# Kap. 3
States of aggregation

Chemical bonds

**Table 3.1** Forces between atoms, ions and molecules

Type of bond	Approximate energy/kJ mol^{-1}	Species involved
Covalent	350	Atoms with partly filled orbitals
Ionic	250	Ions only
Metal	200	Metal atoms
Ion–dipole	15	Ions and polar molecules
Dipole–dipole	2	Stationary polar molecules
Dipole–dipole	0.3	Rotating polar molecules
Dispersion	2	All atoms and molecules
Hydrogen bond	20	N, O or F plus H

$$V(r) = 4V_{min}\left[\left(\frac{r_0}{r}\right)^6 - \left(\frac{r_0}{r}\right)^{12}\right]$$

Van der Waals interactions

Hydrogen bonds

δ− charge

δ+ charge
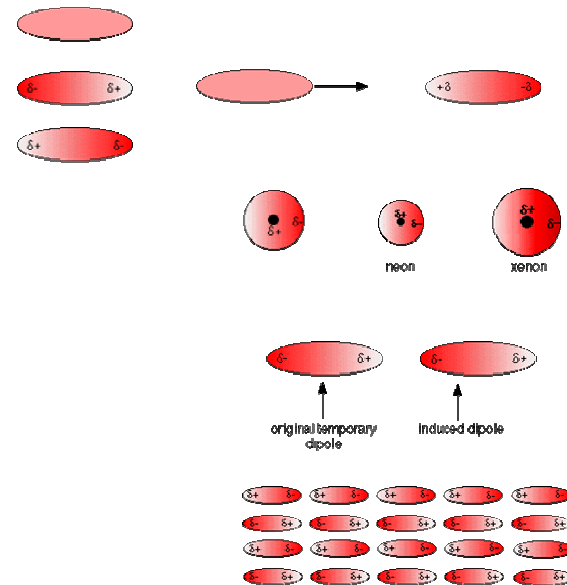
Hydrogen Bonds

Hydrogen bonds
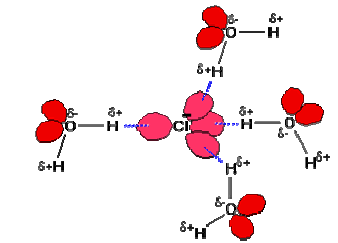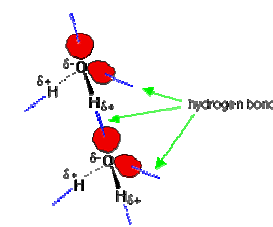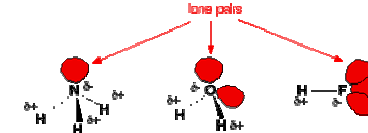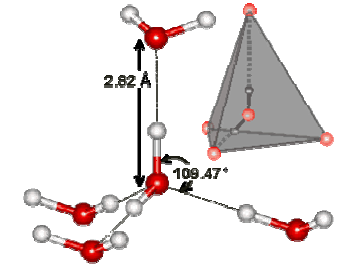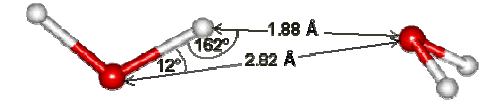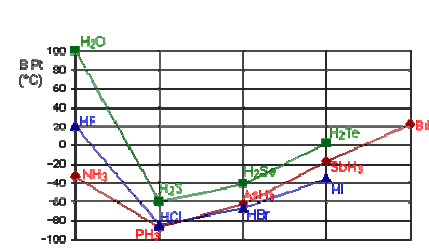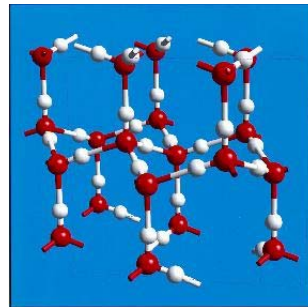

lone pairs
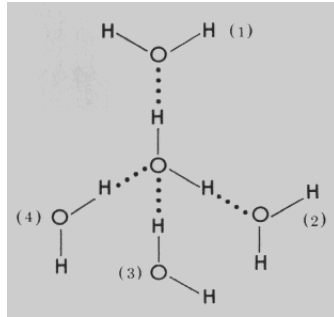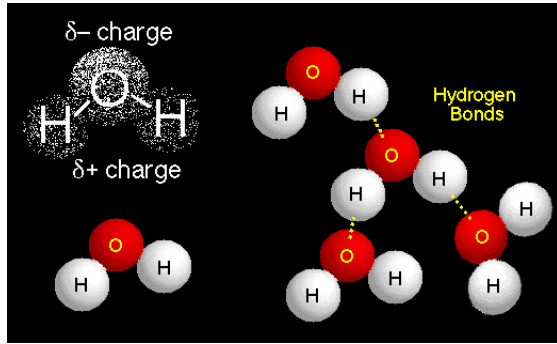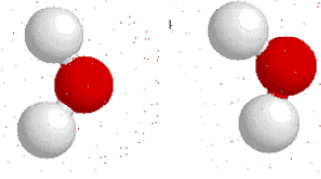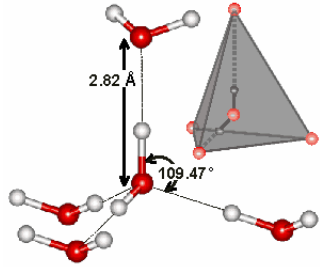
hydrogen bonds

Polymorphism
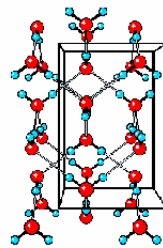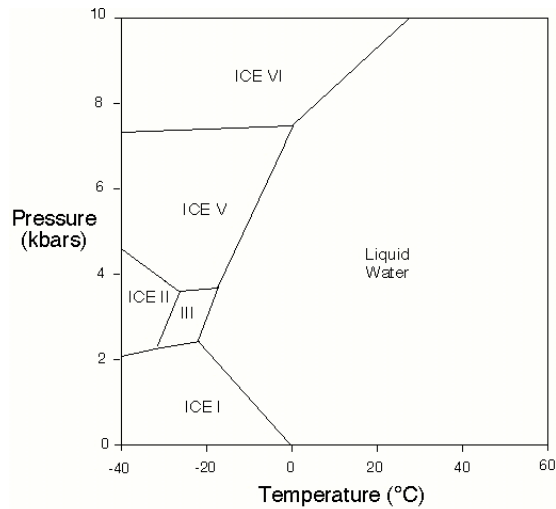
Ice VIII

Ice 1h

Macrostructure -> Microstructure
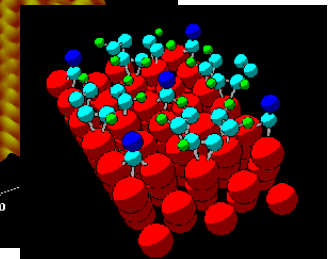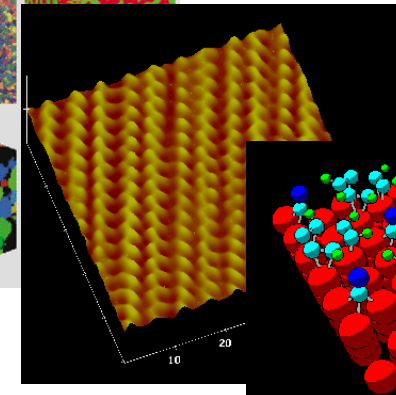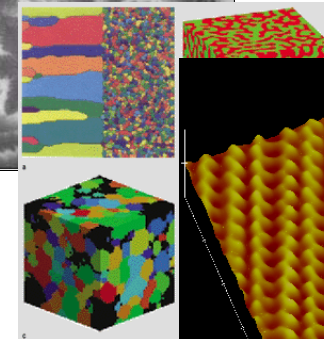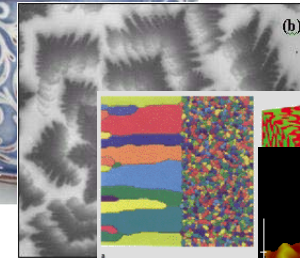
Crystal - amorphous
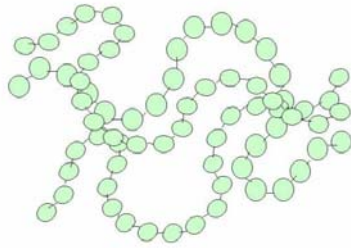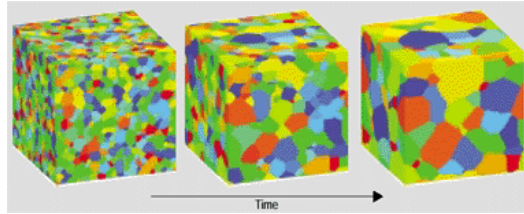
Funtional material
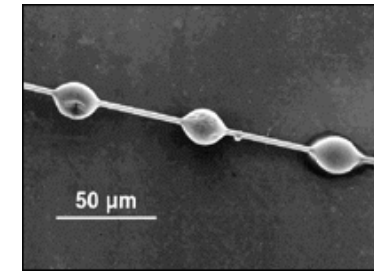
Nanostructures

PbSe Nanocrystals

PbSe Q-dot size series photoluminescence spectra
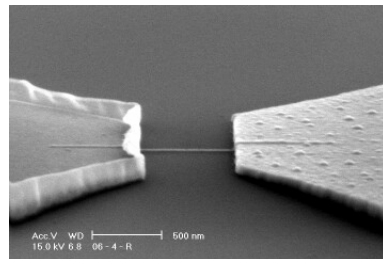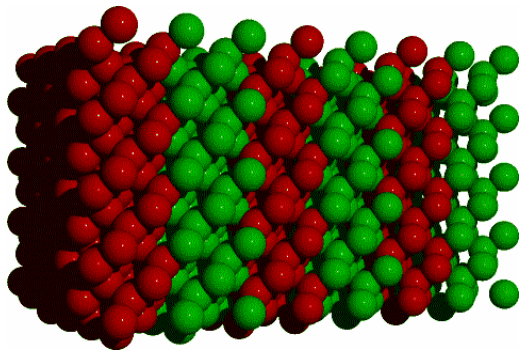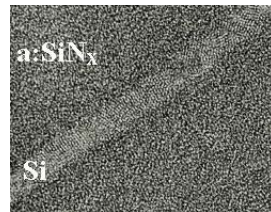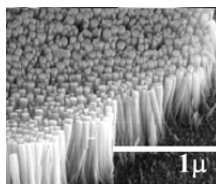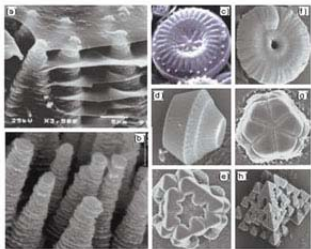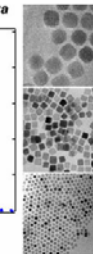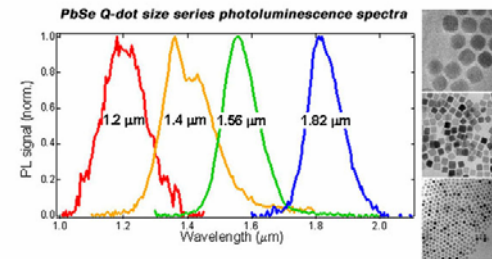
Low-resolution TEM images of monodisperse PbSe spheres, rounded cubes, and cubes

Hi-resolution TEM images of PbSe Q-dots
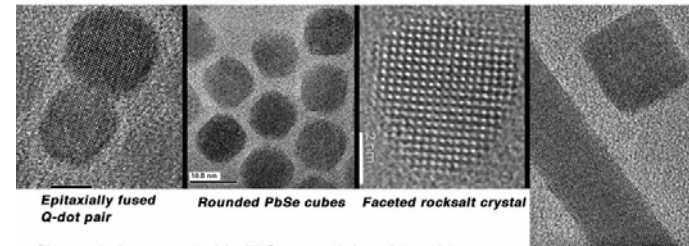
Epitaxially fused Q-dot pair   Rounded PbSe cubes   Faceted rocksalt crystal   PbSe cube and wire comprising oriented fused cubes

Size and shape control in PbSe growth is achieved by controlling temperature, reaction time, solvent/stabilizer identity, and precursor concentration.
Preparations are based on modifications of:
C. B. Murray, et al. IBM Journal of Research and Development 45, 47 (2001) and B. L. Wehrenberg, C. J. Wang, and P. Guyot-Sionnest. J. Phys. Chem. B 106, 10634 (2002)

Emission wavelengths important for the telecommunications industry (1.3 and 1.5 µm) are easily achieved with Q-dot photoluminescence quantum yields as high as ~80%.
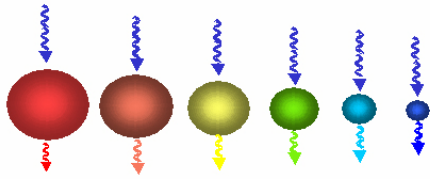
Nanocrystals absorb light then re-emit the light in a different color – the size of the nanocrystal (at the Angstrom scale) determines the color
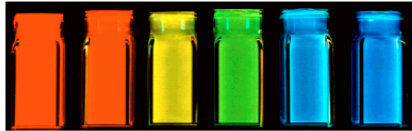
Six different quantum dot solutions are shown excited with a long wave UV lamp

Felice Frankel

500 nm

1 µm
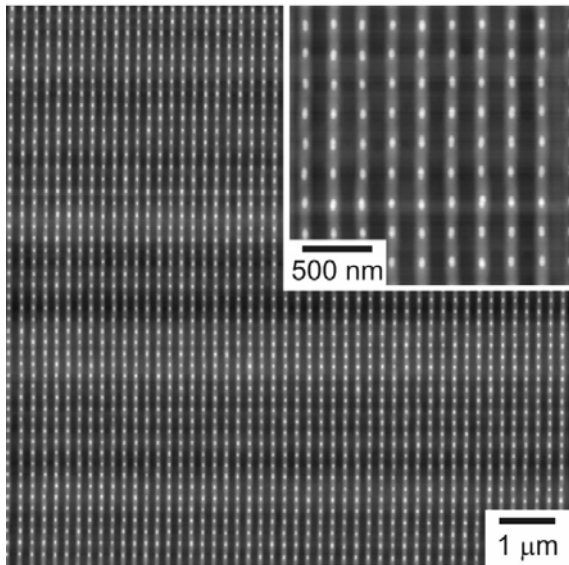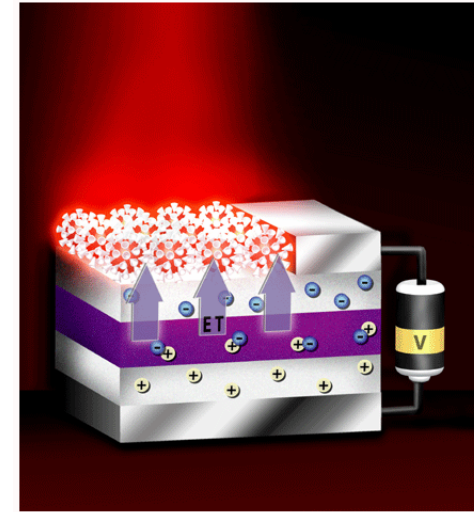
Defects

Perfect Crystal

- A perfect crystal with every atom in the correct position does not exist. Only a hypothetical situation at 0 K

- "Crystals are like people: it is the defects in them which tend to make them interesting!" - Colin Humphreys

- Most materials properties are determined by the crystal defects present.

Defects

Usually few defects:
$$\frac{\text{No. defects}}{\text{No. atoms}} \approx \frac{1}{10^{15}} \quad \text{to } 0.1 - 1\ \%$$

If the defect consentration becomes too high, defect-defect interactions occur.

⬇

Defect clustering

Stoichiometric defects, viz. no ateration in composition

Vacancies (empty possitions)
Interstitial ("between lattice" points)
Wrong type atoms

Vacancies and Interstitials
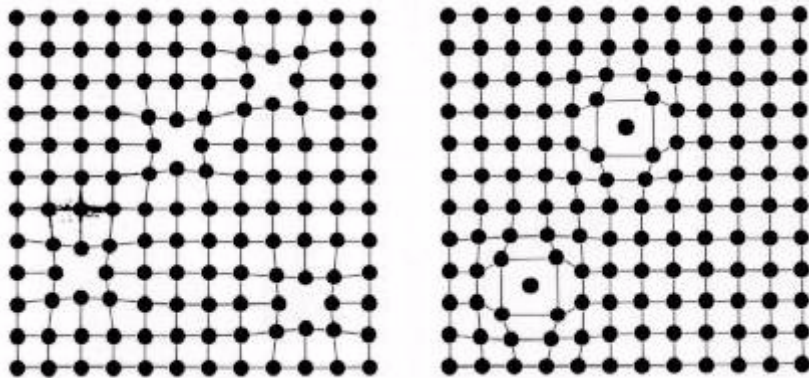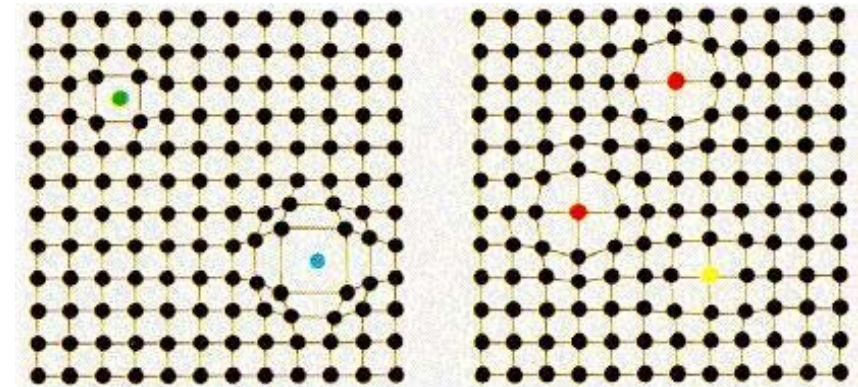
Impurity Atoms

interstitial impurity.

substitutional impurity

The colored atoms are impurity atoms. They are atoms of a different element.

Thermodynamics

Heat of formation   **ΔH**
Configurational entropy   **S = k ln(W)**

Temperature dependency: **ΔG = ΔH − TΔS**

[defects] incrases with temperature

Different types of defects in one phase:
       each type of defect: ΔG$_i$ = ΔH$_i$ − TΔS$_i$

One dominating type of defects.

ΔH

ΔG = ΔH − TΔS

Energy

TΔS
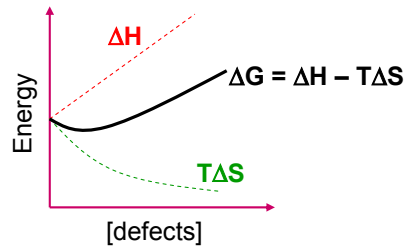
[defects]

Formation of defects:
cost energy but gain entropy

$$\frac{n_d}{N} \approx \exp\left(\frac{-\Delta H}{RT}\right)$$

Schottky defects

The (100) for NaCl-type structure

Equal ammount of anion and cation vacancies

$$V'_{Na}\,^{(-)} \qquad V^{\bullet}_{Cl}\,^{(+)}$$

$$\frac{n_d}{N} \approx \exp\left(\frac{-\Delta H_S}{2RT}\right)$$

Alkaline halides	NaCl-type
Earth alkaline halides	NaCl-type
Cs-halides	CsCl-type
BeO	Wurtsite-type

Table 3.3 The formation enthalpy of Schottky defects, ΔH_S, in some alkali halide compounds of formula *MX*

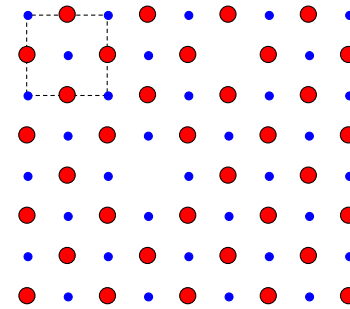| Compound	ΔH_S/J
LiF	3.74×10^{-19}
LiCl	3.39×10^{-19}
LiBr	2.88×10^{-19}
LiI	1.70×10^{-19}
NaF	3.87×10^{-19}
NaCl	3.75×10^{-19}
NaBr	2.75×10^{-19}
NaI	2.34×10^{-19}
KF	4.35×10^{-19}
KCl	4.06×10^{-19}
KBr	3.73×10^{-19}
KI	2.54×10^{-19}

Note: all compounds listed have the *halite* structure
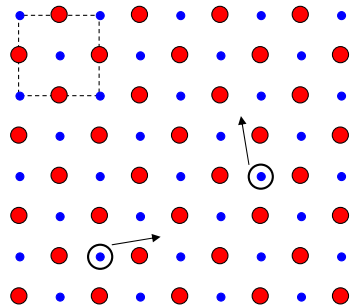
The heat of formation for a Schottky defect: **ΔH$_S$**

Frenkel defects

The (100) for NaCl-type structure

Cation Frenkel defect
Anion Frenkel defect

1/8th of NaCl-t unitcell:
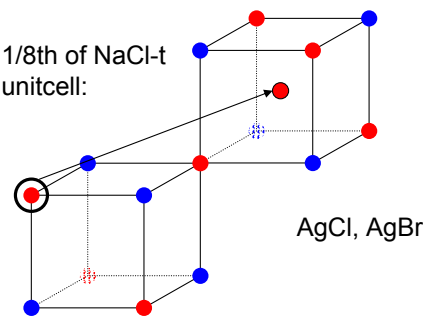
AgCl, AgBr

Movement from a normal to an interstitial position

$$n_f \approx \left(NN^*\right)^{1/2} \exp\left(\frac{-\Delta H_F}{2RT}\right)$$

Example: AgCl
   NaCl-type structure

Ag in octahedra holes
of ccp Cl

Ag in tetrahedre holes
of ccp Cl

Table 3.4 The formation enthalpy of Frenkel defects, ΔH_{Fr} in some compounds of formula *MX* and *MX$_2$*

Compound[a]	ΔH_F/J	Compound[b]	ΔH_F/J
AgCl	2.32×10^{-19}	CaF$_2$	4.34×10^{-19}
AgBr	1.81×10^{-19}	SrF$_2$	2.78×10^{-19}
β-AgI	0.96×10^{-19}	BaF$_2$	3.06×10^{-19}

[a]Frenkel defects on the cation sublattice of *halite* structure compounds.
[b]Frenkel defects on the anion sublattice of *fluorite* structure compounds.

The heat of formation for a Frenkel defect: **ΔH$_{Fr}$**

Kroger-Vink notation

Each defect is represented by a combination of three symbols:

$$X^{\bullet(+1),x(0),'(-1)}_{i,s,X,Y} \qquad Na^x_{Na} \qquad V'_{Na} \qquad Ag^{\bullet}_i$$

Scottky defect

$$Na_{Na} + Cl_{Cl} + V_{Na,S} + V_{Cl,S} \Leftrightarrow V'_{Na} + V^{\bullet}_{Cl} + Na_{Na,S} + Cl_{Cl,S}$$

Thermodynamics

Scottky defect
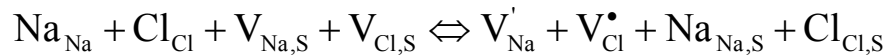
$$Na_{Na} + Cl_{Cl} + V_{Na,S} + V_{Cl,S} \Leftrightarrow V'_{Na} + V^{\bullet}_{Cl} + Na_{Na,S} + Cl_{Cl,S}$$

Constant

$$K = \frac{[V'_{Na}][V^{\bullet}_{Cl}][Na_{Na,S}][Cl_{Cl,S}]}{[Na_{Na}][Cl_{Cl}][V_{Na,S}][V_{Cl,S}]} \quad \Rightarrow \quad K = \frac{[V'_{Na}][V^{\bullet}_{Cl}]}{[Na_{Na}][Cl_{Cl}]}$$

Constant

$$K = \frac{(N_V)^2}{(N - N_V)^2}$$

$$N \cong N - N_V \quad \rightarrow \quad N_V \cong N\sqrt{K}$$
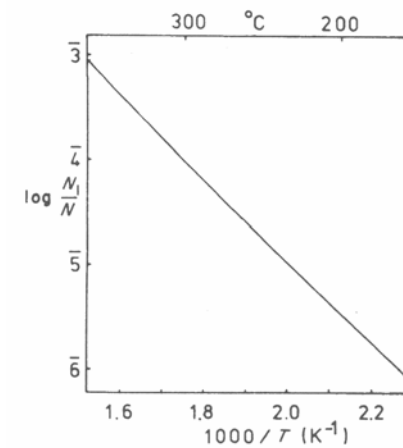
$$K \propto e^{(-\Delta G/RT)}$$
$$K \propto e^{(-\Delta H/RT)}e^{(\Delta S/R)}$$
$$= Ce^{(-\Delta H/RT)}$$
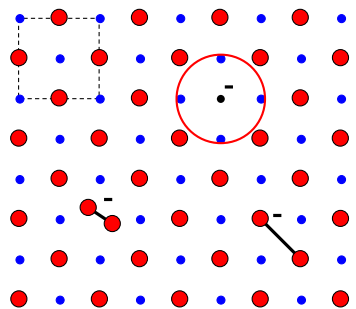$$N_V = N\,Ce^{(-\Delta H/2RT)}$$

Thermodynamics

$$\log_{10}(N_i/N) = \log_{10}(constant) - (\Delta H/2RT)\log_{10}e$$

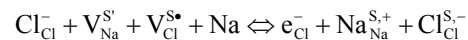# Colour centre, (alkaline halides)

The (100) for NaCl-type structure

H-centre   V-centre

Electron in a box, paramagnetic moment

F-centre

Colour from F-centre:
Dependant om host lattice

LiCl	**3.1 eV**
NaCl	**2.7 eV**
KCl	**2.2 eV**
RbCl	**2.0 eV**

$$Cl^-_{Cl} + V^{S'}_{Na} + V^{S\bullet}_{Cl} + Na \Leftrightarrow e^-_{Cl} + Na^{S,+}_{Na} + Cl^{S,-}_{Cl}$$

Colour:
MX-perfect   colourless
MX ordinary defects (intrinsic)   colourless
Chemical impurities (extrinsic)   colour
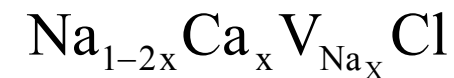**Radiation**   colour
Treatment with extra M   colour

Aliovalent substitution

Extrinsic defects arise on doping pure crystals with aliovalent impurities

NaCl may be doped with CaCl$_2$ to give:

$$Na_{1-2x}Ca_x V_{Na_x} Cl$$

Defect clustering

Defects have effective charge

Defects do perturb the host structure

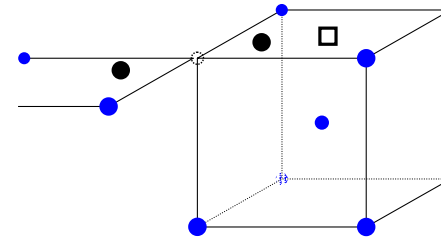**Some interactions** — **"neutral pairs"**

More interactions — **"defect clustering"**

Loads of interaction — **Stable phases with ordered distribution of defects**

eks. Pt. fcc (F) Z=4
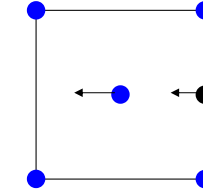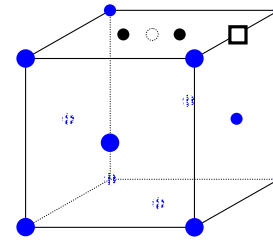
Introduction of an interstitial atom (a defect) creates two defects.
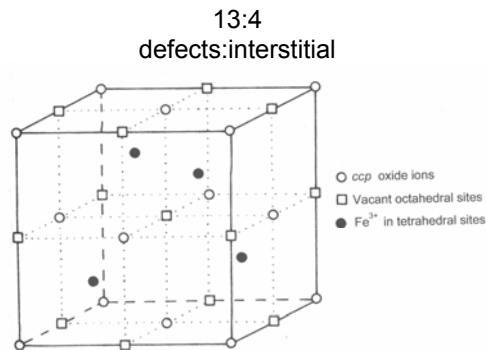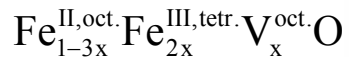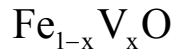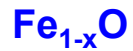
eks. α-Fe. bcc (I) Z=2

Wüstite

$Fe_{1-x}O$ **$Fe^{II}+Fe^{III}$**

$$Fe_{1-x}V_xO$$

$$Fe^{II}_{1-3x}Fe^{III}_{2x}V_xO$$

$$Fe^{II,oct.}_{1-3x}Fe^{III,tetr.}_{2x}V^{oct.}_xO$$

Ordered on a small scale, no long-range order (SRO vs. LRO)

13:4
defects:interstitial

○ ccp oxide ions
□ Vacant octahedral sites
● Fe^{3+} in tetrahedral sites
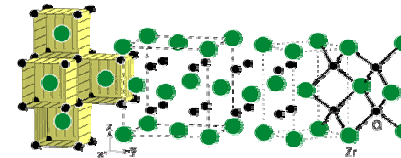
Fig. 5.9 Koch cluster postulated to exist in wüstite, $Fe_{1-x}O$

4:1
8:3
13:4
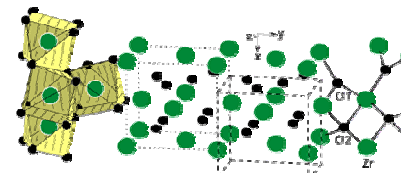16:5   Structur element in Fe_3O_4
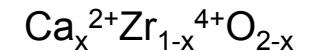
ZrO2

cubic ZrO_2
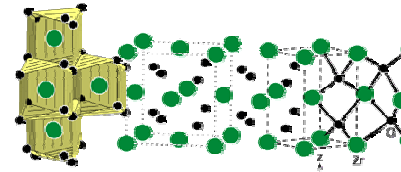
tetragonal ZrO_2

monoclinic ZrO_2

2300 °C

1100 °C

Addition of Ca, Y, Ce or similar may stabilise the high temperature forms to lower temperatures.

$$Ca_x^{2+}Zr_{1-x}^{4+}O_{2-x}$$

Defects are ascribed effective charges

+ ⬇ -

Interactions
"neutral pair"

⬇

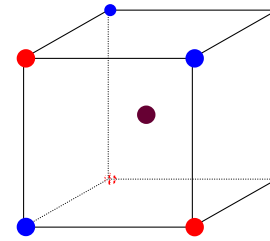Interactions with other pairs
defect clusters

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Smaller areas with ordered defect structures
Predecessor for stable phases with ordering of defects and atoms

Dominating effect

Ionical compounds of NaCl-type structure: **MX**

Regard 1/8 th of the unit cell:

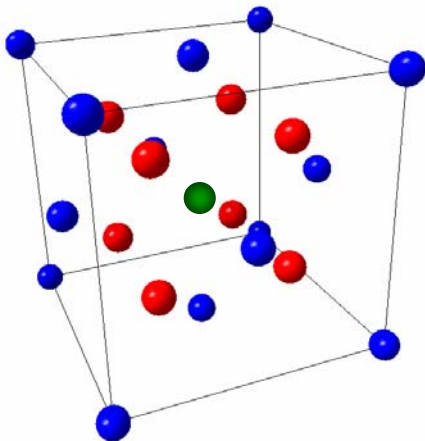If Frenkel defect, then filled tetrahedra possition.

●●$_4$●$_4$ Undesireable

⬇

Schottky defects instead

Dominating effect

Ionical compounds of CaF_2-type structure: **MX$_2$**

●●$_6$●$_8$

Frenkel

Compound	Str. type	Dominating defect
Alkali-halides	NaCl – t. str.	Schottky
Earth alkali halides	NaCl – t. str.	Schottky
AgCl, AgBr	NaCl – t. str.	Cation Frenkel
Cs-halides, TlCl	CsCl – t. str.	Schottky
BeO	würtsite	Schottky
Earthalkali-fluorides, CeO_2, ThO_2	fluorite – t. str.	Anion Frenkel

Solutions

Solution

Intrinsic defects associated with stoichiometric and pure crystals

Extrinsic defects associated with dopants or impurities (0.1 – 1 %)
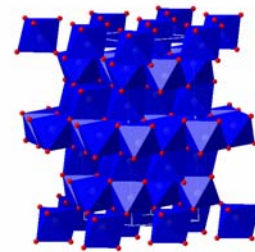
What about dopants > 1% ???
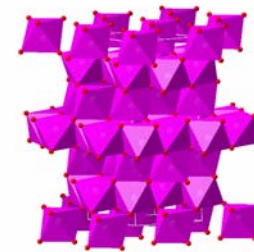
Solid solution

Substitutional solid solution
Interstitial solid solution

Aliovalent substitution

Substitutional solid solution

Al_2O_3 corundum $(Al_{2-x}Cr_x)O_3$ corundum Cr_2O_3 corundum

Al^{3+}
covalent radius 1.18 Å

Cr^{3+}
covalent radius 1.18 Å