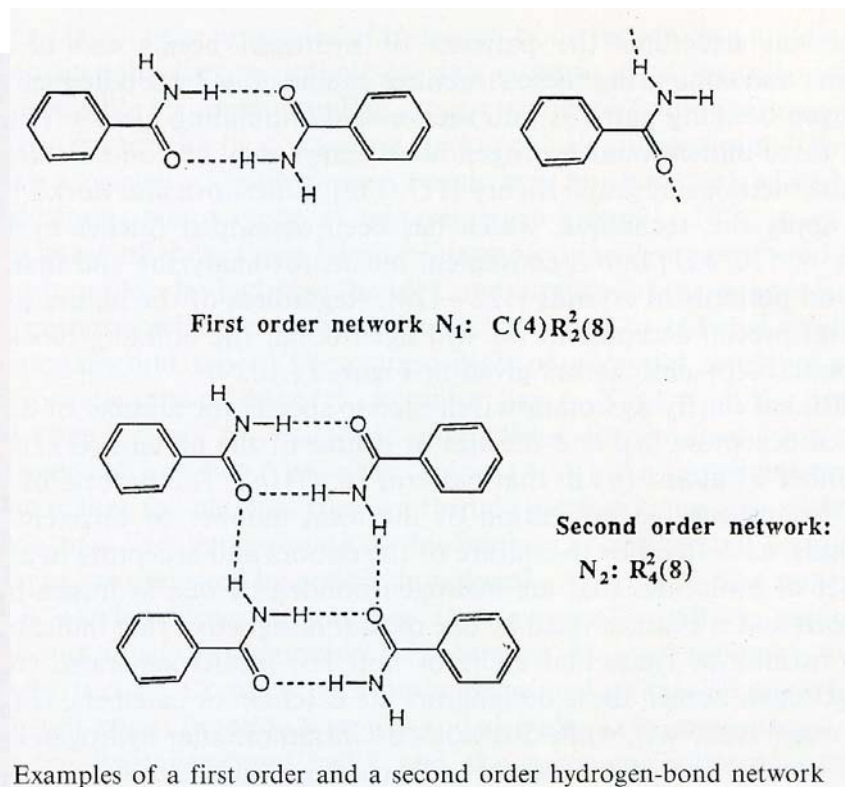
2.4 Hydrogen bonding

Chain (C)

Ring (R)

Dimer (D)

Intramolecular (self) (S)

The four basic pattern types of hydrogen bonds

First order network N_1: $C(4)R_2^2(8)$

Second order network:
N_2: $R_4^2(8)$

Examples of a first order and a second order hydrogen-bond network

Types and structure building of hydrogen bonds

2.4 Hydrogen bonding
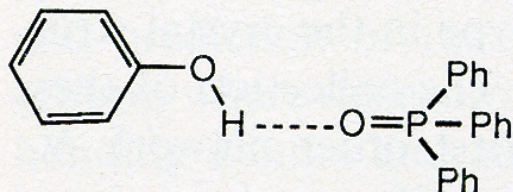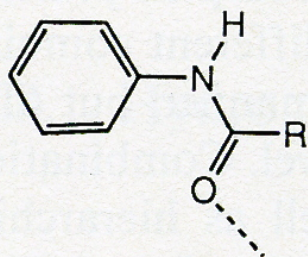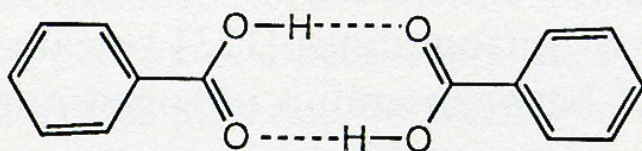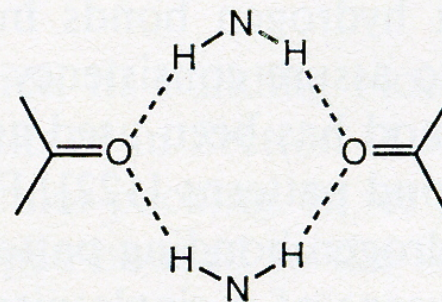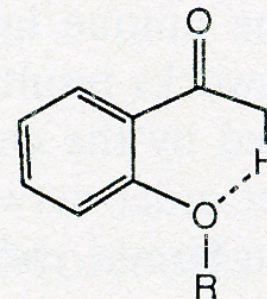
Types and structure building of hydrogen bonds
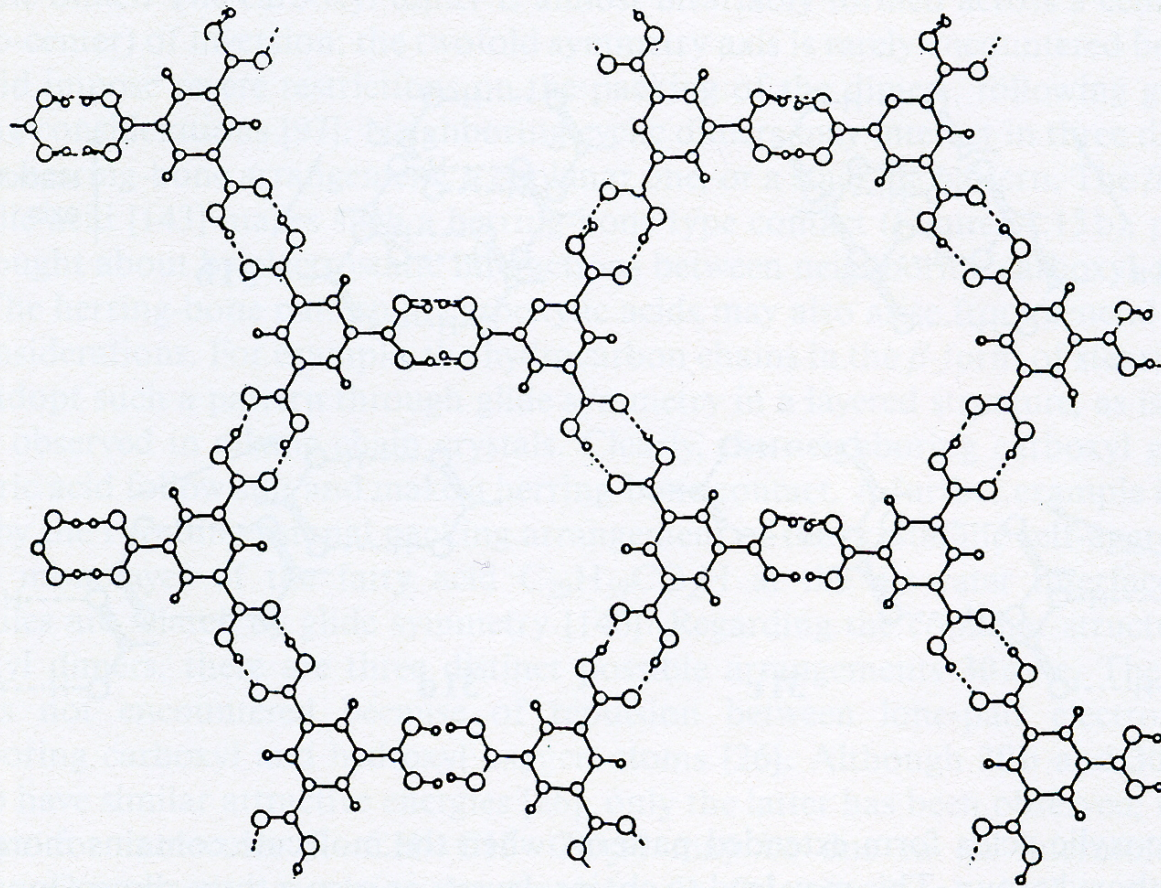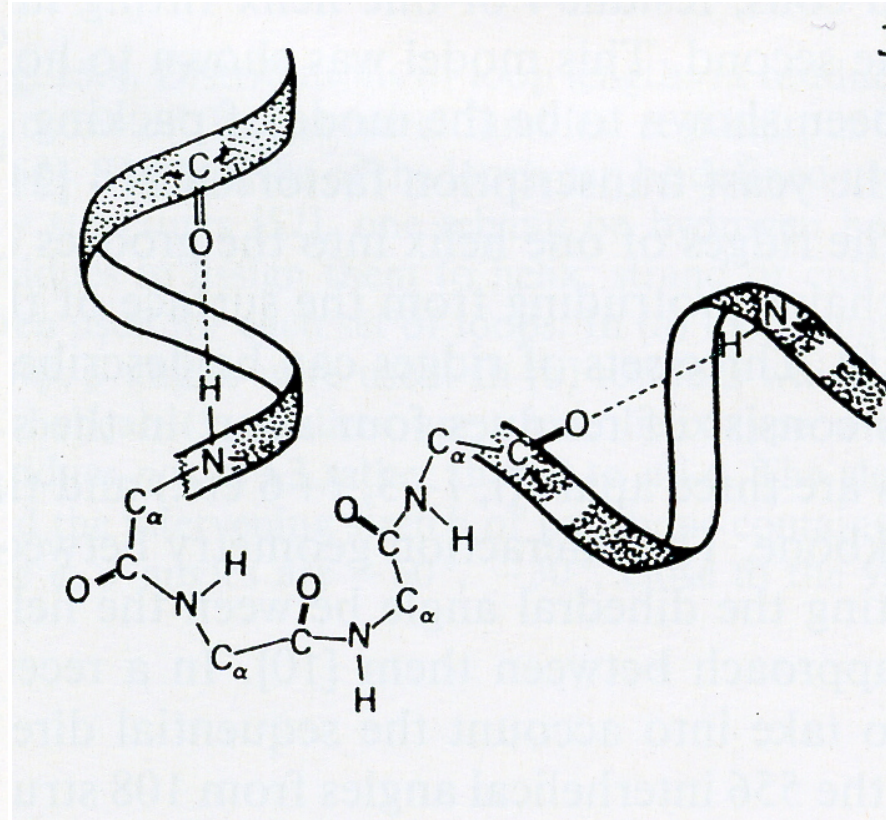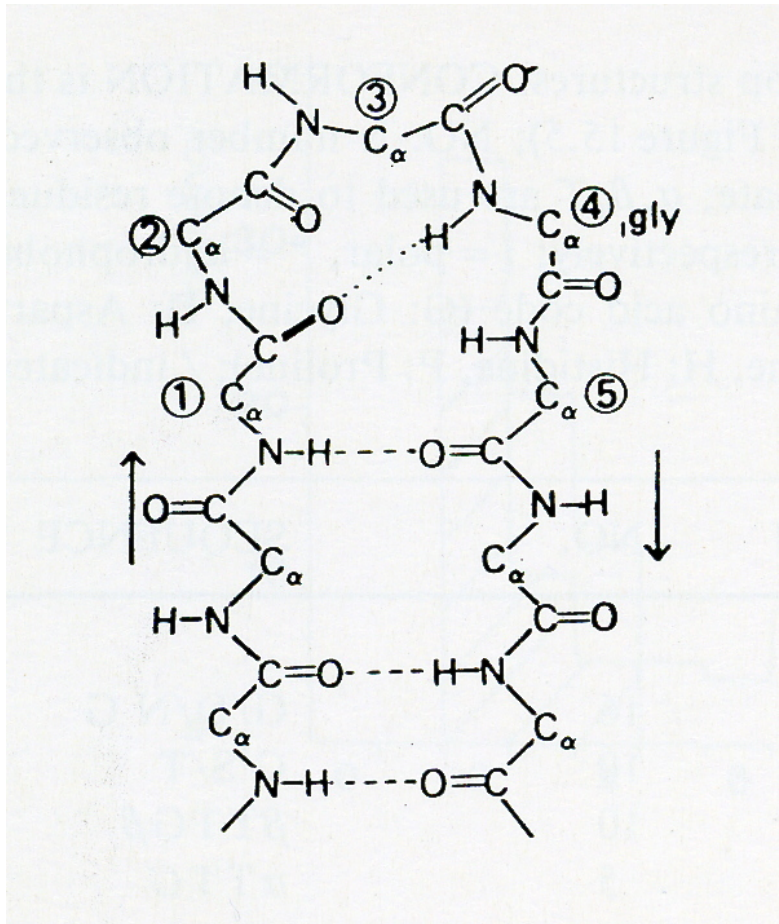(intra and intermolecular hydrogen bonds)

2.4 Hydrogen bonding

Fig. 11.17. 1,3,5-Trimesic acid. The "chicken-wire" motif
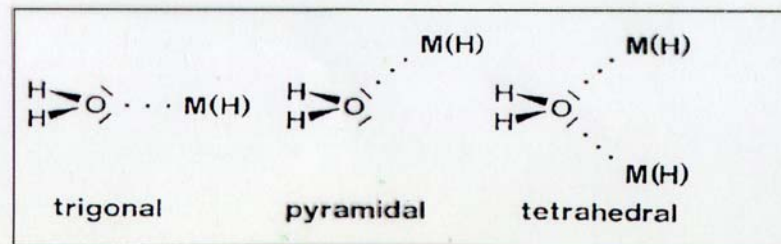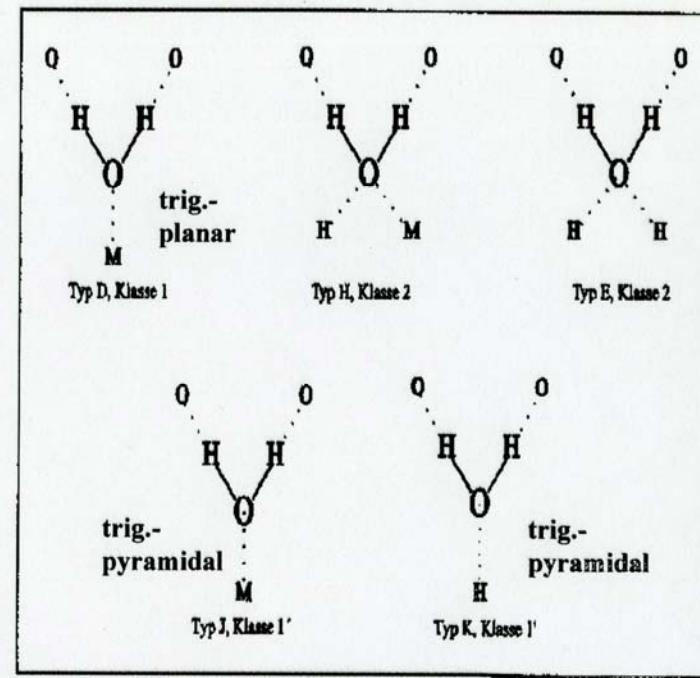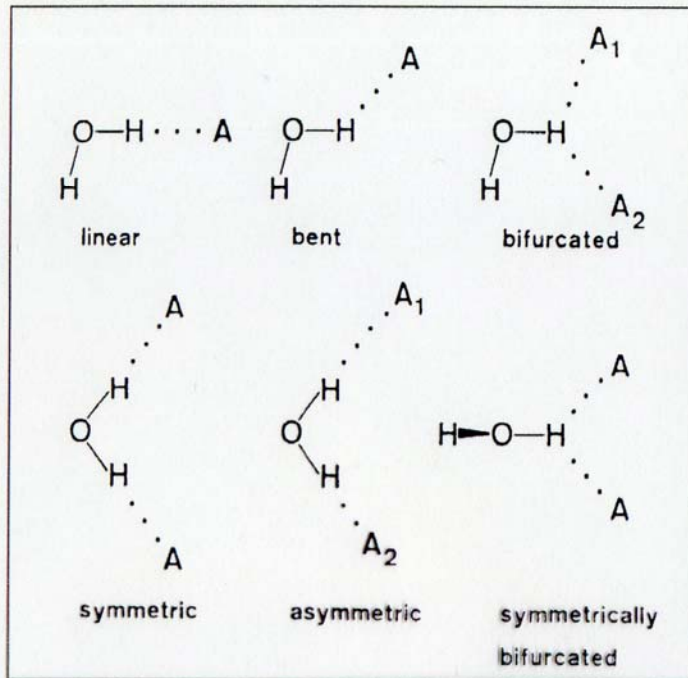
Structure building of hydrogen bonds

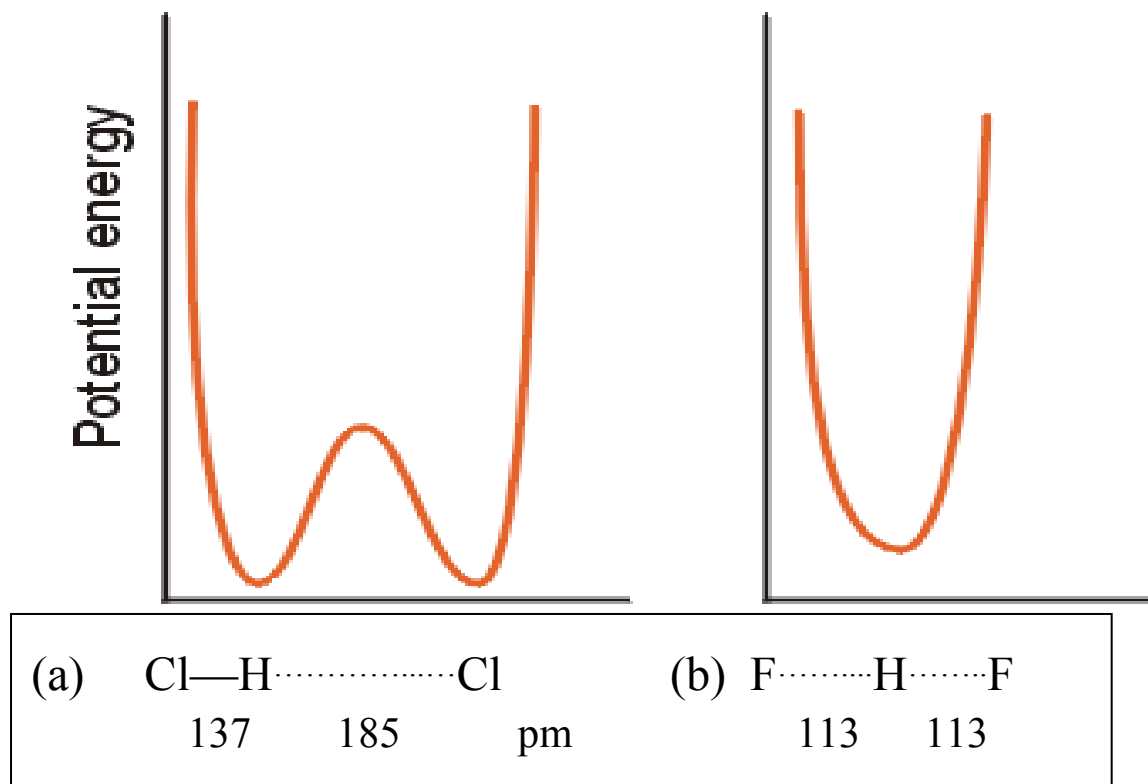# 2.4 Hydrogen bonding

Structure building of hydrogen bonds

2.4 Hydrogen bonding

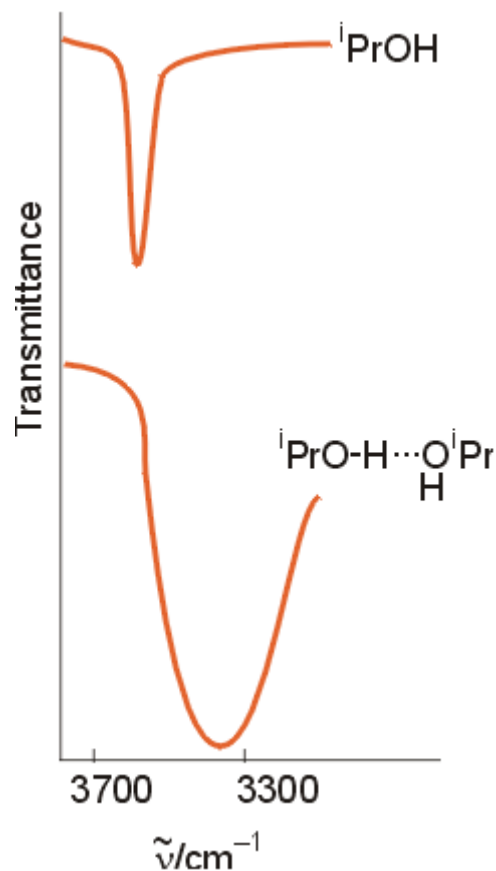Configuration/coordination of water molecules of crystallization

2.4 Hydrogen bonding

Potential energy curves for X-H···X bonds with
(a) double-minimum for weak and (b) single-minimum for strong H-bonds
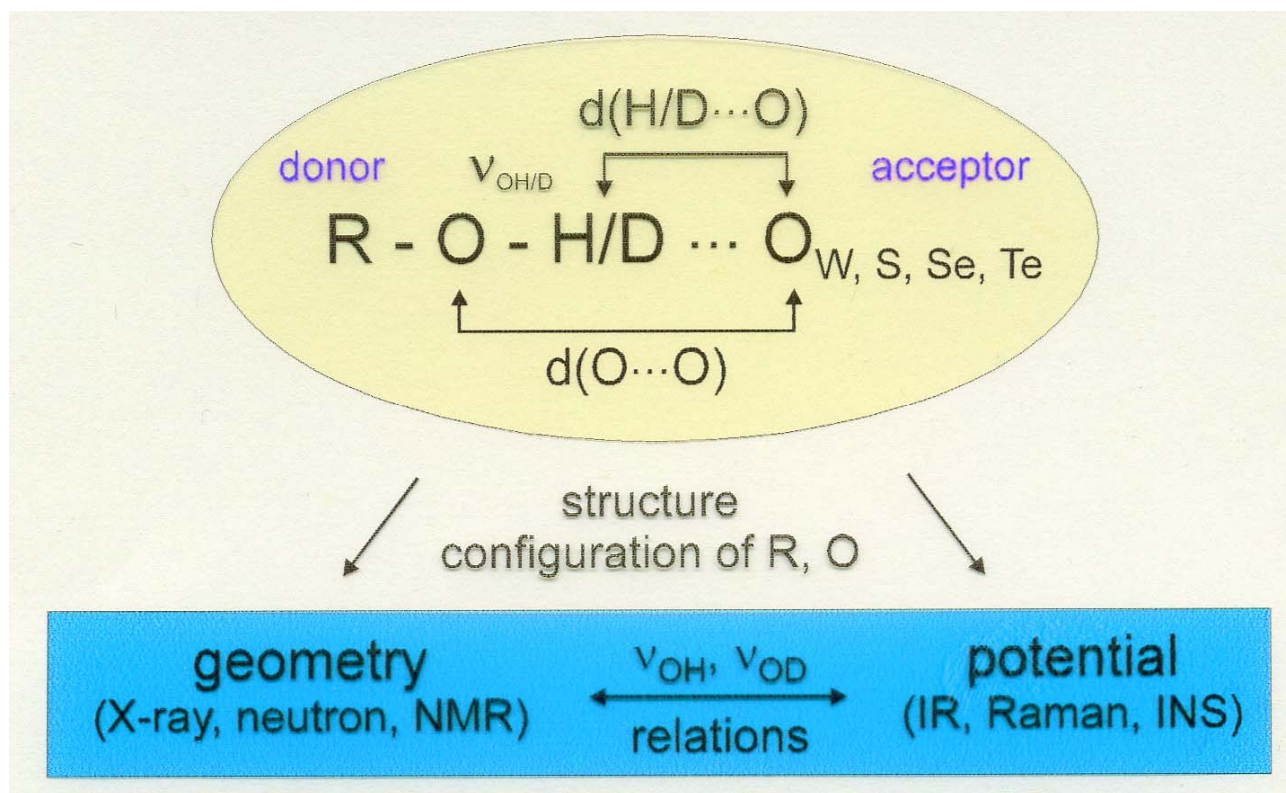
2.4 Hydrogen bonding

Infrared spectra of pure (bottom) and diluted (top) Isopropanol showing the shift and the broadening of the O-H stretching band by hydrogen bonding

2.4 Hydrogen bonding
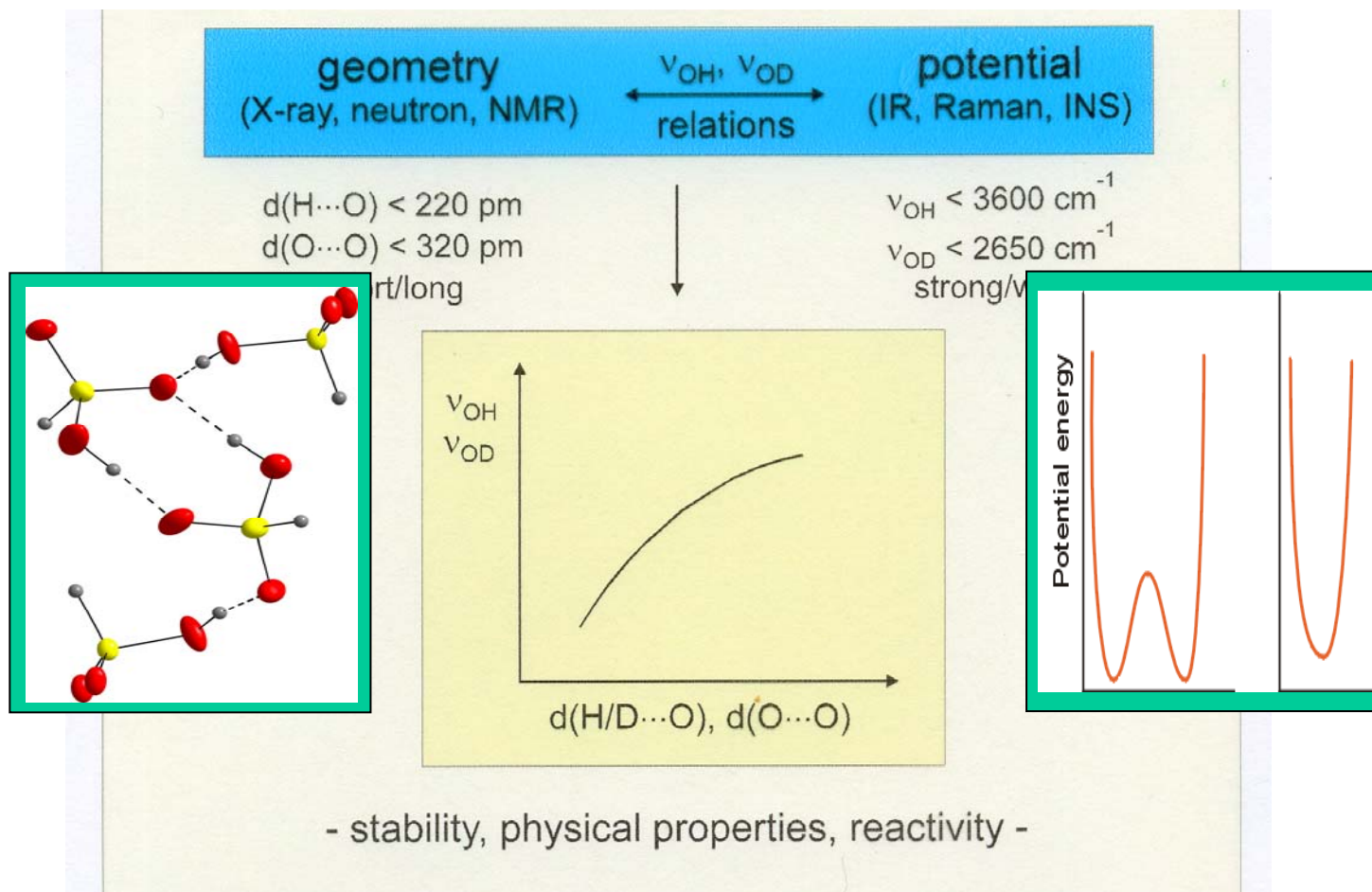
How to investigate/characterize hydrogen bonds?

By systematic investigation of isotypic compounds
(e.g. Oxohydrates $MXO_3 \cdot nH_2O$ (X = S, Se, Te), $M(HSeO_3)_2 \cdot nH_2O$)
with X-ray and neutron diffraction, NMR, IR, Raman, INS

2.4 Hydrogen bonding

How to investigate/characterize hydrogen bonds?

geometry (X-ray, neutron, NMR) ⟷ ν_{OH}, ν_{OD} relations ⟷ potential (IR, Raman, INS)

$d(H\cdots O) < 220$ pm
$d(O\cdots O) < 320$ pm
short/long

$\nu_{OH} < 3600$ cm^{-1}
$\nu_{OD} < 2650$ cm^{-1}
strong/w

ν_{OH}
ν_{OD}

$d(H/D\cdots O)$, $d(O\cdots O)$

Potential energy
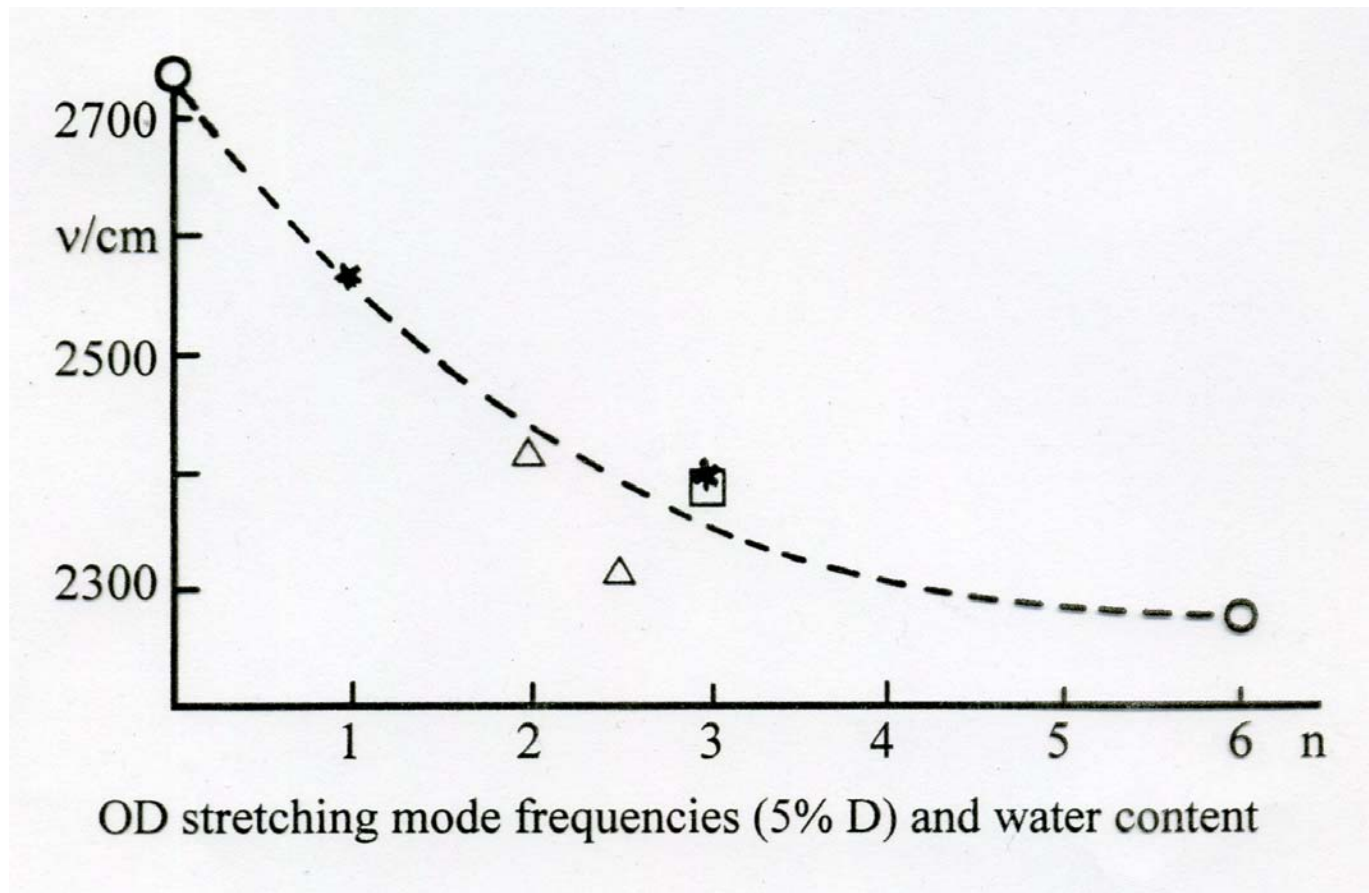
- stability, physical properties, reactivity -

By systematic investigation of isotypic compounds
and correlation of the structural, spectroscopic and theoretical data
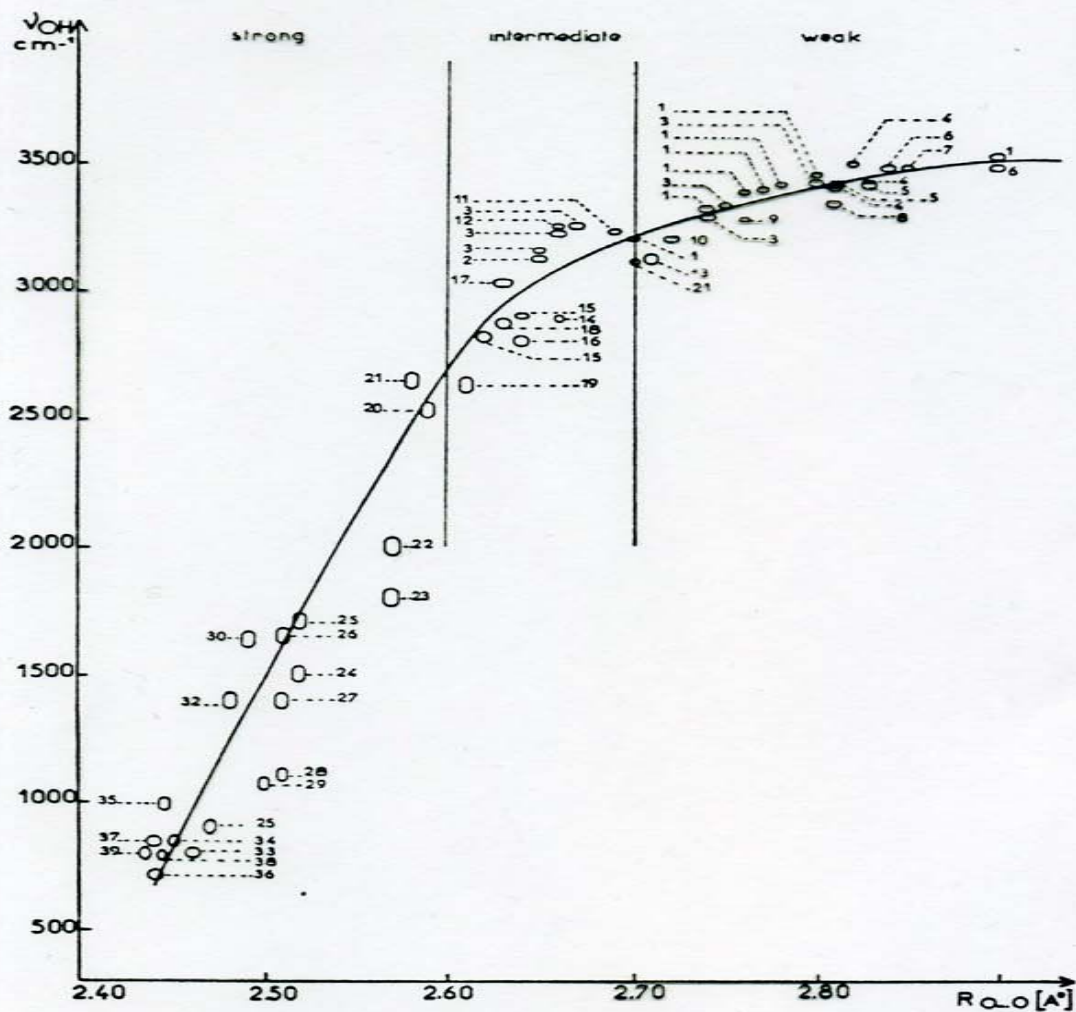
2.4 Hydrogen bonding
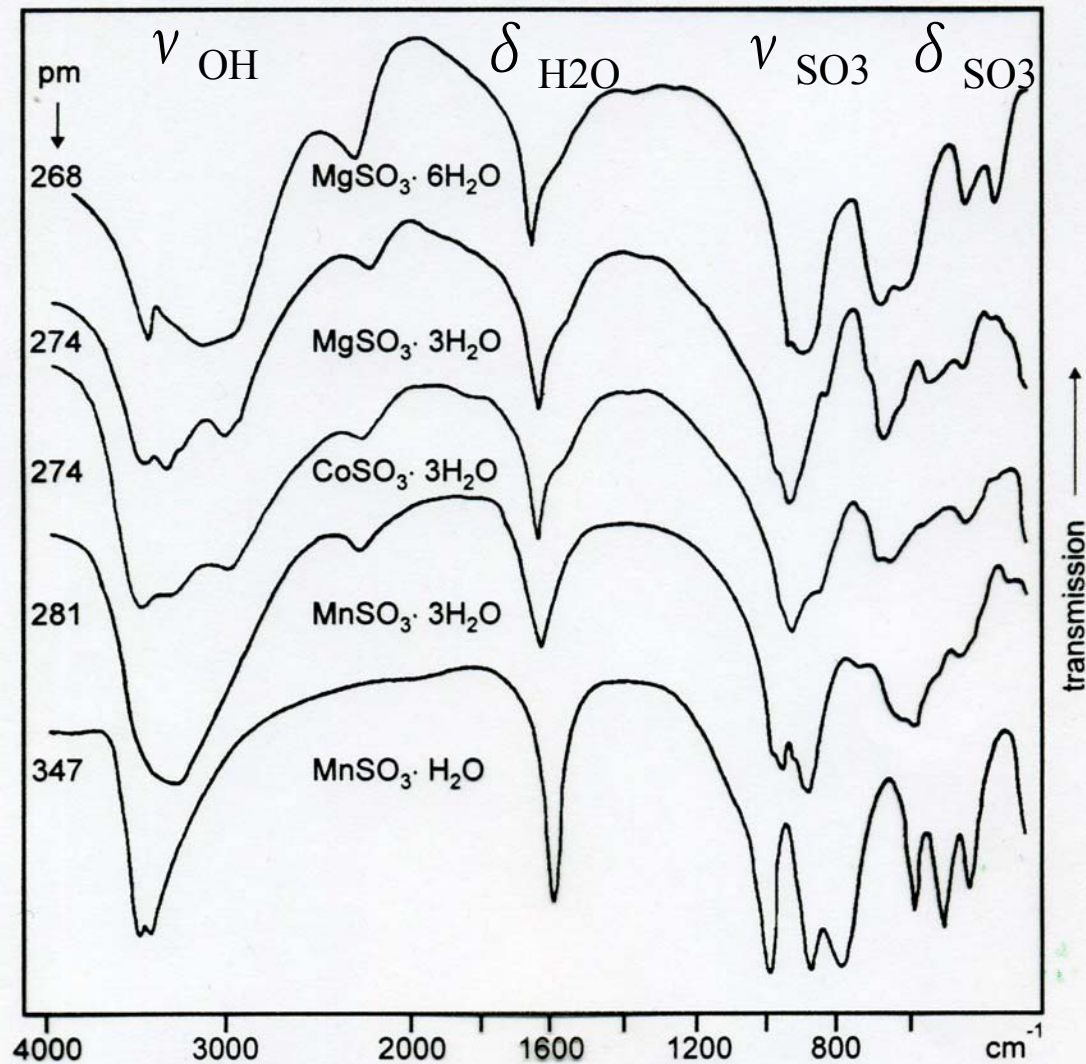
IR spectra and H-bond distances of several sulphite hydrates
(Lutz et al. 1977, Engelen, 1983)

2.4 Hydrogen bonding

OD stretching mode frequencies (5% D) and water content
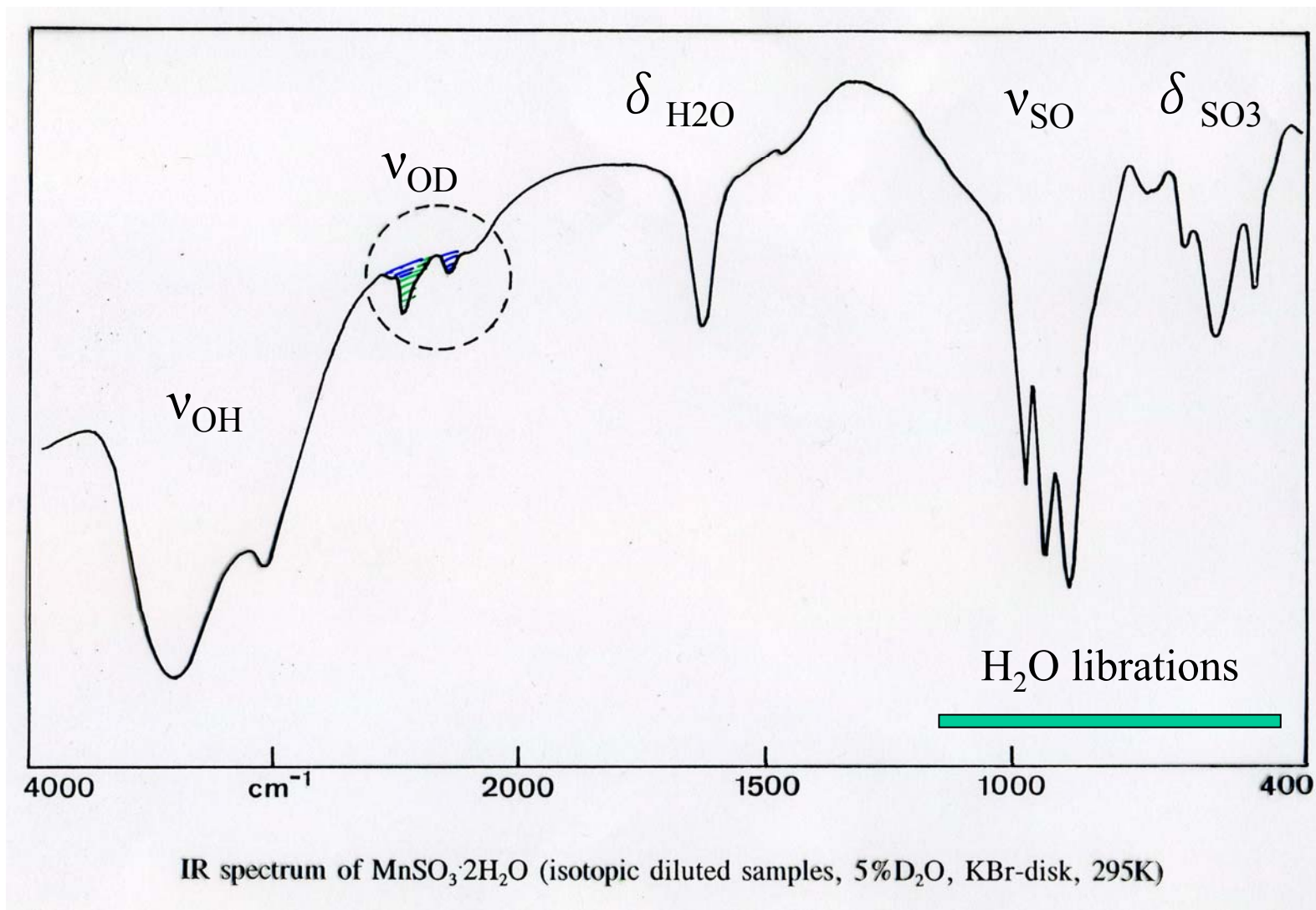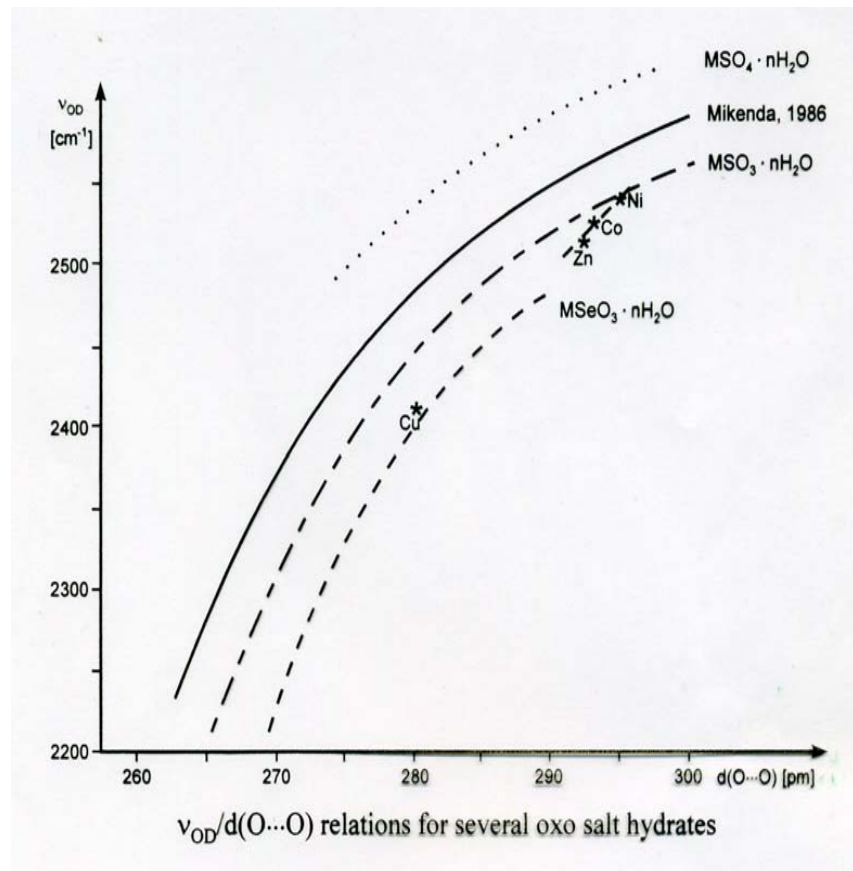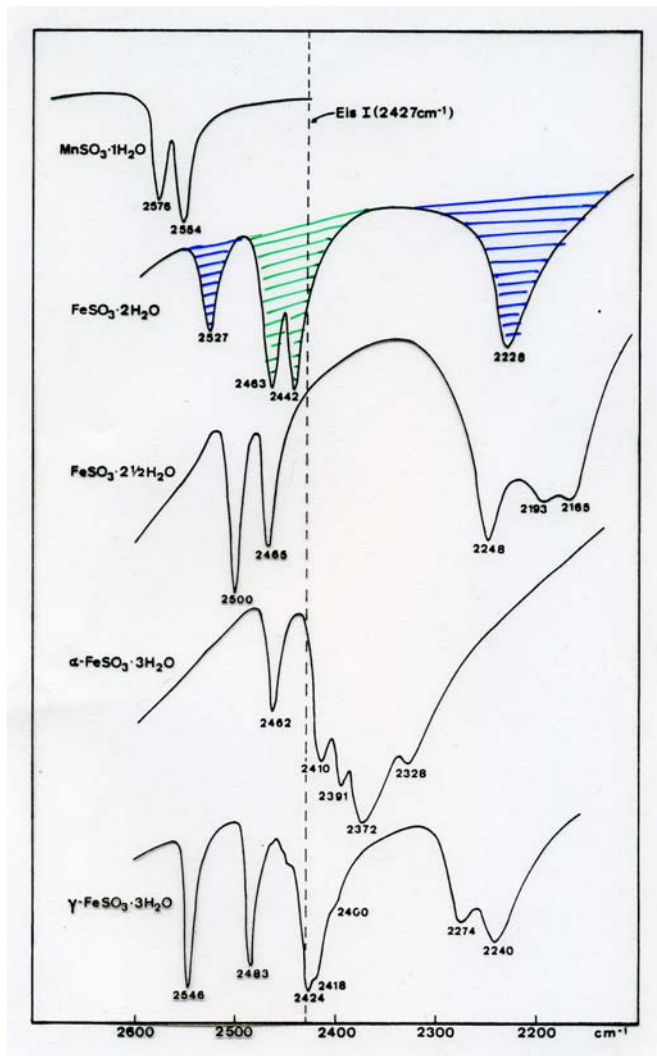
Relation between OH stretching frequency, ν_{OH}, and R(O⋯O) distance (Novak, 1974)

2.4 Hydrogen bonding

IR spectrum of $MnSO_3 \cdot 2H_2O$ (isotopic diluted samples, 5%D_2O, KBr-disk, 295K)

2.4 Hydrogen bonding

IR spectra and $\nu_{OD}/d(O{\cdots}O)$ relations of some salt hydrates

2.4 Hydrogen bonding

WHAT IS A HYDROGEN BOND?

A *hydrogen bond* exists when a hydrogen atom is bonded to two or more other atoms. Since the hydrogen atom has only one orbital (1s) at sufficiently low energy, hydrogen bonds are mainly electrostatic in nature but covalent and repulsive orbital-orbital interactions are also present.

The *strength of hydrogen bonds* is governed by

(i) the inherent hydrogen bond donor strength (acidity) of the hydrogen atom and the acceptor capability of the respective acceptor group,

(ii) collective effects, as cooperative, competitive, and synergetic effects, which increase or decrease the inherent donor strengths and acceptor capabilities,

(iii) structural features, as the number of acceptor groups, e. g. two-center, three-center (bifurcated), etc. hydrogen bonds, and the hydrogen bond angles $X-H{\cdots}Y$ and $H{\cdots}Y-Z$ built by the donor (X), acceptor (Y), and H atoms (linear or bent), and

(iv) packing effects and constraints of the respective crystal structure.

2.4 Hydrogen bonding

STRENGTH OF HYDROGEN BONDS

In the case of *weak and very weak hydrogen bonds*, the respective bonding is mainly electrostatic in nature with attractive and repulsive charge-charge, charge-dipole, charge-induced dipole, and charge-multipole interactions between the partially positive charged hydrogen atom and the negative charged areas of the acceptor atom *Y*.

In the case of *strong and very strong hydrogen bonds*, in addition to the Coulomb forces, covalent bonding phenomena via orbital-orbital overlap attractive and closed-shell repulsive forces are of some importance.

2.4 Hydrogen bonding

STRENGTH OF HYDROGEN BONDS

The *strength of hydrogen bonds in inorganic solids* is governed by both the hydrogen-bond donor strength of the hydrogen-bond donor X and the hydrogen-bond acceptor capability of the hydrogen-bond acceptor Y.

For the formation of hydrogen bonds two rules have been established:

(i) All hydrogen-bond acceptors available in a molecule will be engaged in hydrogen bonds as far there are available donors.

(ii) The hydrogen-bond acceptors will be saturated in order of decreasing strength of the hydrogen bonds formed.

Both the hydrogen-bond donor strengths and the hydrogen-bond acceptor capabilities, are modified by additional phenomena like the synergetic, the cooperative, and the anti-cooperative or competitive effects. The various effects are highly non-additive.

2.4 Hydrogen bonding

Hydrogen-bond donor strength and acceptor capability

The *synergetic effect* describes the increase of the strength of a hydrogen bond through metal ions coordinated to the donor atom X.

The *cooperative effect* means the increase of the donor strength of a hydrogen-bond donor if the donor concurrently acts also as acceptor for a second hydrogen bond.

The *anti-cooperative* or *competitive effect* means the decrease of the strength of hydrogen bonds due to the decrease of

(i) the donor strength e.g. through coordination (*donor competitive effect*) or

(ii) the acceptor capability (*acceptor competitive effect*) of the entities involved in the respective hydrogen bonds.

Both may be caused by the different coordination of the donor and acceptor atoms X and Y.

2.4 Hydrogen bonding

Hydrogen-bond donor strength and acceptor capability

The *acceptor capability* primarily depends on the gas-phase basicity of the hydrogen-bond acceptor groups to hydrogen atoms. It is modified by the *acceptor competitive effect* due to the coordination and bond strength of the acceptor atom Y, e.g. by

(i)   the receipt of more than one hydrogen bonds,

(ii) the total number of atoms coordinated to the acceptor atom,

(iii) the strength of the $Y–Z$ bonds of the hydrogen-bond acceptor group, and

(iv) the deviation from the most favorable hydrogen-bond acceptor angle $H\cdots Y–Z$.

In the case of $O–H\cdots Y$ hydrogen bonds, the relative acceptor capability range as $ClO_4^- < NO_3^- < BrO_3^- < IO_3^- < I^- < Br^- < H_2O < Cl^- << SO_4^{2-} < SeO_4^{2-} < SO_3^{2-} < SeO_3^{2-} < PO_4^{3-} < F^- < OH^-$ (*hydrogen-bond acceptor series*).

The *donor strengths* of common hydrogen-bond donors range as $OH^- < SH^- < NH_2^- < NH_3 < H_2O < HSeO_3^- < H_{5-n}IO_6^{n-} < H_3O^+$. It is governed by both the positive partial charge at the acid hydrogen atom, and the strength and hybridization of the $X–H$ bond of the donor molecule. The donor strength is increased due to the cooperative and the synergetic effects and decreased due to the anti-cooperative/donor competitive effect.

2.4 Hydrogen bonding

Hydrogen-bond donor strength and acceptor capability

In the case of the *synergetic effect*, i. e., bonding of the donor atom X to metal atoms, the X–H bonds of the donor are both weakened and polarized with increasing strength of the respective M–X bonds and, hence, the acidity of the respective hydrogen atom and the donor strength are increased.

The synergetic effect increases with increasing charge and decreasing size of the respective metal ions as well as with increasing covalence of the M–X bonds. The latter is particularly strong in the case of Cu^{2+}, Zn^{2+}, and Pb^{2+} ions.

In the case of the *cooperative effect*, the X–H bond of the hydrogen-bond donor is weakened because the donor atom X acts concurrently as hydrogen-bond acceptor and hydrogen-bond donor, and, hence, acidity and donor strength of the respective hydrogen atom are increased.

2.5 Molecular interactions and packing of molecules

Interaction/Energy	Bonding	Distance relation
Covalent bonding (complex)	very strong	~ 1/r (long-range)
Ionic bonding (monopole-monopole) $$E = -\frac{Z^+ \cdot Z^-}{4\pi\varepsilon_0} \cdot \frac{1}{r}$$	very strong	~ 1/r (long-range)
Repulsive forces (nuclei, core electrons) $$E = +k \cdot \frac{1}{r^n}$$	extreme strong repulsive	~ $1/r^n$ (n = 5-12) (extreme short-range)
Ion-dipol ($Z^\pm$ = charge of ion, μ = q·r) $$E = -\frac{\left|Z^\pm\right| \cdot \mu}{4\pi\varepsilon_0} \cdot \frac{1}{r^2}$$	strong	~ $1/r^2$ (short-range)

**Interactions, forces and energies in solids**

2.5 Molecular interactions and packing of molecules

Interaction/Energy	Bonding	Distance relation
Dipol-dipol (dipolar molecules) $$E = -\frac{2\mu_1 \cdot \mu_2}{4\pi\varepsilon_0} \cdot \frac{1}{r^3}$$	moderately strong	~ $1/r^3$ (short-range)
Ion-induced dipole $$E = -\frac{1}{2} Z^2 \alpha \cdot \frac{1}{r^4}$$ (z: charge of ion, α: polarizability)	weak	~ $1/r^4$ (very short-range)
Induced dipole-induced dipol (dispersion, van der Waals, London) $$E = -\mu^2 \alpha \cdot \frac{1}{r^n}$$	very weak	~ $1/r^n$ (n = 6-8) (extreme short-range)

Interactions, forces and energies in Solids

2.5 Molecular interactions and packing of molecules

Molecular Interactions in HCN Crystals

This dipolar molecule ($\mu = 1 \cdot 174$) has two crystalline modifications, both consisting of parallel linear H-bonded chains $\cdots H\!-\!C\!\equiv\!N\cdots H\!-\!C\!\equiv\!N\cdots$ $H\!-\!C\!\equiv\!N\cdots$ with a transition between the two forms at 170 K resulting in slightly different chain packing (Figure 6-28). The crystal internal energy
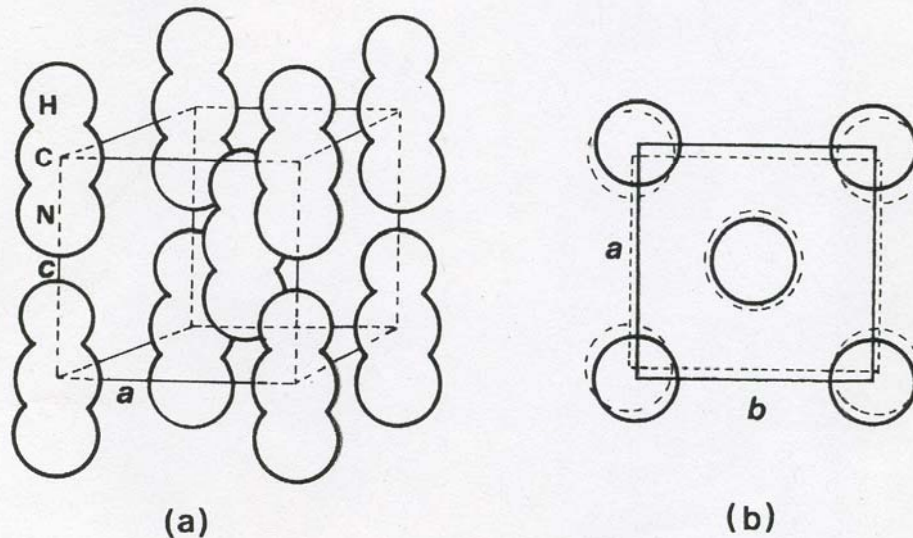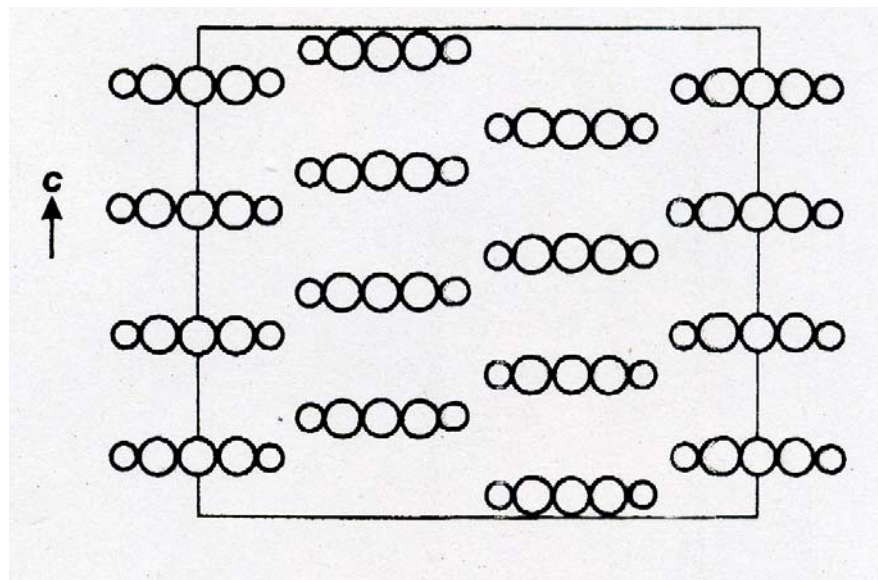
Figure 6-28 The structures of crystalline HCN. (a) The chains of H-bonded molecules. (b) The slightly different modes of packing in the high (—) and low (- - -) temperature phases. (Rae (1969))

Space filling packing/arrangement of H-bonded polar molecules
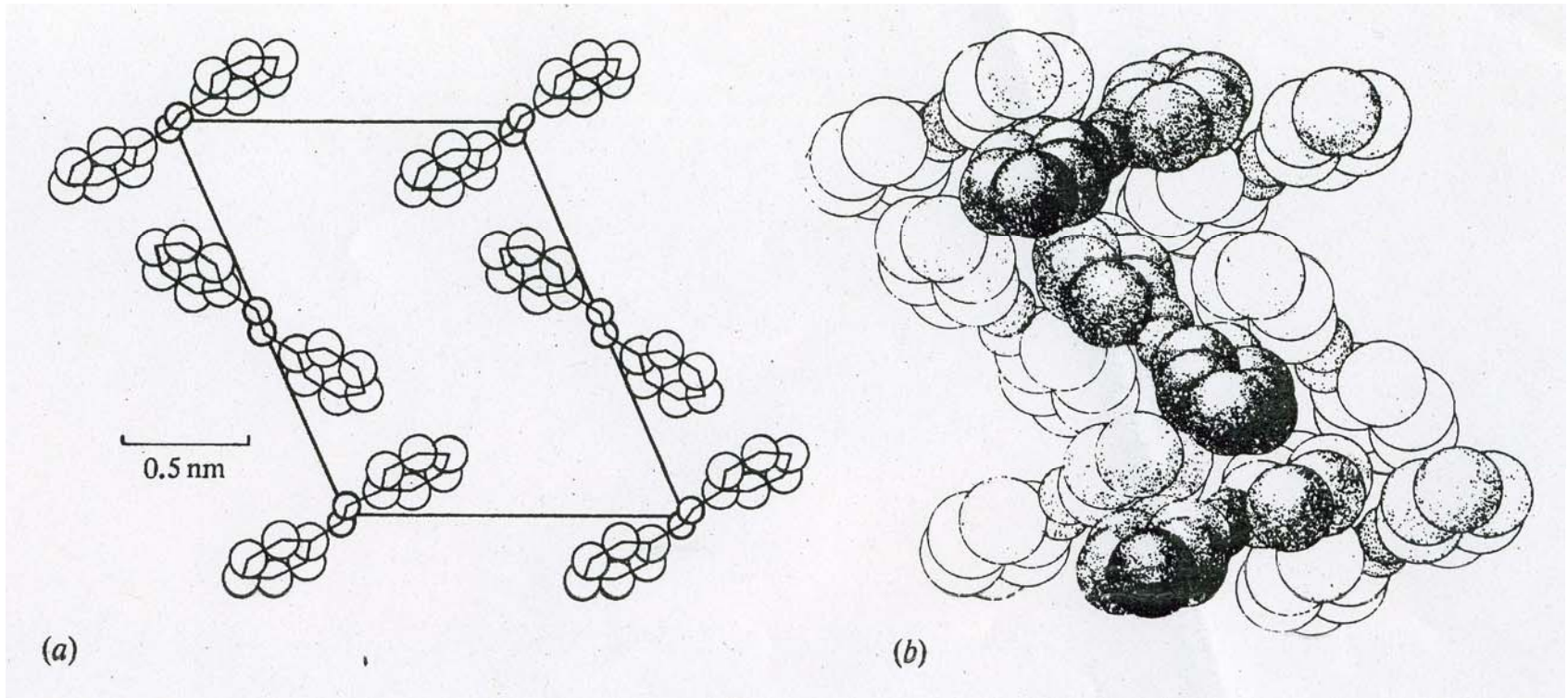
2.5 Molecular interactions and packing of molecules
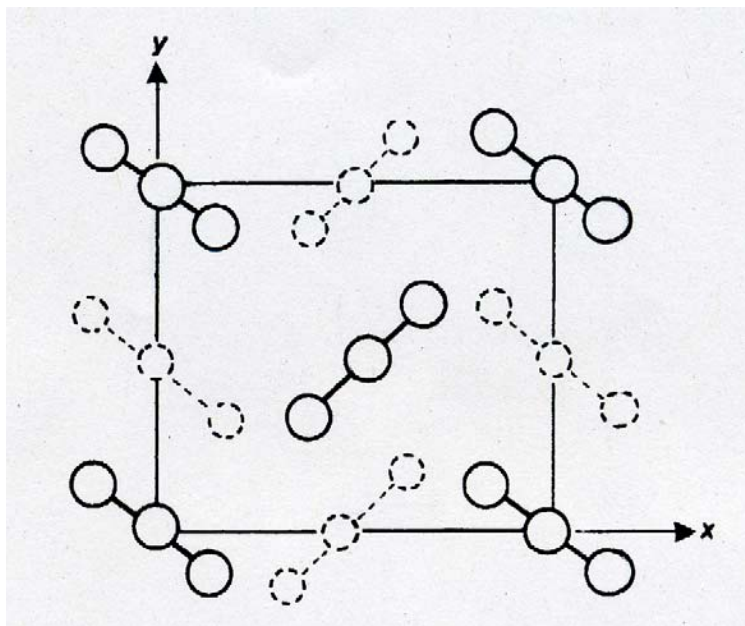
The crystal structure of benzene (H··π-bonds?)

The columnar crystal structure of sym-triazine (H··N bonds?)

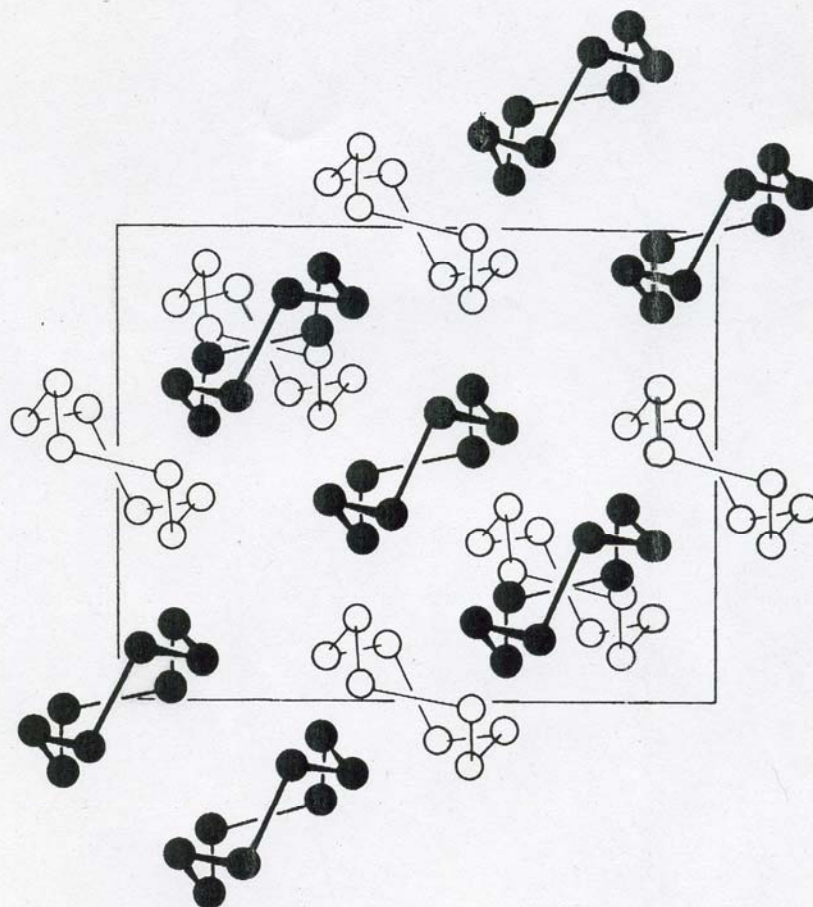Space filling packing/arrangement of non-polar molecules

2.5 Molecular interactions and packing of molecules

Space filling packing/arrangement of non-polar molecules
(a) at height 0 and (b) at height 0 and 1/2

2.5 Molecular interactions and packing of molecules

Figure 6-11 The packing of S_8 rings in crystalline orthorhombic sulphur. (Modified from *Fundamentals of Inorganic Crystal Chemistry* by H. Krebs. © 1968 McGraw-Hill Book Company (UK) Ltd. Used with permission)

Space filling packing/arrangement of non-polar molecules (d⋯d repulsion?)

# 2.5 Molecular interactions and packing of molecules
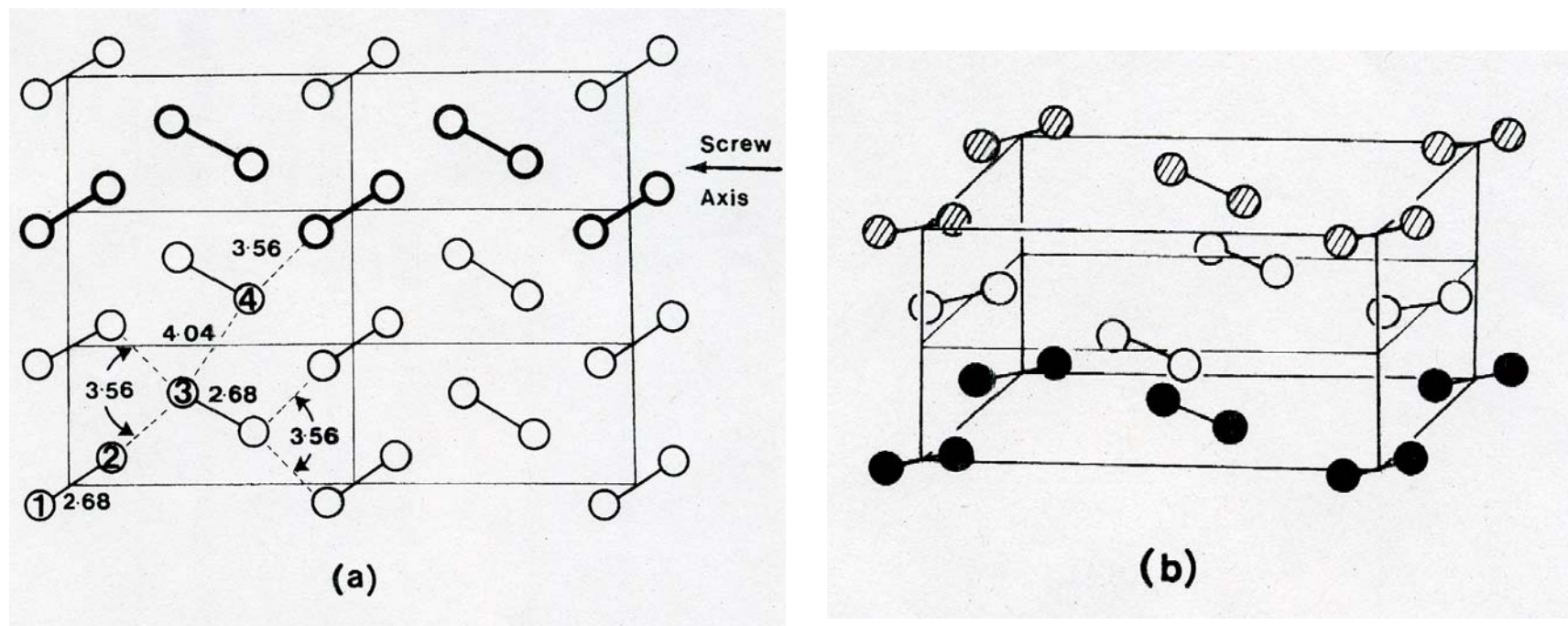
Figure 6-10 (a) Detail of one layer of the iodine crystal. (b) The layer stacking found in crystalline chlorine, bromine and iodine. Note the formal analogy with c.c.p. (From *Fundamentals of Inorganic Crystal Chemistry* by H. Krebs. © 1968 McGraw-Hill Book Company (UK) Ltd. Used with permission)

Space filling packing/arrangement of non-polar molecules
($\rightarrow 2_1$ symmetry)

# 2.5 Molecular interactions and packing of molecules

(a)

(b)

(c)
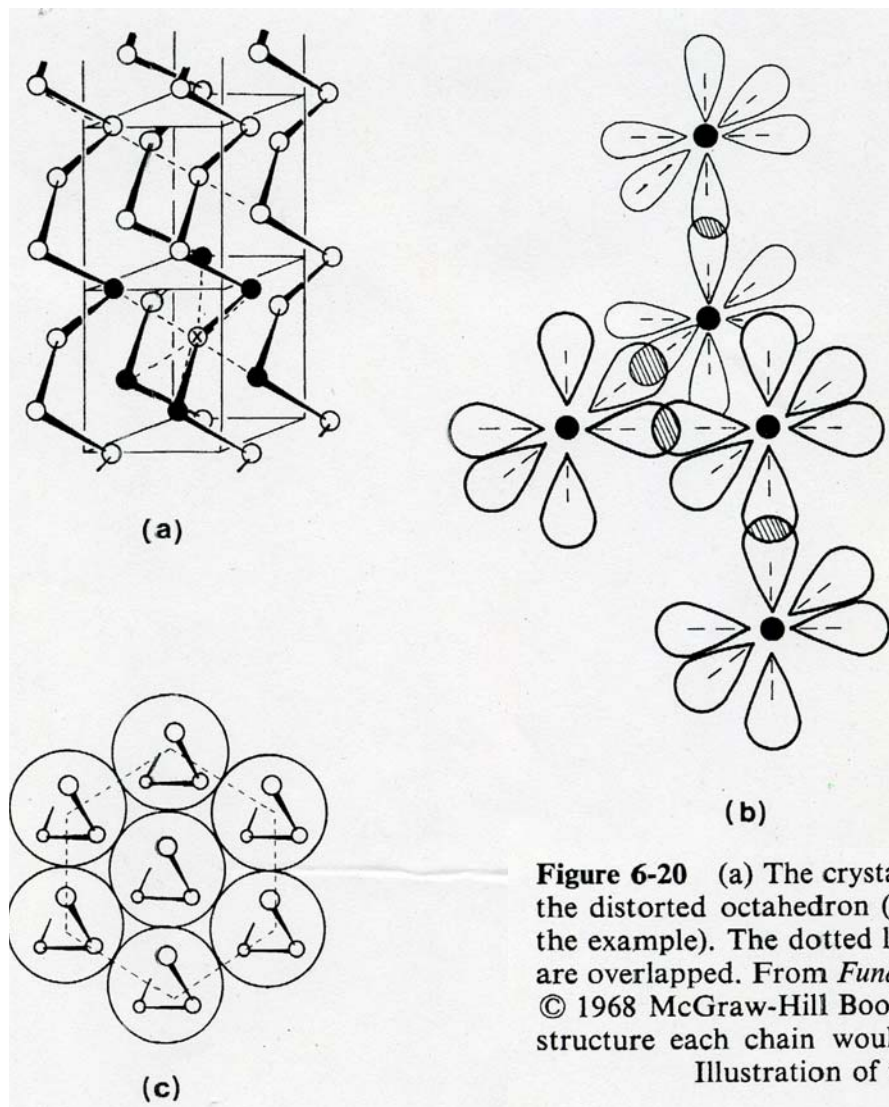
Influence of space filling, free electron pairs and configurat. requirements on molecular arrangement (Se and Te like octahedral surroundings)

Figure 6-20 (a) The crystal structure of hexagonal selenium and tellurium. Note the distorted octahedron (black atoms) formed about each atom (x is taken as the example). The dotted lines indicate the directions in which the sp^3d^2 hybrids are overlapped. From *Fundamentals of Inorganic Crystal Chemistry* by H. Krebs. © 1968 McGraw-Hill Book Company (UK) Ltd. Used with permission). (b) The structure each chain would have if only *p*-orbitals were used in bonding. (c) Illustration of the packing of the chains (cf. Figure 3-1b)

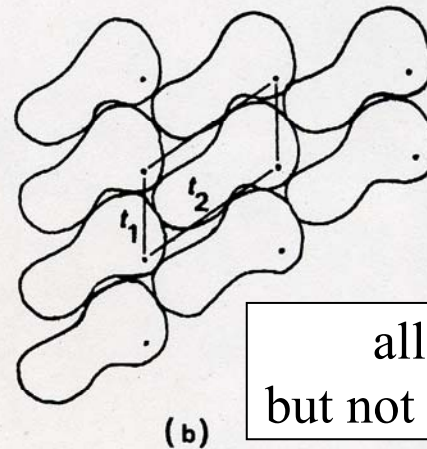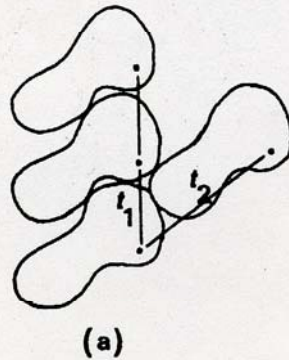Space filling packing/arrangement of non-polar molecules

2.5 Molecular interactions and packing of molecules
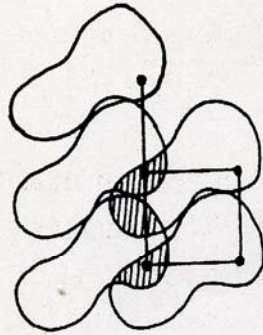
not allowed!

Figure 6-2   Illustration of the unsuitability of a rectangular lattice for arranging arbitrarily shaped molecules. (Kitaigorodskii (1961))
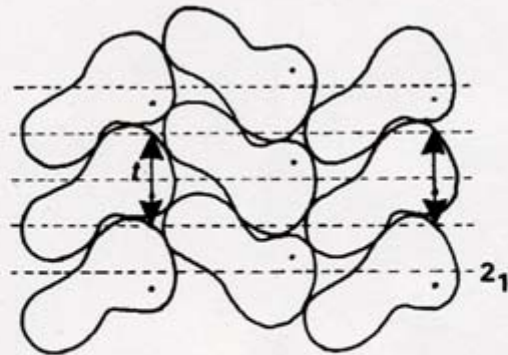
allowed!
but not rectangular

(a)

(b)

Figure 6-3   A close-packed planar layer of non-directionally bonded molecules of arbitrary shape. (a) A chain of type 1 (see text) to which one additional molecule has been added, determining the second translational repeat, t_2. (b) More of the layer. (Kitaigorodskii (1961))
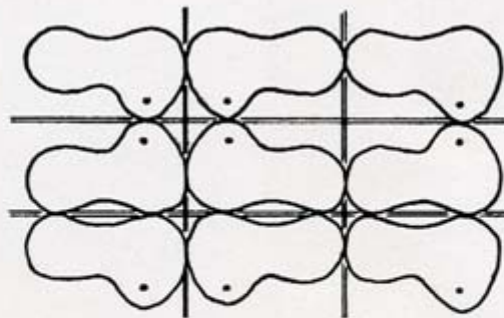
Space filling packing/arrangement of arbitrarily shaped non-polar molecules after Kitaigorodskii

2.5 Molecular interactions and packing of molecules

allowed!
forming of 2_1

Figure 6-4   Another close-packed layer of molecules formed from chains of type 1. (Kitaigorodskii (1961))

not allowed!

Figure 6-5   An undesirable form of molecular packing derived from chains of type 5. (Kitaigorodskii (1961))

Space filling packing/arrangement of non-polar molecules after Kitaigorodskii

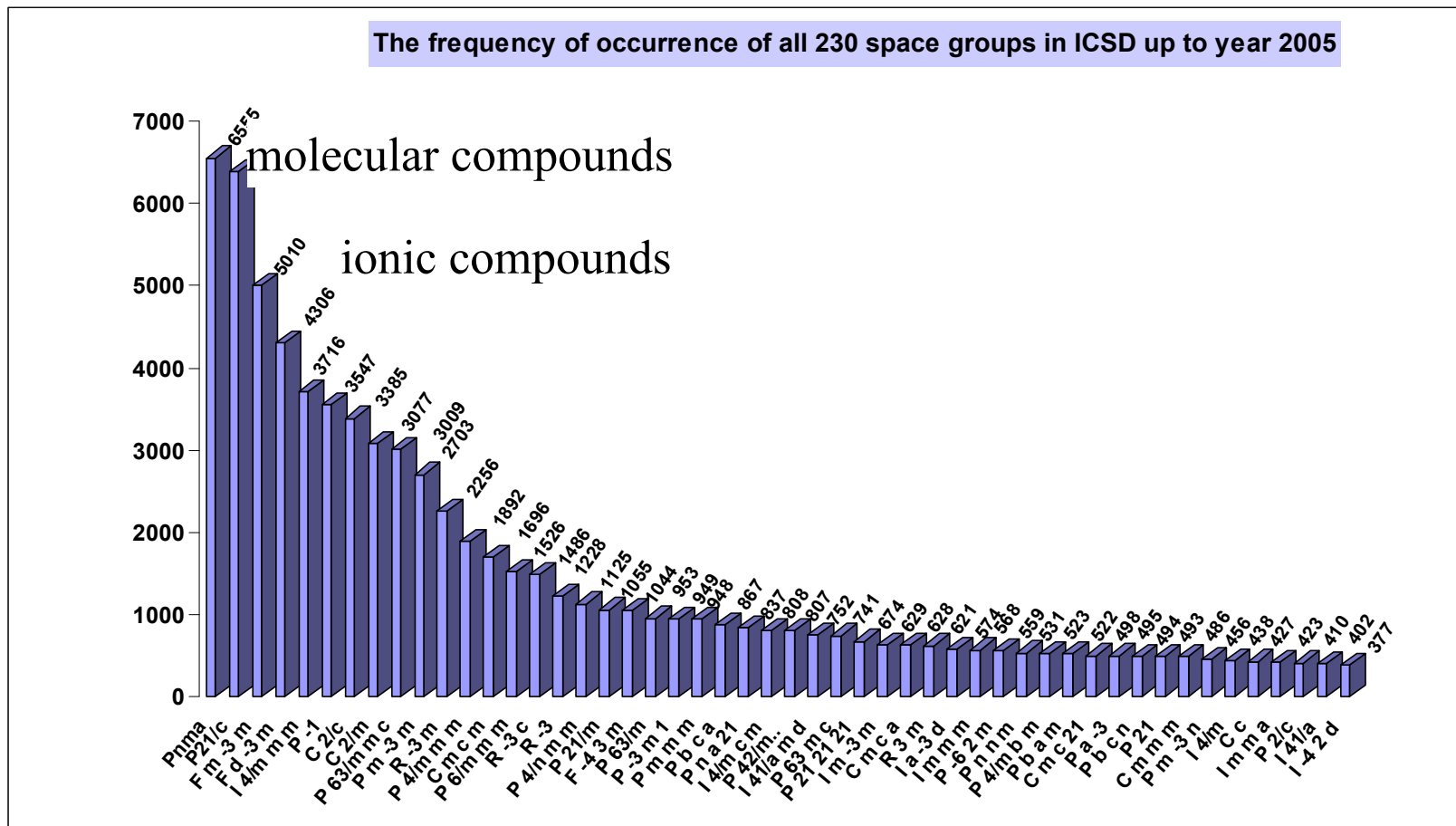# 2.5 Molecular interactions and packing of molecules

Table 1. Most-probable space groups for molecular crystals (A. I. Kitaigorodskii, *Organic Chemical Crystallography*, Consultants Bureau, New York, 1961)

Inherent molecular symmetry	1, 2, m		$\bar{1}$, 2, m mmm		mmm				222	
Molecular symmetry in crystal	1		$\bar{1}$		2		m		2	
	Space group	Z	Space group	Z	Space group	Z	Space group	Z	Space group	Z
Space group and multiplicity (Z) of position occupied by the molecule	$P\bar{1}$	2,4	$P\bar{1}$	1,2	$C2/c$	4	Pmc	4	$C2/c$	4
	$P2_1$	2,4	$P2_1/c$	2,4	$P2_12_12$	2,4	Cmc	4	$P2_12_12$	2,4
	$P2_1/c$	4	$C2/c$	4	$Pbcn$	4	$Pnma$	4	$Pbcn$	4
	Pca	4	$Pbca$	4						
	Pna	4								
	$P2_12_12_1$	4								

P represents a primitive unit cell, i.e., atoms at corners only. A C-centred cell has twice as many atoms as its equivalent cell but the axes are more conveniently arranged.

Packing/arrangement of arbitrarily shaped non-polar molecules according to Kitaigorodskii mostly results in
space groups with 2_1 and/or c symmetry like $P2_1/c$, $Pnma$ or $P2_12_12_1$

2.5 Molecular interactions and packing of molecules

The frequency of occurrence of all 230 space groups in ICSD up to year 2005

molecular compounds

ionic compounds

Space group population statistics of inorganic compounds

2.5 Molecular interactions and packing of molecules

Space group frequency of the 30 most frequent space groups in the ICSD of the year 2005

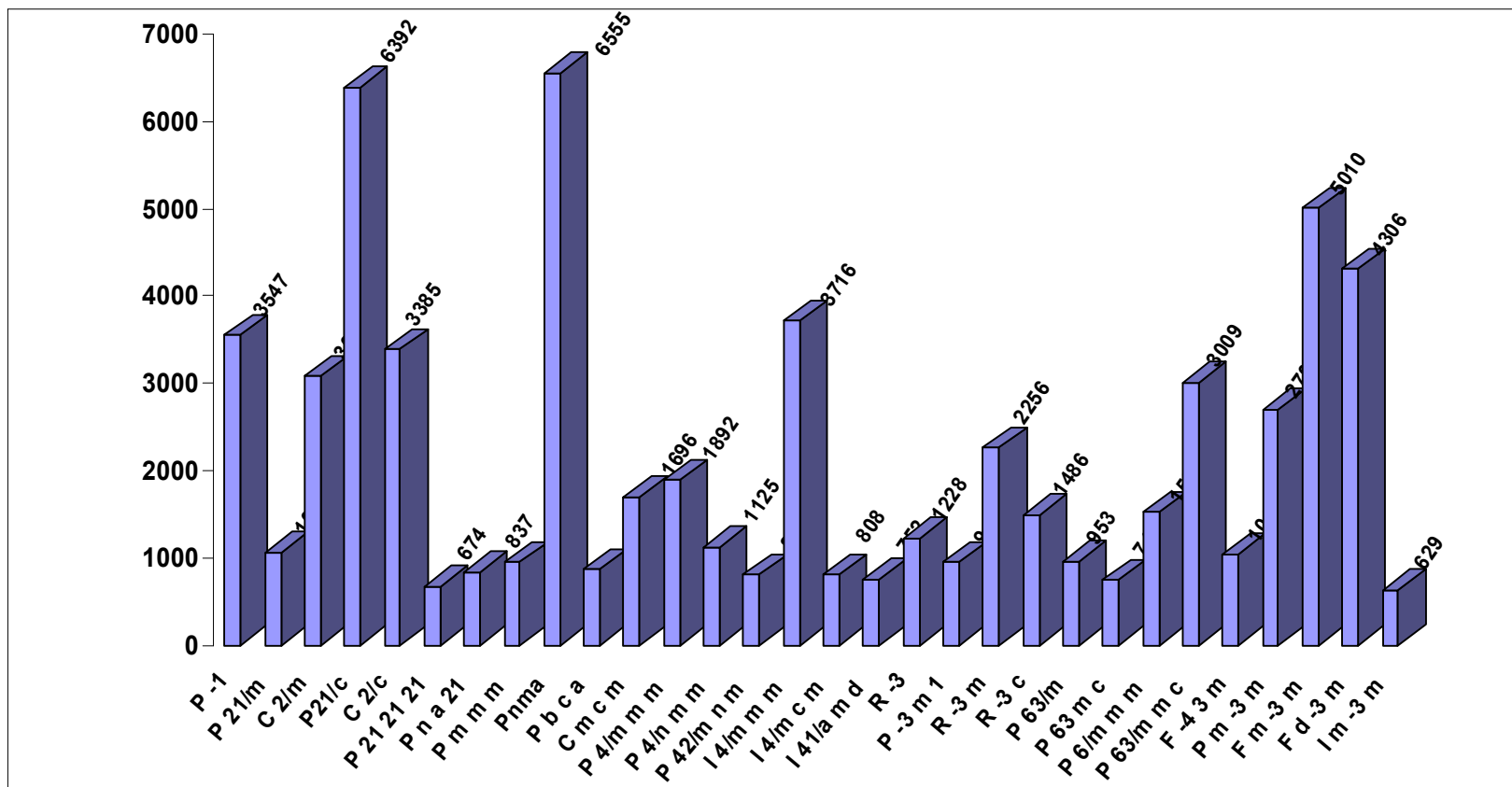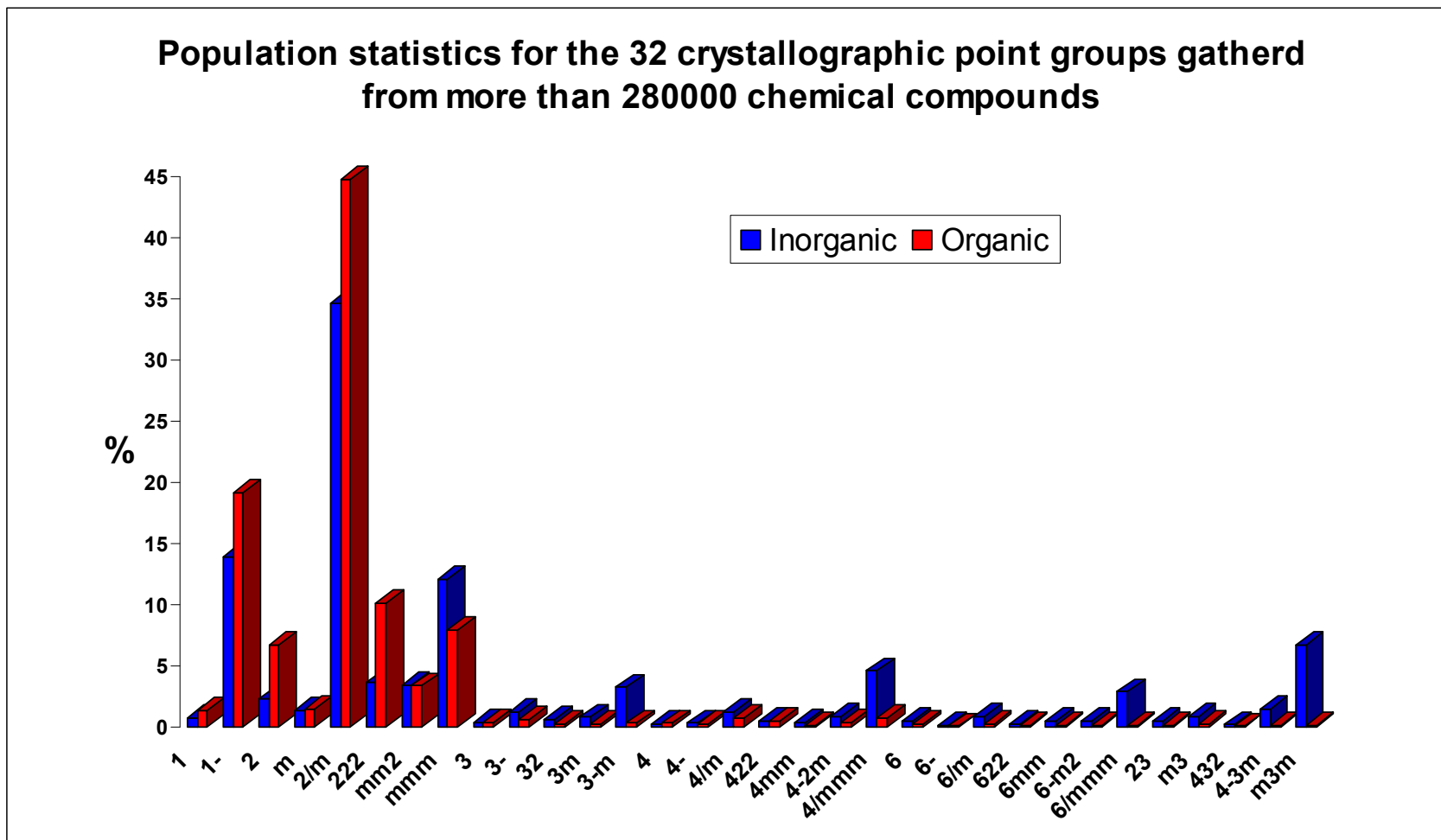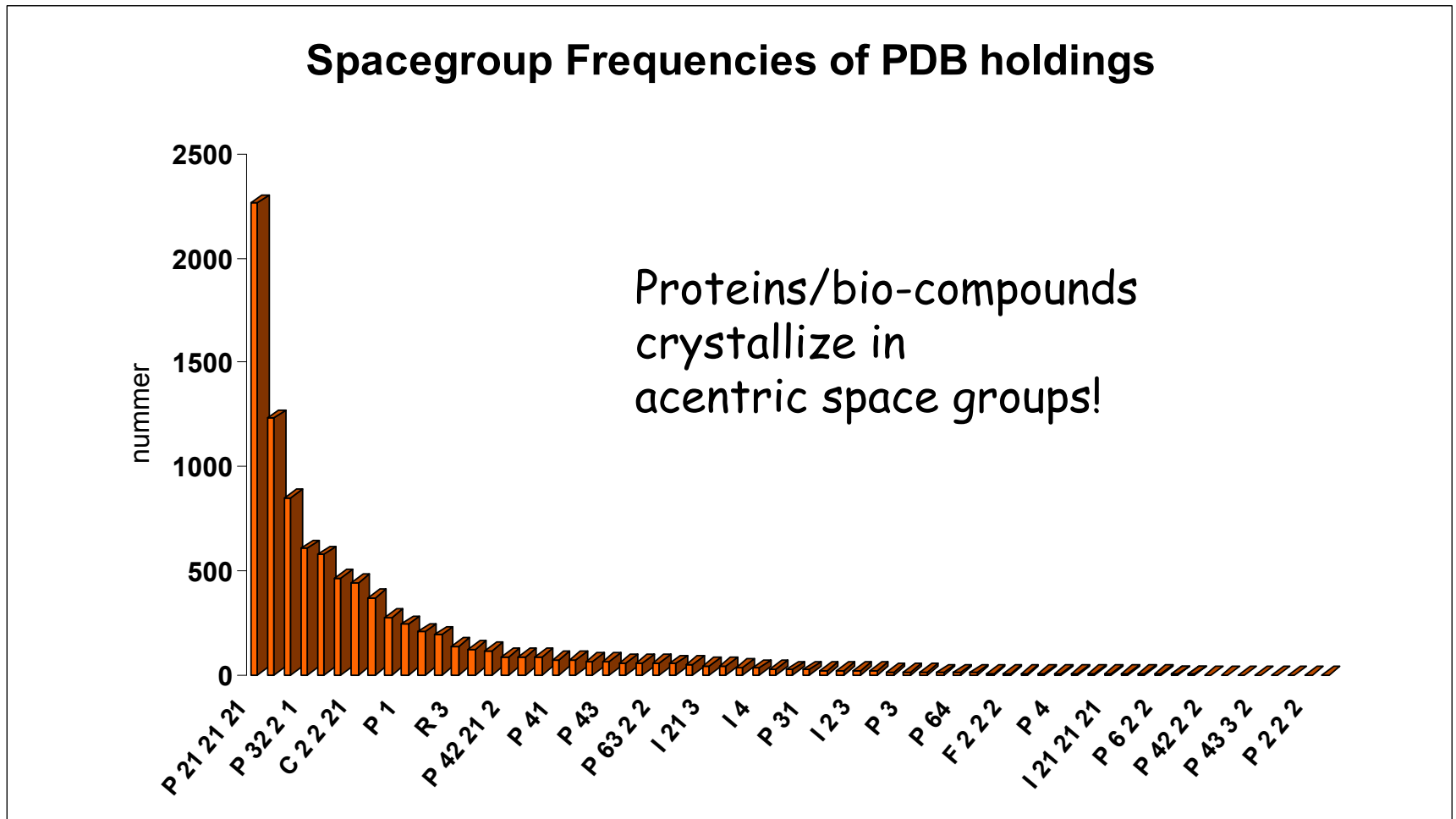Space group population statistics of inorganic compounds

2.5 Molecular interactions and packing of molecules

Point group population statistics of organic and inorganic compounds

2.5 Molecular interactions and packing of molecules

Spacegroup Frequencies of PDB holdings

Proteins/bio-compounds crystallize in acentric space groups!

Point group population statistics of proteins/bio-compounds

2.6 Models, Rules and Principles of Bonding/Building of Solids

1. Hard spheres (ionic radii)
- Victor M. GOLDSCHMIDT's ionic radii:
    - Complete set of ionic radii (CN = 6) based on standard radii (O^{2-}, F^-)
- PAULING's set of ionic radii (crystal radii)
- SHANNON's set of ionic radii: crystallographic information and bond-valence ideas (Shannon's (IR) radii have replaced those of Goldschmidt and Pauling)
    - Radius of H^+ is negative (-0.38Å) !!
- Structure-sorting maps
    - PETTIFOR
    - MOOSER-PEARSON

2. Electrostatics
- BORN-HABER cycle
- Coulomb-energy
    - MAPLE (HOPPE)

3. Pauling's rules
- A series of 5 rules concerning the stability of complex ionic crystals established by Linus PAULING

2.6 Models, Rules and Principles of Bonding/Building of Solids

4. Volume Increments (BILTZ, HOPPE)
- The total molar volume is approximated by the sum of individual volume increments characteristic for individual particles (atoms, ions, ionic groups)
- Obtained by statistical analysis of a large number of crystal structures

5. Bond-valence Method (BROWN, TRÖMEL, etc.)
- Bond-length-bond-strength method based on Pauling's second rule

6. Quantum Chemical Approaches
– Molecular Orbital, Energy bands, Band model
- Hückel MO
- HSAB (Pearson)
    – Hard and soft acids and bases
    – Can be expressed in terms of quantum chemical quantities using DFT
– Valence Bond (rarely used in solid state chemistry)
– Electron gas

2.6 Models, Rules and Principles of Bonding/Building of Solids

7. Intermetallic Phases
- LAVES phases
  - Packing dominated inter metallic phases of the composition AB_2
  - Three structure types: $MgCu_2$, $MgZn_2$ and $MgNi_2$
- ZINTL phases
  - Transition between metallic and ionic bonding (Zintl anion)
  - Cations: alkaline and alkaline-earth metals
  - Anions: 14. group (salt-like) and group 11.-13. (alloys)

8. Symmetry Principles (e.g. Curie)
  - Relationship between the symmetry of structural units and crystal symmetry

9. Molecular Packing (KITAIGORODSKI, O'KEEFFE)