

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

Consider metallic alloys

Interstitial solid solution

Atoms enters interstitial positions in the host structure.

The host structure may be expanded but not altered.

H_2 in Pt



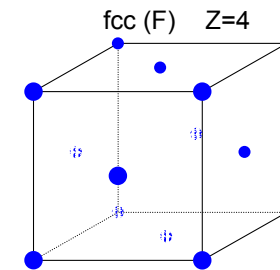
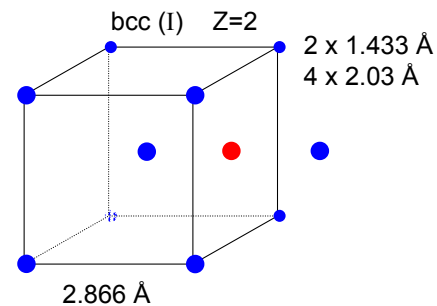
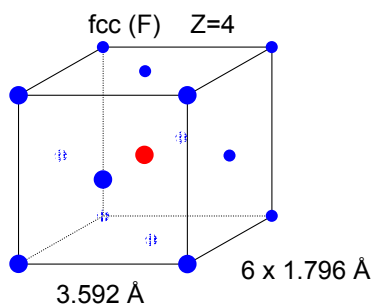
Interstitial solid solution

Fe-C system

δ -Fe (bcc) \rightarrow 0.1 % C $T_m = 1534$ °C

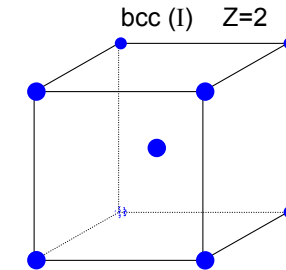
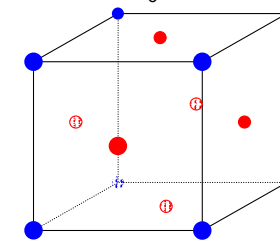
γ -Fe (fcc) \rightarrow 2.06 % C < 1400 °C

α -Fe (bcc) \rightarrow 0.02 % C < 910 °C



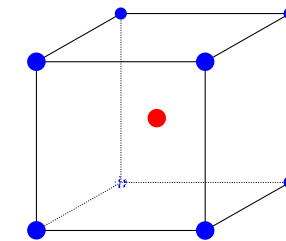
Disordered $Cu_{0.75}Au_{0.25}$
High temp

Low temp
Ordered Cu_3Au



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

Low temp
Ordered CuAu

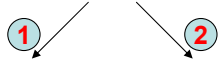


Aliovalent substitution

Substitution with ions of different charge

Need charge compensation mechanism

Substitution by higher valence cations



Cation vacancies

Interstitial anions

Substitution by lower valence cations



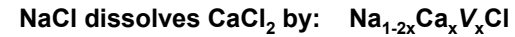
Anion vacancies

Interstitial cations

Aliovalent substitution

① Cation vacancies, Substitution by higher valence

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



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



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.



Aliovalent substitution

③ Anion vacancies, Substitution by lower valence

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



Aliovalent substitution

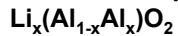
4 Interstitial cations, Substitution by lower valence

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

Common mechanism

Must be holes present to accomodate additional atoms

Si⁴⁺ can be replaced by Al³⁺ and interstitial Li⁺

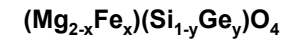


Aliovalent substitution

5 Double substitution

Two substitutions take place simultaneously

In olivines, Mg²⁺ can be replaced by Fe²⁺ at the same time as Si⁴⁺ is replaced by Ge⁴⁺

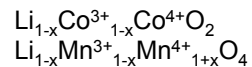


Aliovalent substitution

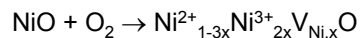
6 Charge compensations

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

Li⁺ in LiCoO₂, or LiMn₂O₄



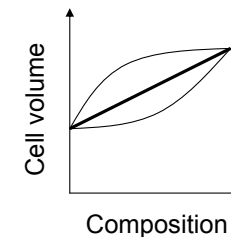
NiO takes up additional oxygen by formation of cation vacancies



How to analyze solid solution

X-ray diffraction

- Fingerprint to analyze end members
- Vegard's law to analyze composition



Density measurements

- Will differentiate between interstitial and vacancy mechanisms

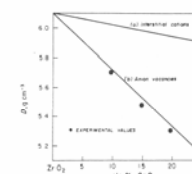


Fig. 5.15 Density data for cubic CaO-stabilized zirconia solid solutions for samples fired from 1600°C. (Data from Dienes and Roy, *Solid State Commun.*, 3, 113, 1965)

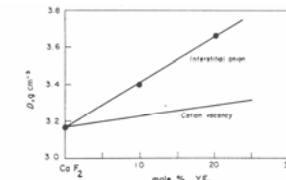
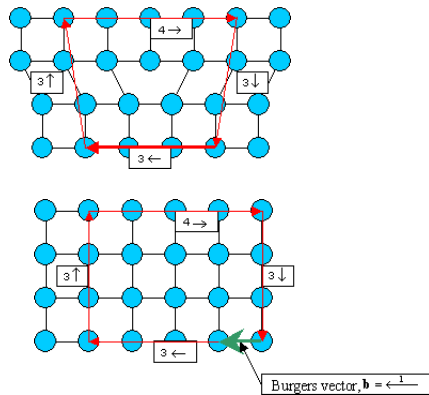
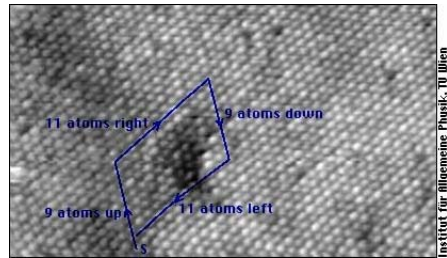
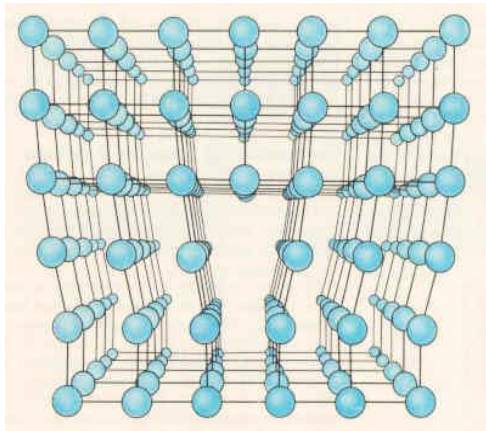


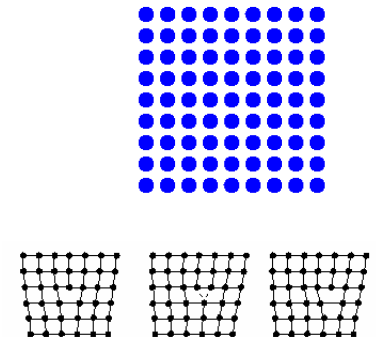
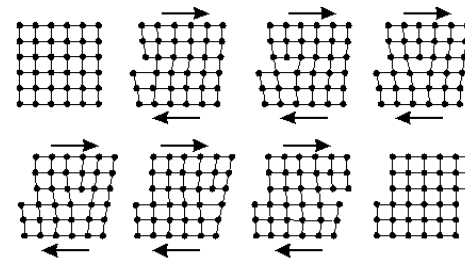
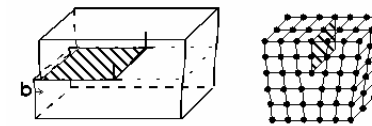
Fig. 5.16 Density data for solid solutions of YF₃ in CaF₂. (From Kingery, Bowen and Uhlmann, *Introduction to Ceramics*, Wiley, New York, 1976)

Line defects

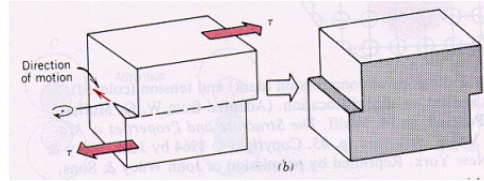
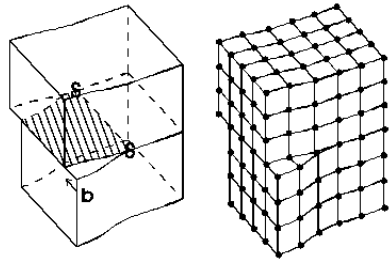
Edge dislocations



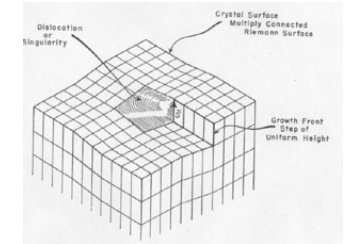
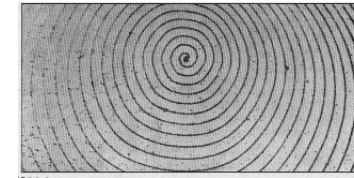
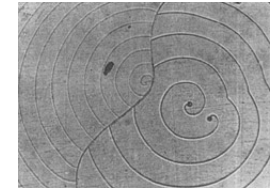
Edge dislocations



Screw dislocations



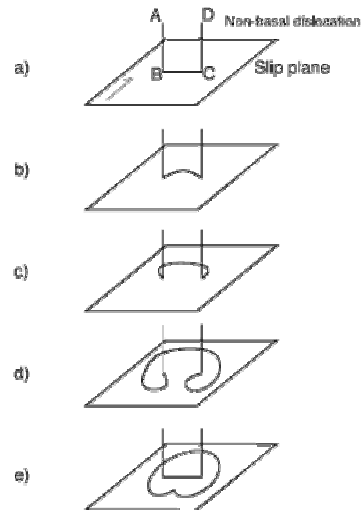
Screw dislocations



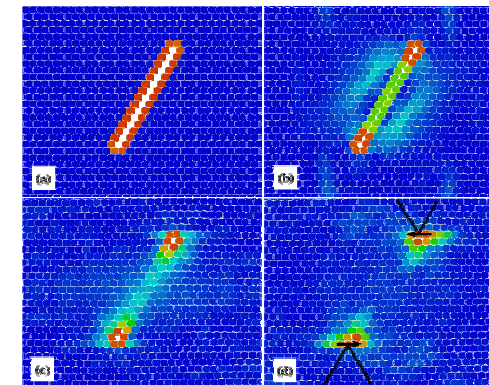
Screw dislocation at surface of SiC single crystal. Dark lines are individual atomic steps at the surface. (Fig. 5.3-2 in Schaffer et al.)

Dislocation loop

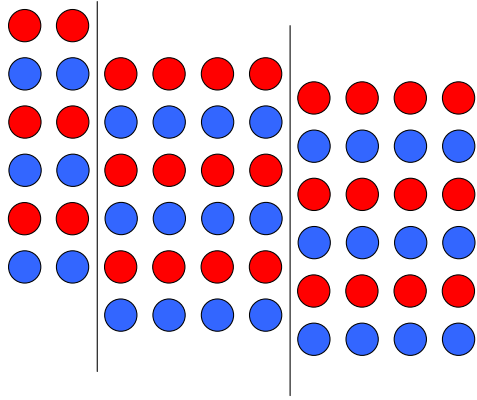
A Frank-Read source for the multiple initiation of dislocation loops. A dislocation is pinned in the basal plane at two ends by either impurities or an immobile non-basal dislocation. If a shear stress is resolved onto the basal plane, the dislocation line becomes unstable and begins to bow. With increasing 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.



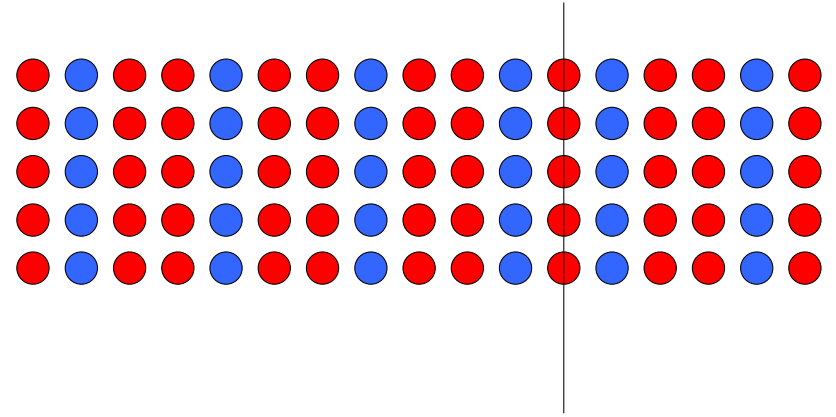
Formation of dislocations



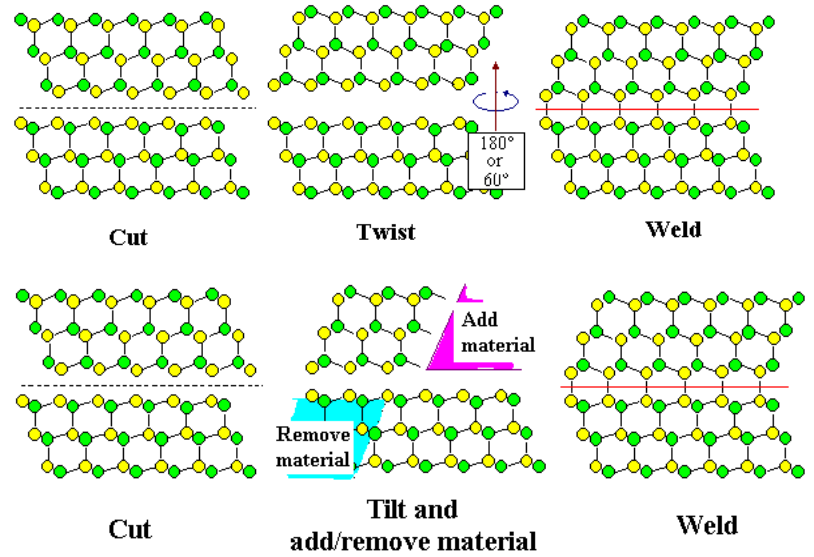
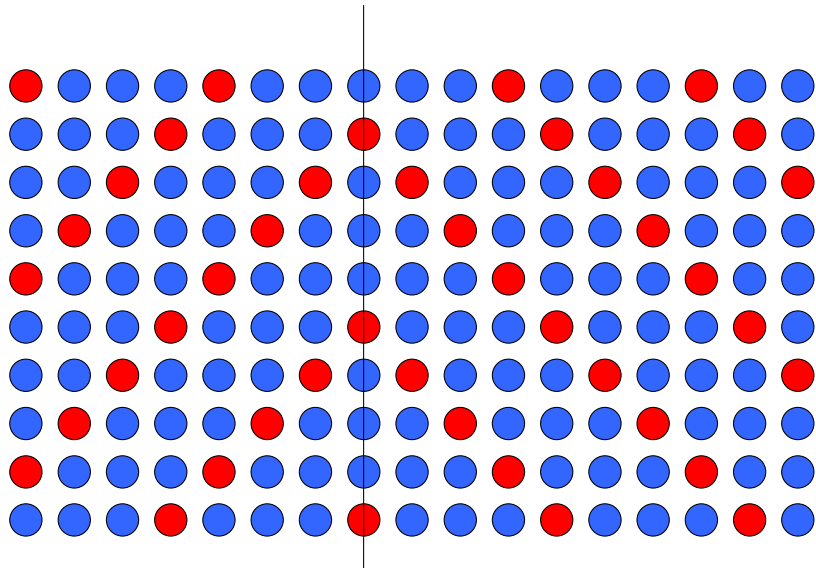
Antiphase

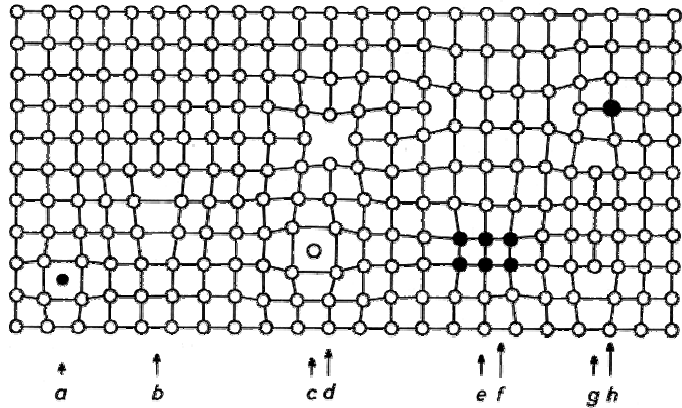


Shear plane



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

Pure metals tend to be soft and ductile and thus have limited usefulness. One of the most common ways of strengthening metals is to mix them with other chemical elements to form an alloy. The simplest type of alloy is one in which the minor component is randomly dispersed in the crystal structure of the major component. This is called a solid solution. There are two classes of solid solutions, **substitutional solid solutions** and **interstitial solid solutions**.

Substitutional solid solutions are those in which the atoms of the minor component (*solute*) are substituted for the atoms of the major component (*solvent*) on the lattice positions normally occupied by the solvent atoms. Usually there is a limit to the maximum amount of solute (*solubility limit*) that can be added to the solvent before the structure changes to a more complex form. There are a few binary (two component) alloy systems where the solubility limit is 100%. Obviously before this can occur the two components must have the same crystal structure and these systems are often referred to as *isomorphous* systems. An example is the Cu-Ni system where both copper and nickel have the FCC crystal structure. There are other requirements in order to have extensive solid solubility: the two components must have similar atomic radii, similar electronegativities, and similar number of electrons in their outer shells (similar number of *valence* electrons). It is difficult to quantify these requirements exactly but it is perhaps useful to study a few examples. Cu-Ni (100% solid solubility); The atom sizes differ by about 2%, the electronegativities are the same, the crystal structures are the same, the valences are confusing since table 2.4 shows the electron configuration of Ni to be $[\text{Ar}]3d^84s^2$ and the electron configuration of Cu is $[\text{Ar}]3d^{10}4s^1$. However, these configurations apply to isolated atoms. In the solid it is thought that one of the Ni 4s electrons occupies a d state since the magnetic moment of Ni in the solid is 0.6 Bohr magnetons instead of the 2 that would be expected if there were 2 unpaired d electrons.

Cu-Ag (limited solid solubility, <1% at room temperature). The atomic size difference is 12% and all other factors are favorable. Copper and silver both have the FCC structure, the electronegativities differ by 0.4, and the valences are similar.

[Topic 6 Outline](#)

Interstitial solid solutions are those in which the solute atoms occupy the interstitial positions (holes between the atoms) in the crystal lattice of the solvent. Interstitial solid solutions always have limited solubility of the solute. One of the requirements for measurable solubility is that the solute atom must be small to fit into the interstitial positions of the solvent. Electronegativity differences are also important. For example carbon shows measurable interstitial solubility in iron while oxygen and fluorine do not even though the atoms are smaller than the carbon atom.

Example problem 4.3 of the text shows how to calculate the largest interstitial void radius in the FCC lattice. In homework set 4 we calculated the diameter of the largest interstitial that would just fit into the tetrahedral interstitial void in BCC vanadium as 0.038nm. There is another type of interstitial position in the BCC which is an octahedral position located at the centers of each face and also at the edges of each face. This can be seen to have a maximum interstitial radius of $(a-2R)/2 = a(1 - 31/2)/2 = .0699a = .0204\text{nm}$ for V.

Point Defects in Ionic Crystals

Ionic crystals unlike other solids are made up of charged ions.

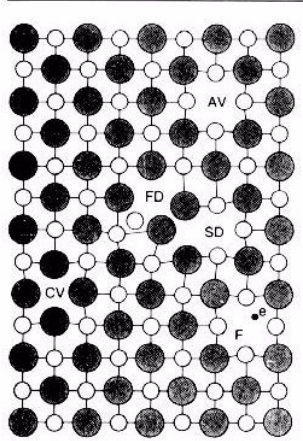
Point defects in ionic crystal are charged.

Charge neutrality must always be maintained.

Forces between Charges

The attractive force between unlike charges and the repulsive force between like charges are called coulombic forces. If one took 45 pounds of protons in a ball one foot in diameter and placed it in the center of the moon, the protons, which repel each other, would fly apart with such force that it would blow apart the moon.

Defect Complexes



B FD - Frenkel defect -
cation vacancy and
cation interstitial. SD -
Schottky defect -
anion and cation
vacancies.

Cotterill 1985