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

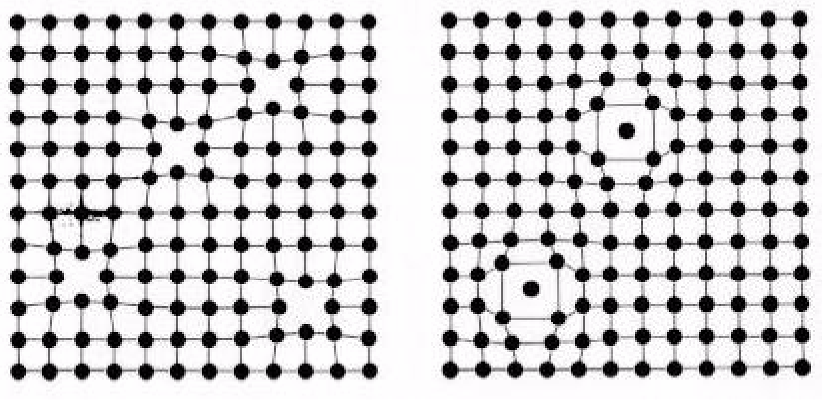
Stoichiometric defects, viz. no ateration in composition

Vacancies (empty possitions)

Interstitial (”between lattice” points)

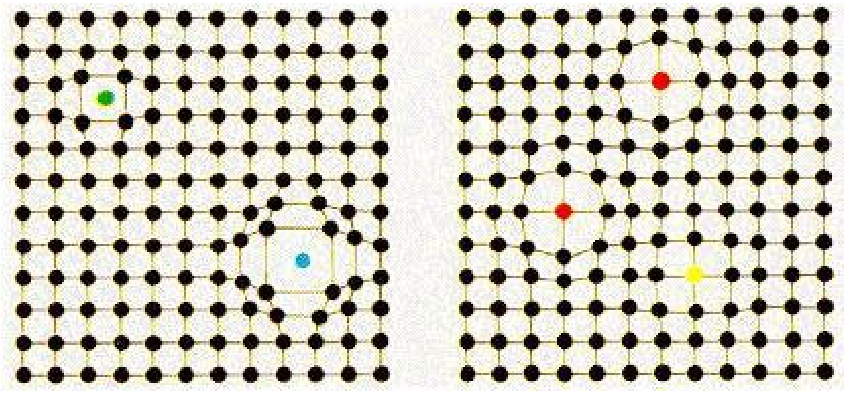
Wrong type atoms

Vacancies and Interstitials



Cotterill 1985

Impurity Atoms



interstitial impurity.

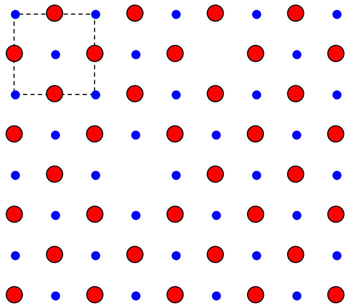
substitutional impurity

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

Cotterill 1985

Schottky defects

The (100) for NaCl-type structure



Equal ammount of anion and cation vacancies

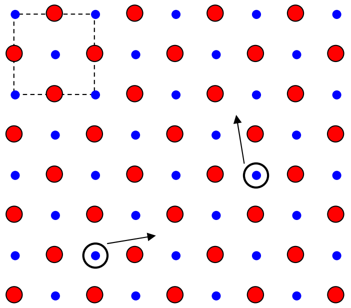
V'_{Na} (-) $V^{\bullet}_{Cl}$ (+)

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_{Sch}

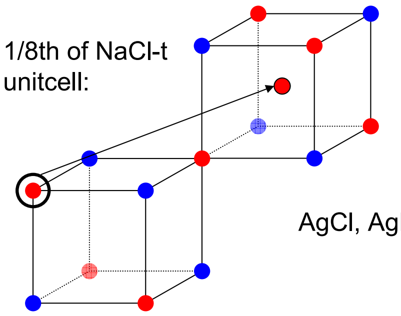
Frenkel defects

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

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}

Thermodynamics

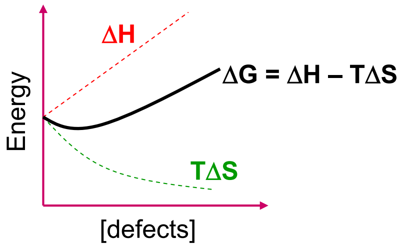
Heat of formation **ΔH**
Configurational entropy **$S = k \ln(W)$**

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

Kroger-Vink notation

Each defect is represented by a combination of three symbols:

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

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

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

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

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

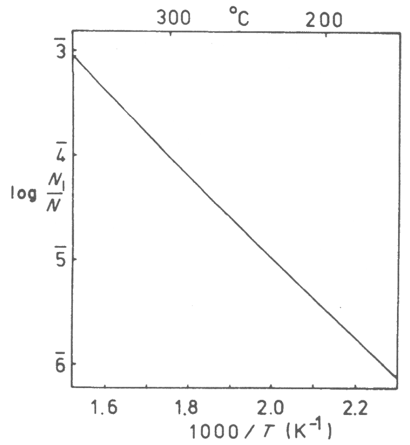
$$K \propto e^{(-\Delta H/RT)} e^{(\Delta S/R)}$$

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

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

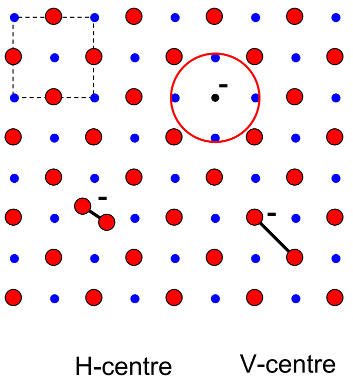
Thermodynamics

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



Colour centre, (alkaline halides)

The (100) for NaCl-type structure



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:

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

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**

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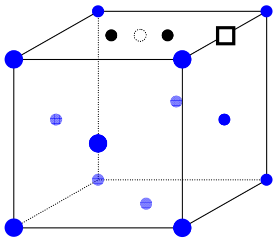
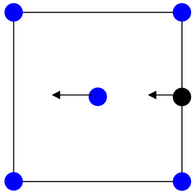
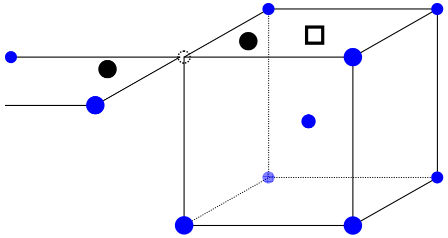
eks. Pt. fcc (F) Z=4





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

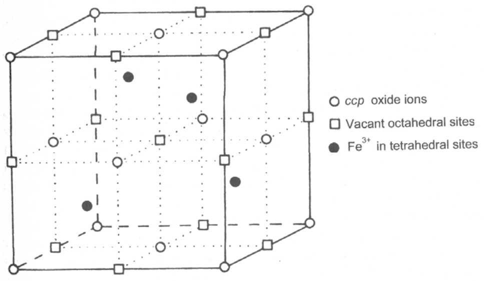


Fig. 5.9 Koch cluster postulated to exist in wüstite, $Fe_{1-x}O$

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

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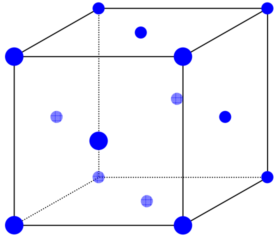
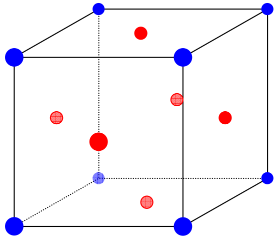
fcc (F) Z=4

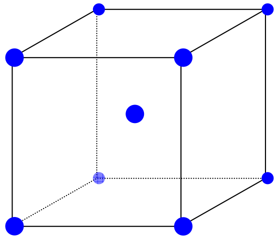


Disordered $Cu_{0.75}Au_{0.25}$
High temp

Low temp
Ordered Cu_3Au

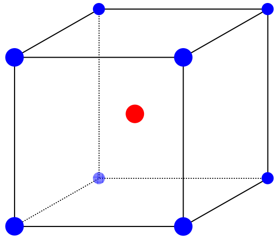


bcc (I) Z=2



Disordered $Cu_{0.50}Au_{0.50}$
High temp

Low temp
Ordered CuAu



Defects are ascribed effective charges

\+ ⬇ -

Interactions
”neutral pair”

⬇

Interactions with other pairs
defect clusters

⬇

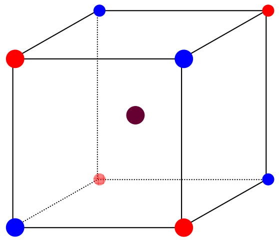
Smaller areas with ordered defect structures
Predecessor for stable phases with ordering of defects and atoms

---

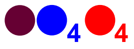
Dominating effect

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

Regard 1/8 th of the unit cell:



If Frenkel defect, then filled tetrahedra possition.



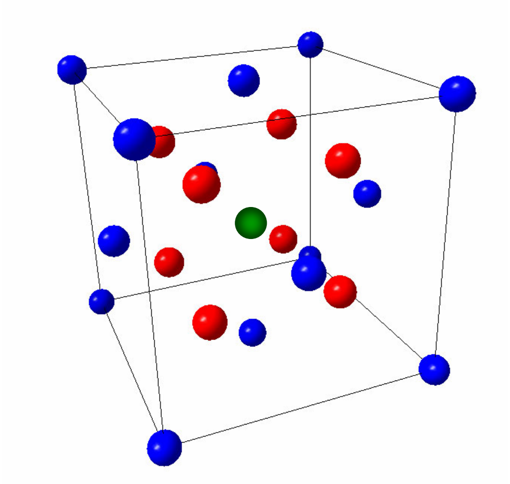
Undesireable

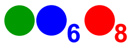
⬇

Schottky defects instead

Dominating effect

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





Frenkel

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**

Solution

Intrinsic defects associated with stoichiometric and pure crystals

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

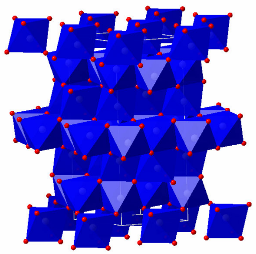
What about dopants > 1% ???

Solid solution

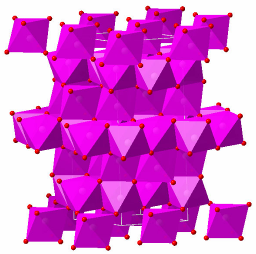
Substitutional solid solution
Interstitial solid solution

Aliovalent substitution

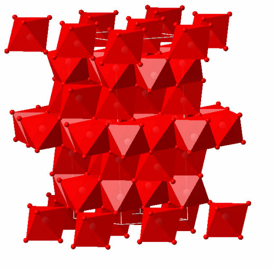
Substitutional solid solution



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 > ΔH vs. 0 < ΔH)

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
$LiCrO_2$ - $LiCr_{1-x}Al_xO_2$ - $LiAlO_2$

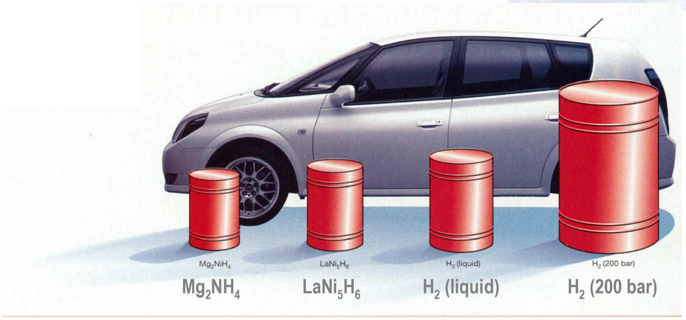
Consider metallic alloys

Interstitial solid solution

Atoms enters intersitital positions in the host structure.

The host structure may be expanded but not altered.

H_2 in Pt



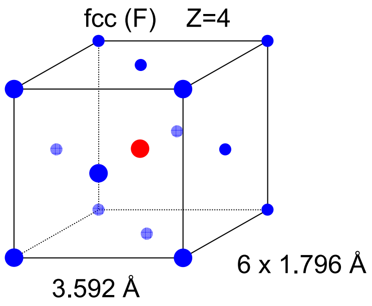
Interstitial solid solution

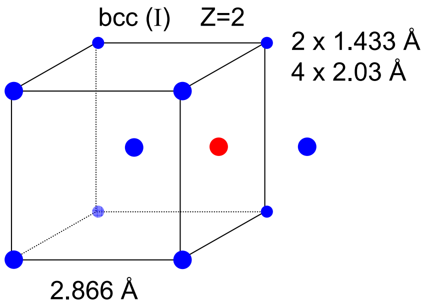
Fe-C system

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

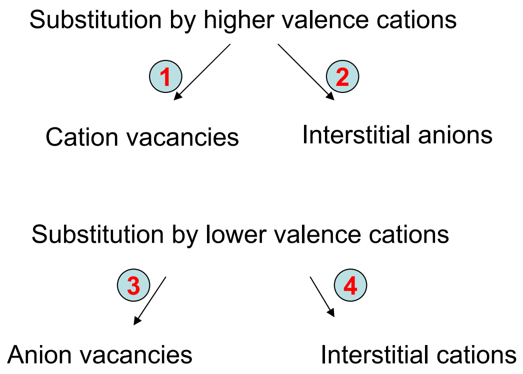




Aliovalent substitution

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 $LiMn_2O_4$

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

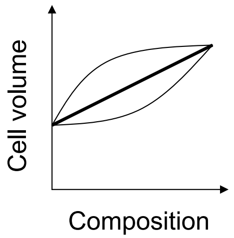
NiO takes up additional oxygen by formation of cation vacancies

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

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

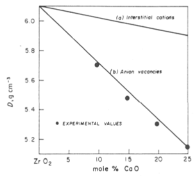


Fig. 5.15 Density data for cubic CaO-stabilized zirconia solid solutions for samples quenched from 1600°C. (Data from Diness and Roy, *Solid State Commun.*, 3, 123, 1965)

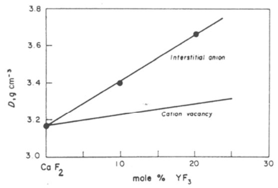


Fig. 5.16 Density data for solid solutions of YF_3 in CaF_2 (From Kingery, Bowen and Uhlmann, *Introduction to Ceramics*, Wiley, New York, 1976)