Kap. 3
States of aggregation

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: $\frac{\text{No. defects}}{\text{No. atoms}} \approx \frac{1}{10^{15}}$ to 0.1 – 1 %

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

⇓

Defect clustering

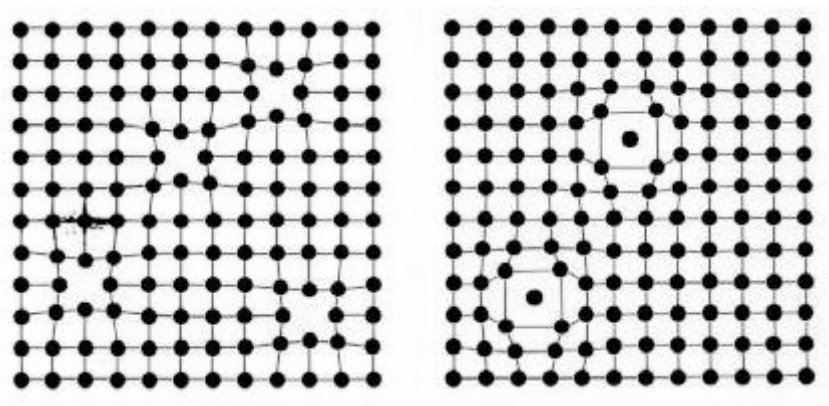
Stoichiometric defects, viz. no ateration in composition

Vacancies (empty possitions)

Interstitial ("between lattice" points)

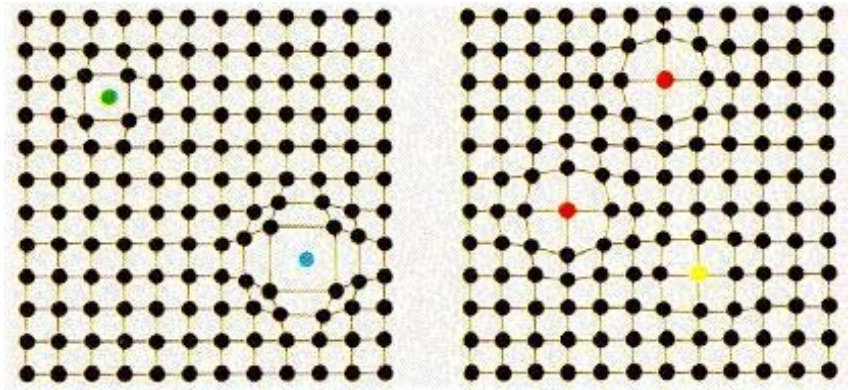
Wrong type atoms

Vacancies and Interstitials



Cotterill 1985

Impurity Atoms



interstitial impurity.

substitutional impurity

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

Cotterill 1985

Thermodynamics

Heat of formation ΔH

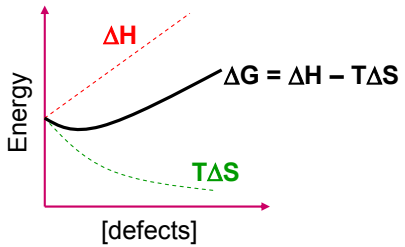
Configurational entropy $S = k \ln(W)$

Temperature dependency: $\Delta G = \Delta H - T\Delta S$

[defects] incrases with temperature

Different types of defects in one phase:
each type of defect: $\Delta G_i = \Delta H_i - T\Delta S_i$

One dominating type of defects.

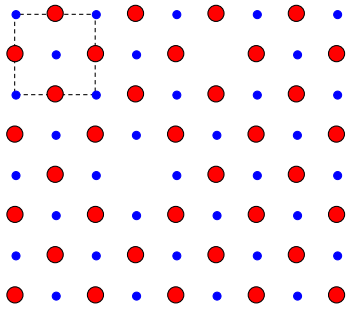


Formation of defects:
cost energy but gain entropy

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

Schottky defects

The (100) for NaCl-type structure



Equal ammount of anion and cation vacancies

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

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

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

The heat of formation for a Schottky defect: ΔH_S

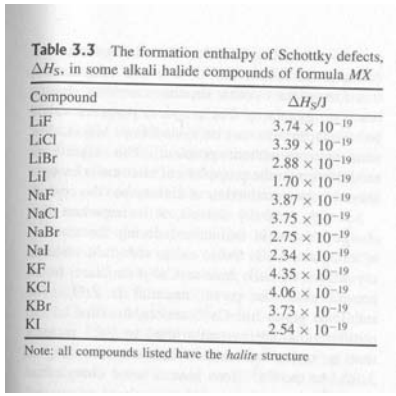


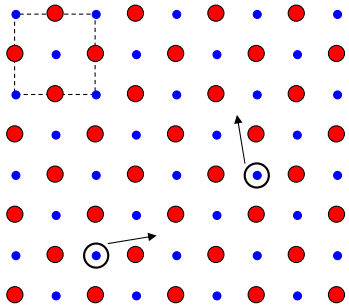
Table 3.3 The formation enthalpy of Schottky defects, ΔH_S, in some alkali halide compounds of formula *MX*

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

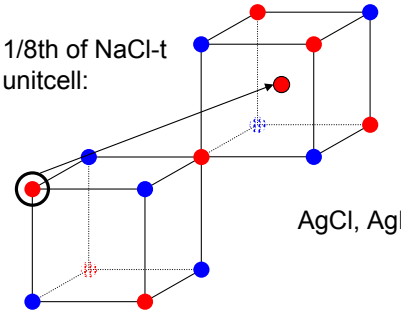
Frenkel defects

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

The heat of formation for a Frenkel defect: ΔH_{Fr}

Table 3.4 The formation enthalpy of Frenkel defects, ΔH_F, 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.

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

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

Constant

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

$$N \cong N - N_V \quad \rightarrow \quad N_V \cong N\sqrt{K}$$

$$K \propto e^{(-\Delta G/RT)}$$

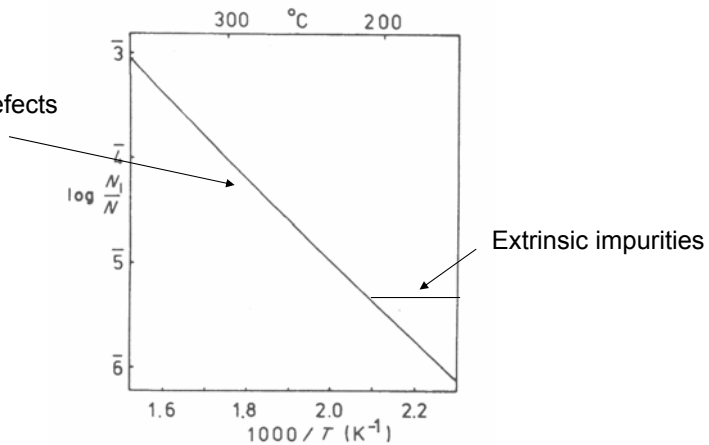
$$K \propto e^{(-\Delta H/RT)} e^{(\Delta S/R)}$$

$$= Ce^{(-\Delta H/RT)}$$

$$N_V = N\,Ce^{(-\Delta H/2RT)}$$

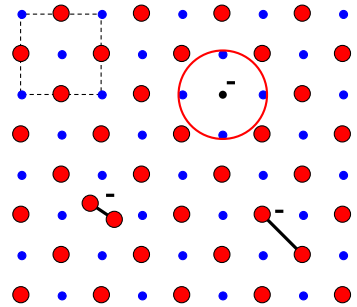
Thermodynamics

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



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

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

Colour:

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

Stoichiometry

Many solid materials are non-stoichiometric
– all that really matters is charge balance

Non-stoichiometry is common amongst transition metal compounds
– Fe_xO where $0.957 > x > 0.833$
– $YBa_2Cu_3O_{7-x}$, $1 > x > 0$

Non-stoichiometry can control properties

Non-stoichiometric compounds

Non-stoichiometric compounds

TiO_x	"TiO"	$0.65 < x < 1.25$
	"TiO_2"	$1.998 < x < 2.000$
VO_x	"VO"	$0.79 < x < 1.29$
Mn_xO	"MnO"	$0.848 < x < 1.000$
Ni_xO	"NiO"	$0.999 < x < 1.000$
$Li_xV_2O_5$		$0.2 < x < 0.33$

Non-stoichiometric compounds

Table 5.5 Approximate composition ranges for some non-stoichiometric compounds

Compound		*Composition range**
TiO_x	[≈TiO]	$0.65 < x < 1.25$
	[≈TiO_2]	$1.998 < x < 2.000$
VO_x	[≈VO]	$0.79 < x < 1.29$
Mn_xO	[≈MnO]	$0.848 < x < 1.000$
Fe_xO	[≈FeO]	$0.833 < x < 0.957$
Co_xO	[≈CoO]	$0.988 < x < 1.000$
Ni_xO	[≈NiO]	$0.999 < x < 1.000$
CeO_x	[≈Ce_2O_3]	$1.50 < x < 1.52$
ZrO_x	[≈ZrO_2]	$1.700 < x < 2.004$
UO_x	[≈UO_2]	$1.65 < x < 2.25$
$Li_xV_2O_5$		$0.2 < x < 0.33$
Li_xWO_3		$0 < x < 0.50$
TiS_x	[≈TiS]	$0.971 < x < 1.064$
Nb_xS	[≈NbS]	$0.92 < x < 1.00$
Y_xSe	[≈YSe]	$1.00 < x < 1.33$
V_xTe_2	[≈VTe_2]	$1.03 < x < 1.14$

*Note that all composition ranges are temperature-dependent and the figures here are intended only as a guide.

Aliovalent substitution

Extrinsic defects arise on doping pure crystals with aliovalent impurities

NaCl may be doped with $CaCl_2$ to give:

$$Na_{1-2x}Ca_xV_{Na_X}Cl$$

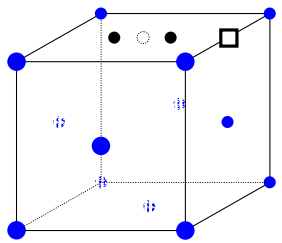
Defect clustering

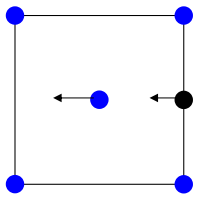
Defects have effective charge

Defects do perturb the host structure

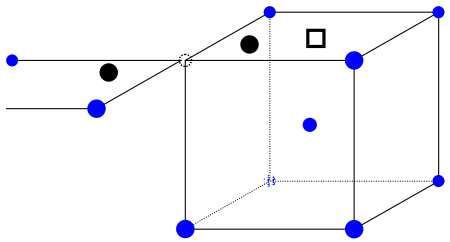
Some interactions	**"neutral pairs"**
More interactions	**"defect clustering"**
Loads of interaction	**Stable phases with ordered distribution of defects**

eks. Pt. fcc (F) Z=4





Introduction of an interstitial atom (a defect) creates two defects.



eks. α-Fe. bcc (I) Z=2

Wüstite

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

13:4
defects:interstitial

$$Fe_{1-x}V_xO$$

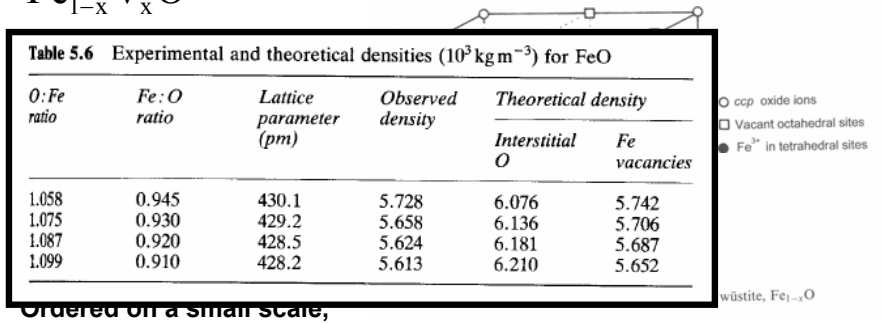


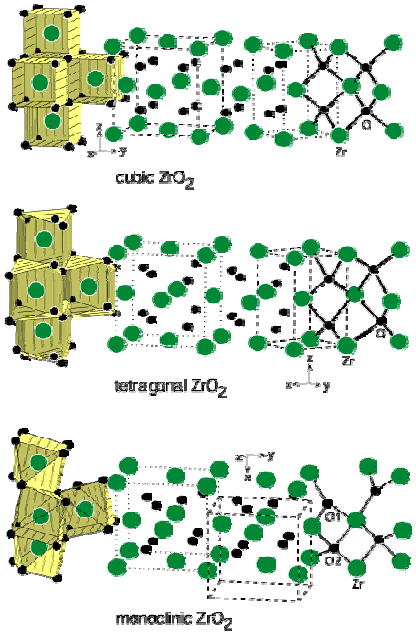
Table 5.6 Experimental and theoretical densities ($10^3\,kg\,m^{-3}$) for FeO

O:Fe ratio	*Fe:O ratio*	*Lattice parameter (pm)*	*Observed density*	*Theoretical density*	
				Interstitial O	*Fe vacancies*
1.058	0.945	430.1	5.728	6.076	5.742
1.075	0.930	429.2	5.658	6.136	5.706
1.087	0.920	428.5	5.624	6.181	5.687
1.099	0.910	428.2	5.613	6.210	5.652

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

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

ZrO2



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

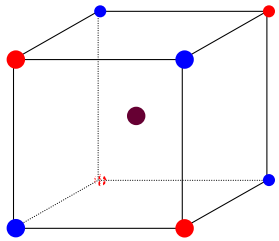
⇓

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.

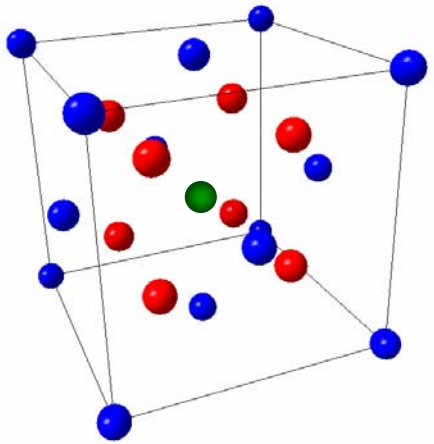
Undesireable

⇓

Schottky defects instead

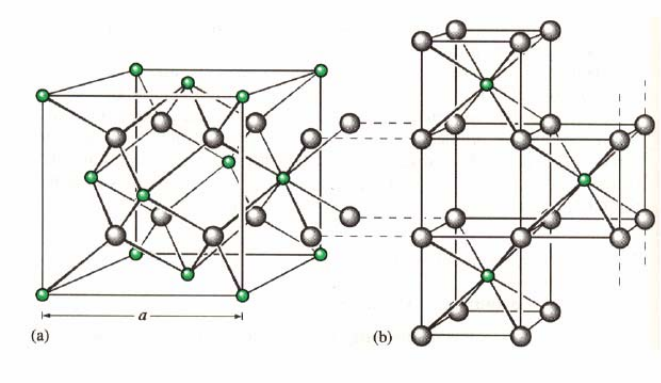
Dominating effect

Ionical compounds of CaF_2-type structure: **MX_2**



Frenkel

The fluorite structure

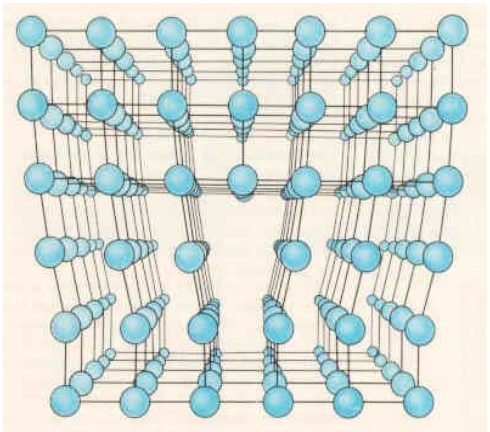


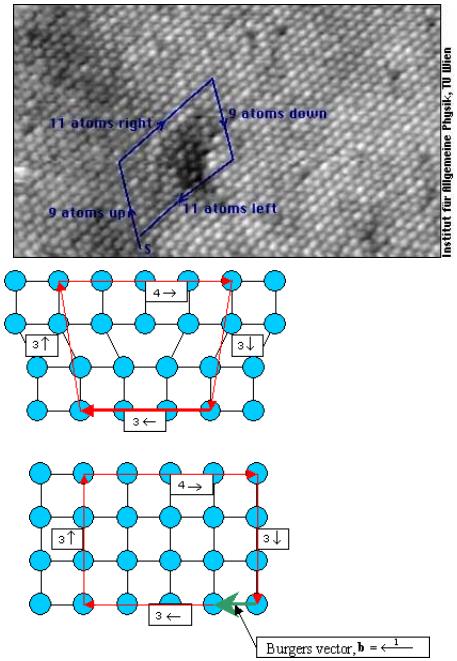
UO_{2+x} incorporates interstitial oxygen

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

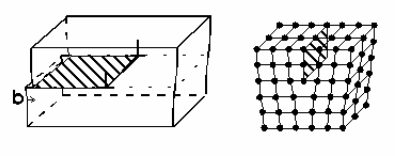
Line defects

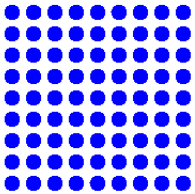
Edge dislocations

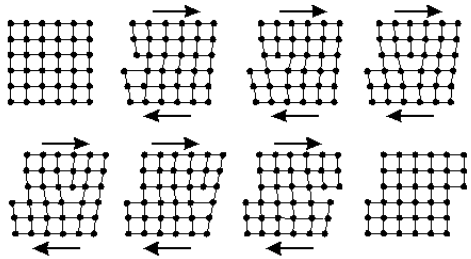


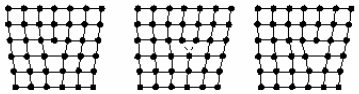


Edge dislocations

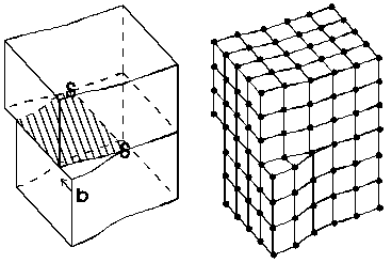


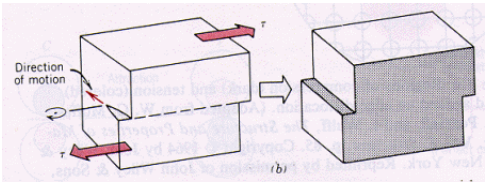




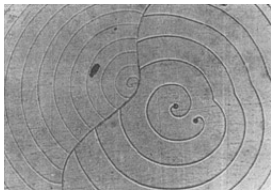


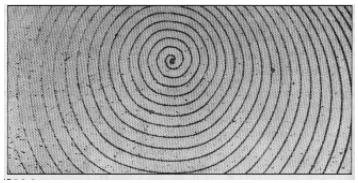
Screw dislocations

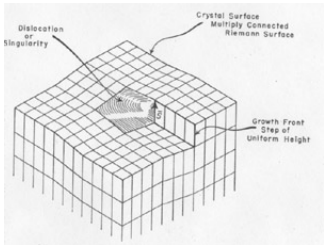




Screw dislocations

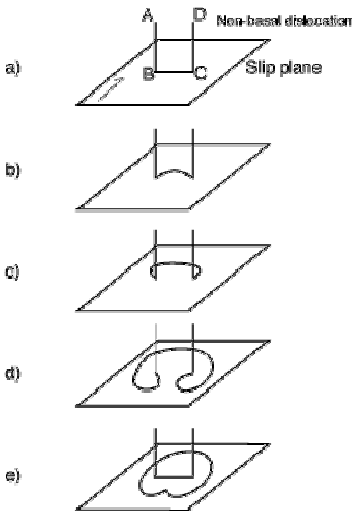






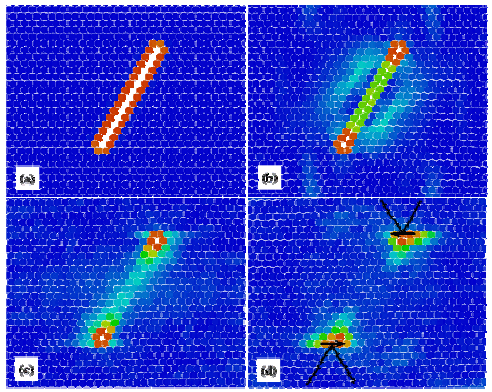
Screw dislocation at surface of SiC single crystal. Dark lines are individual atomic steps at the surface. (Fig. 5.3-2 in Schaffer et al.)

Dislocation loop

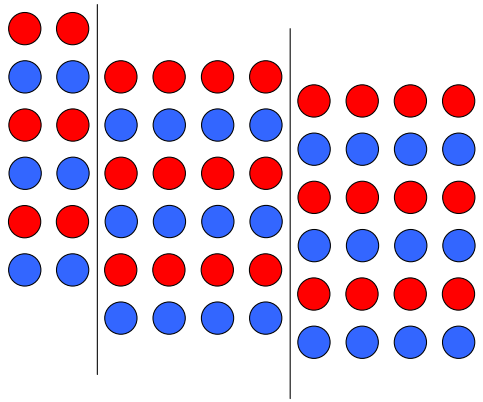


A Frank-Read source for the multiple initiation of dislocation loops. A dislocation is pinned in the basal plane at two ends by either impurities or an immobile non-basal dislocation. If a shear stress is resolved onto the basal plane, the dislocation line becomes unstable and begins to bow. With increasing stress, the line bows back onto itself to produce a new loop that is free to propagate, and a section that remains pinned which may initiate more loops.

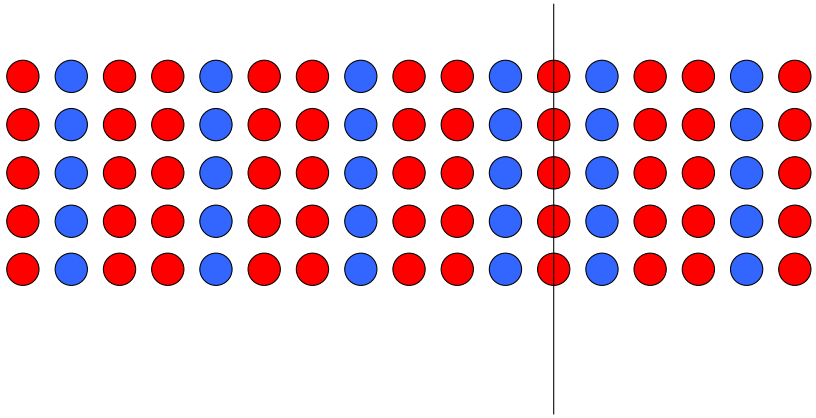
Formation of dislocations



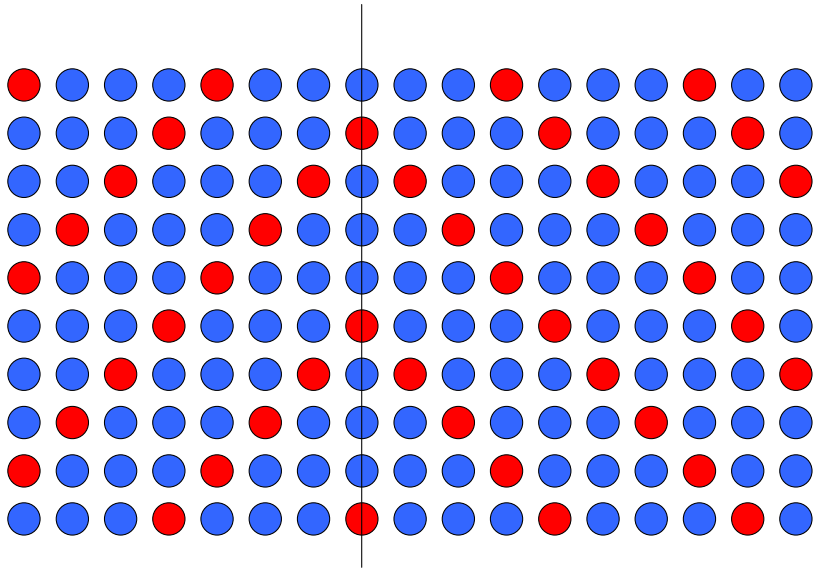
Antiphase

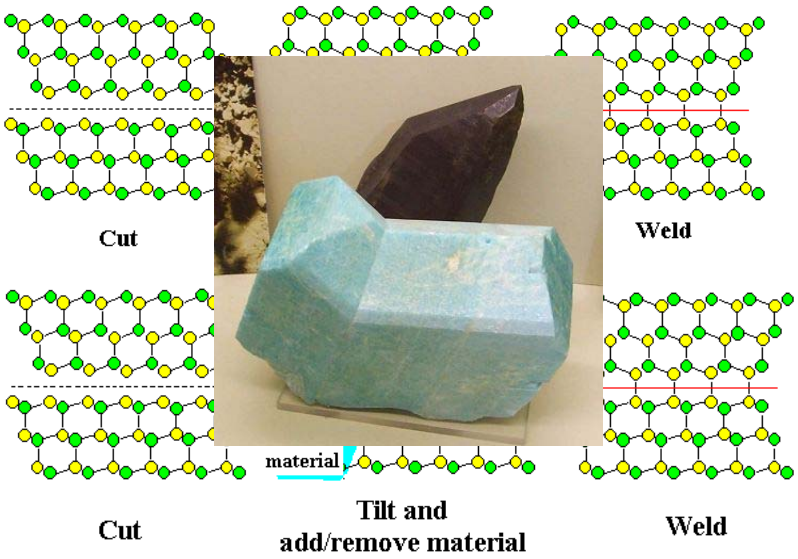


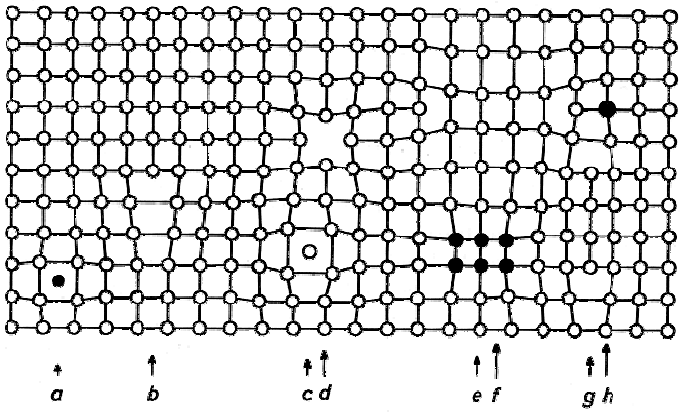
Shear plane



Twin plane







a) Interstitial impurity atom
b) Edge dislocation
c) Self interstitial atom
d) Vacancy
e) Precipitate of impurity atoms
f) Vacancy type dislocation loop
g) Interstitial type dislocation loop
h) Substitutional impurity atom

Solutions

Solution

Intrinsic defects associated with stoichiometric and pure crystals

Extrinsic defects associated with dopants or impurities (0.1 – 1 %)

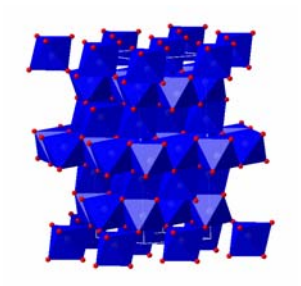
What about dopants > 1% ???

Solid solution

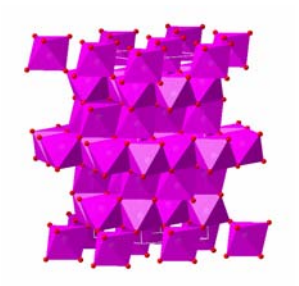
Substitutional solid solution
Interstitial solid solution

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

Substitutional solid solution

For substitutional solid solution to form:

The ions must be of same charge

The ions must be similar in size.
(For metal atoms < 15% difference)
(a bit higher for non-metals)

High temperature helps – increase in entropy
($0 > \Delta H$ vs. $0 < \Delta H$)

The crystal structures of the end members must be isostructural for complete solid solubility

Partial solid solubility is possible for non-isostructural end members
Mg_2SiO_4 (Mg in octahedras) - Zn_2SiO_4 (Zn in tetrahedras)

Preference for the same type of sites
Cr^{3+} only in octahedral sites, Al^{3+} in both octahedra and tetraheda sites
$LiCrO_2$ - $LiCr_{1-x}Al_xO_2$ - $LiAlO_2$

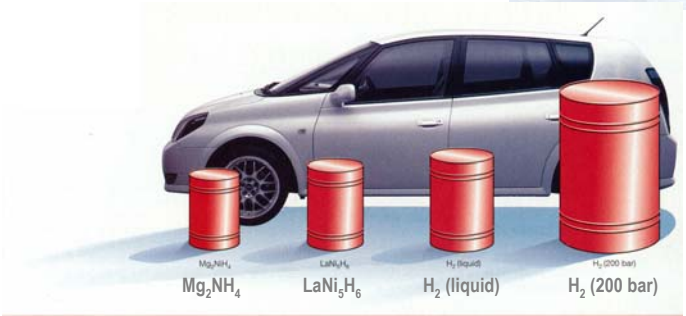
Consider metallic alloys

Interstitial solid solution

Atoms enters intersititial positions in the host structure.

The host structure may be expanded but not altered.

H_2 in Pt



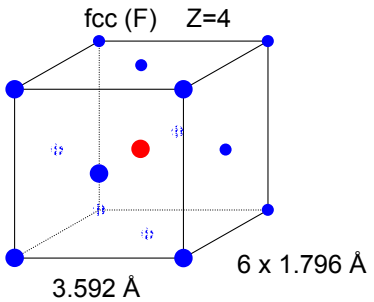
Interstitial solid solution

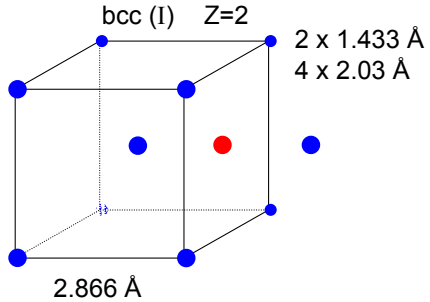
Fe-C system

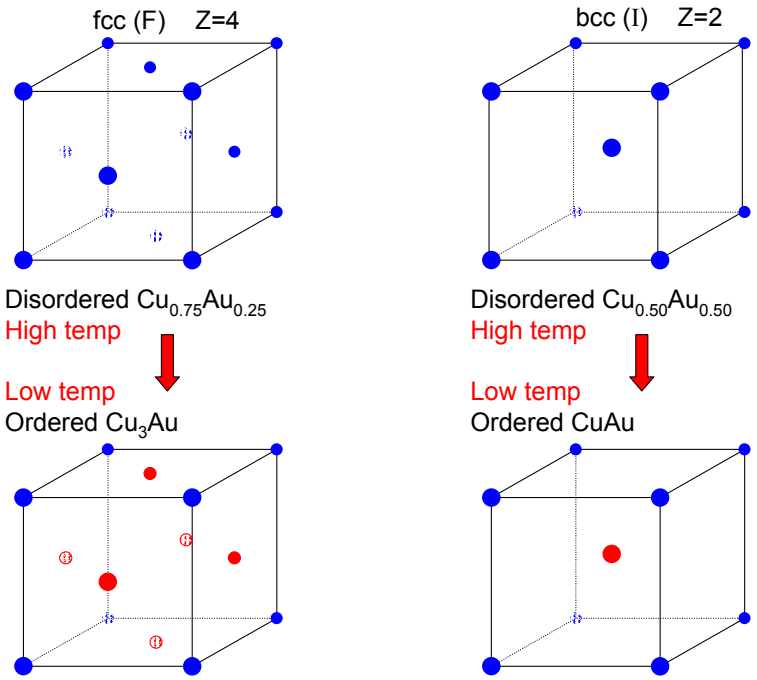
δ-Fe (bcc) -> 0.1 % C Tm = 1534 °C

γ-Fe (fcc) -> 2.06 % C < 1400 °C

α-Fe (bcc) -> 0.02 % C < 910 °C







Aliovalent substitution

Substitution with ions of different charge

Need charge compensation mechanism

Substitution by higher valence cations

1 → Cation vacancies

2 → Interstitial anions

Substitution by lower valence cations

3 → Anion vacancies

4 → Interstitial cations

Aliovalent substitution

1 Cation vacancies, Substitution by higher valence

Preserve charge neutrality by leaving out more cations than those that are replaced.

NaCl dissolves $CaCl_2$ by: $Na_{1-2x}Ca_xV_xCl$

Ca^{2+} vil have a net excess charge of +1 in the structure and attract Na^+ vacancies which have net charge -1

Mg^{2+} may be replaced by Al^{3+} : $Mg_{1-3x}Al_{2+2x}V_xO_4$

Aliovalent substitution

2 Interstitial anions, Substitution by higher valence

Preserve charge neutrality by inserting more anions interstitially.

Not common mechanism due to the large size of the anions.

CaF_2 may dissolve some YF_3 : $Ca_{1-x}Y_xF_{2+x}$

Aliovalent substitution

3 Anion vacancies, Substitution by lower valence

Preserve charge neutrality by leaving out anions as cations are replaced.

ZrO_2 dissolve CaO by anion vacancies : $Zr_{1-x}Ca_xO_{2-x}V_x$

Aliovalent substitution

4 Interstitial cations, Substitution by lower valence

Preserve charge neutrality by inserting more cations interstitially, not necessarily of same kind.

Common mechanism

Must be holes present to accomodate additional atoms

Si^{4+} can be replaced by Al^{3+} and interstitial Li^+
$Li_x(Al_{1-x}Al_x)O_2$

Aliovalent substitution

5 Double substitution

Two substitutions take place simultaneously

In olivines, Mg^{2+} can be replaced by Fe^{2+} at the same time as Si^{4+} is replaced by Ge^{4+}

$(Mg_{2-x}Fe_x)(Si_{1-y}Ge_y)O_4$

Aliovalent substitution

6 Charge compensations

Cations or anions may be inserted/removed from the structure and compensated by reduction/oxidation of the catons in the structure.

Li^+ in $LiCoO_2$, or $LiMn_2O_4$

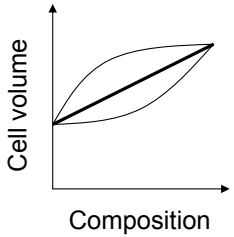
$Li_{1-x}Co^{3+}{}_{1-x}Co^{4+}O_2$
$Li_{1-x}Mn^{3+}{}_{1-x}Mn^{4+}{}_{1+x}O_4$

NiO takes up additional oxygen by formation of cation vacancies

$NiO + O_2 \rightarrow Ni^{2+}{}_{1-3x}Ni^{3+}{}_{2x}V_{Ni,x}O$

How to analyze solid solution

X-ray diffraction
- Fingerprint to analyze end members
- Vegards law to analyze composition



Density measurements
- Will differensiate between interstitial and vacancy mechanisms

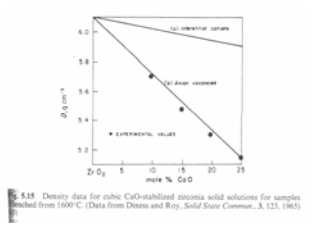


Fig. 5.15 Density data for cubic CaO-stabilized zirconia solid solutions for samples fired from 1600°C. (Data from Diness and Roy, *Solid State Commun.*, 3, 123, 1965)

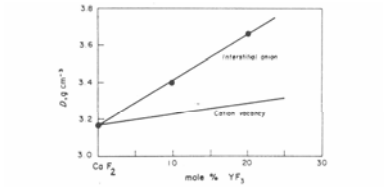


Fig. 5.16 Density data for solid solutions of YF_3 in CaF_2 (From Kingery, Bowen and Uhlmann, *Introduction to Ceramics*, Wiley, New York, 1976)

States

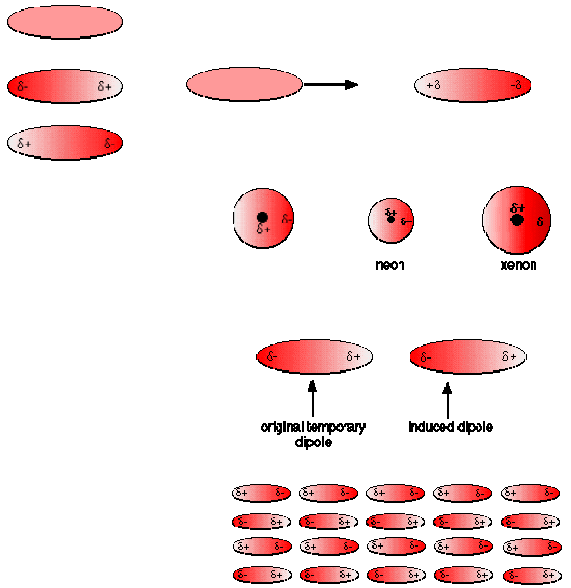
Chemical bonds

Table 3.1 Forces between atoms, ions and molecules

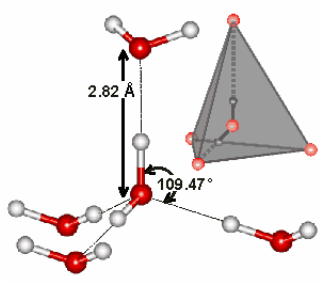
Type of bond	Approximate energy/kJ mol^{-1}	Species involved
Covalent	350	Atoms with partly filled orbitals
Ionic	250	Ions only
Metal	200	Metal atoms
Ion–dipole	15	Ions and polar molecules
Dipole–dipole	2	Stationary polar molecules
Dipole–dipole	0.3	Rotating polar molecules
Dispersion	2	All atoms and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

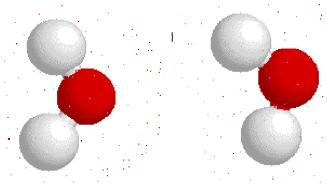
$$V(r) = 4V_{\min}\left[\left(\frac{r_0}{r}\right)^6 - \left(\frac{r_0}{r}\right)^{12}\right]$$

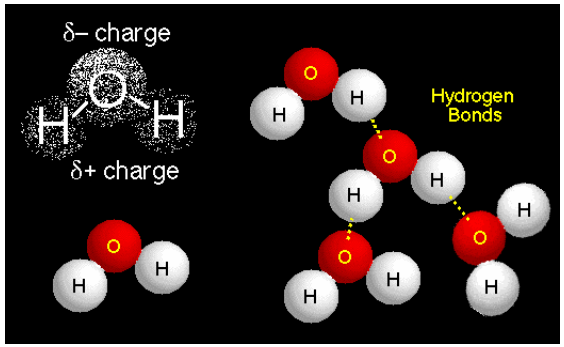
Van der Waals interactions

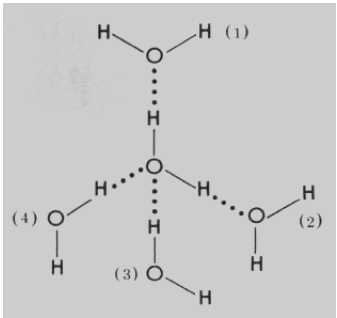


Hydrogen bonds

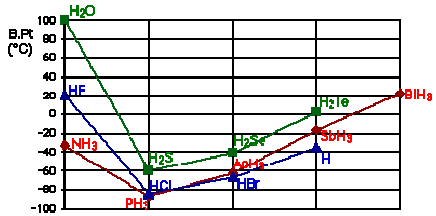


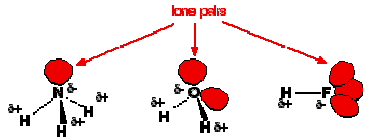


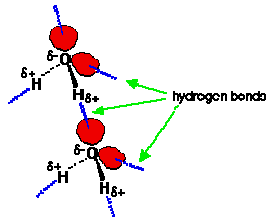


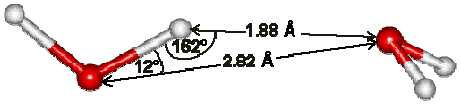


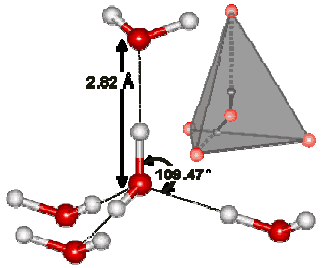
Hydrogen bonds

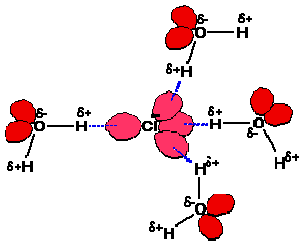




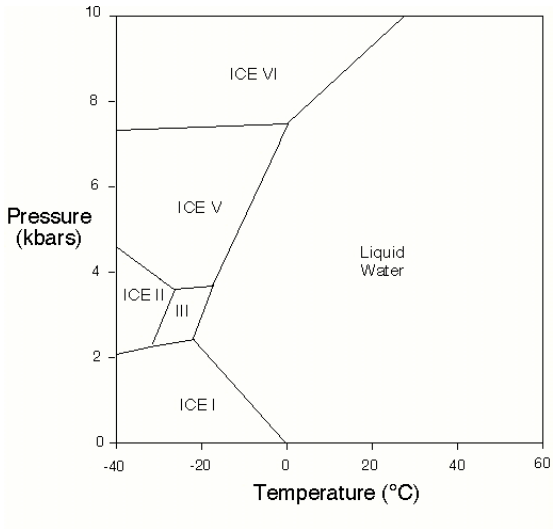


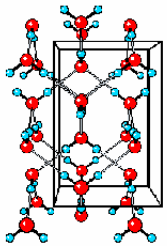




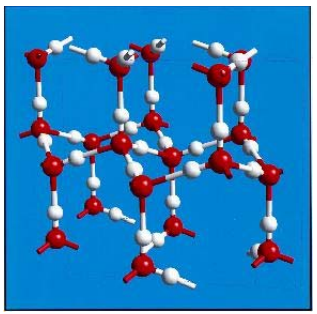


Polymorphism



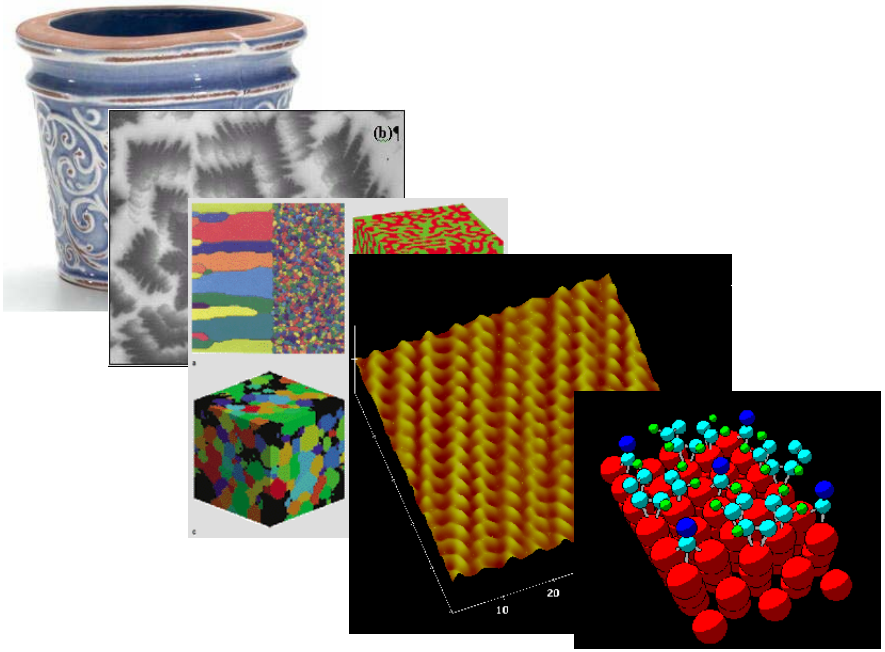


Ice VIII

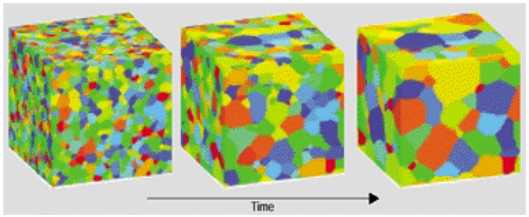


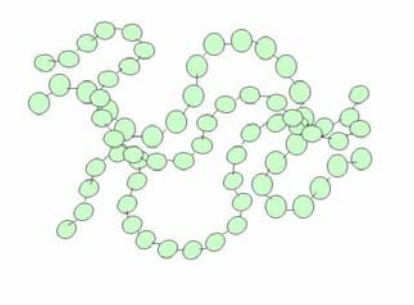
Ice 1h

Macrostructure -> Microstructure

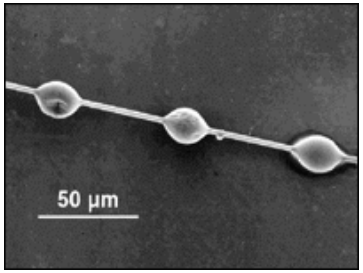


Crystal - amorphous

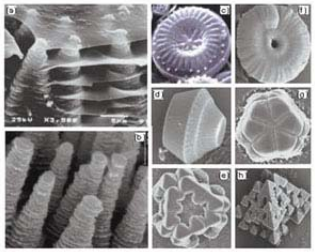


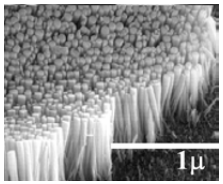


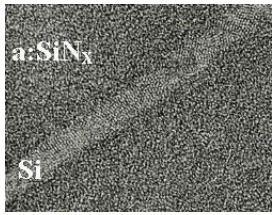
Funtional material

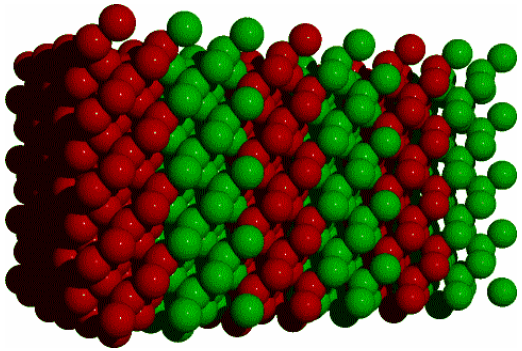


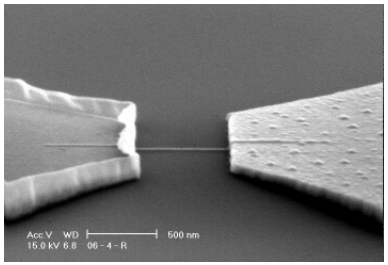
Nanostructures





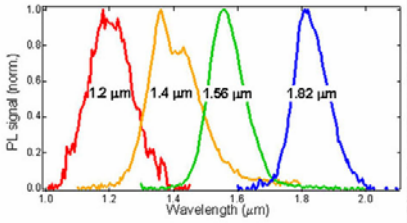


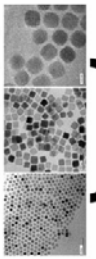




PbSe Nanocrystals

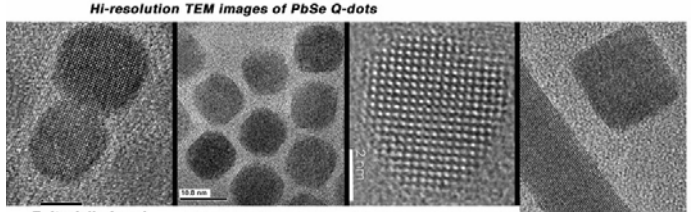
PbSe Q-dot size series photoluminescence spectra





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

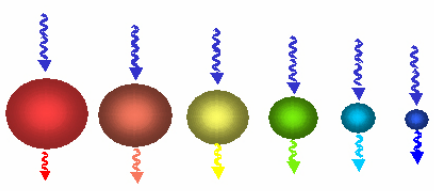
Rounded PbSe cubes

Faceted rocksalt crystal

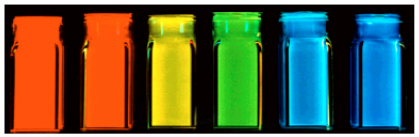
PbSe cube and wire comprising oriented fused cubes

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



Felice Frankel

Six different quantum dot solutions are shown excited with a long wave UV lamp