Crystal Structure

CRYSTAL STRUCTURES
Lecture 3

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Structure & Defects

1.7.4 Spacing between planes

In a cubic system with lattice parameter (unit cell side) a, the (hkl) planes are separated by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.$$

Proof: We know (from first year Maths) that we can write the equation of a plane as

$$\hat{\mathbf{n}}.\mathbf{r} = d \qquad (1)$$

where $\hat{\mathbf{n}}$ is a unit vector perpendicular to the plane and $\mathbf{r}$ is the vector position of a point in the plane, $\mathbf{r} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$. Basically, $\hat{\mathbf{n}}$ defines the orientation, d tells us how far the plane is from the origin: for a family of planes hkl there will be a plane through the origin too, and so d is the interplanar spacing.

For the (hkl) planes in a lattice with lattice parameter a, we know that the intercepts of the planes on the axes are a/h, a/k and a/l. So the equation of the plane is

$$hx + ky + lz = a. \qquad (2)$$

But the unit vector normal to the plane is

$$\hat{\mathbf{n}} = \frac{h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}}}{\sqrt{h^2 + k^2 + l^2}} \qquad (3)$$

and thus

$$\hat{\mathbf{n}}.\mathbf{r} = \frac{hx + ky + lz}{\sqrt{h^2 + k^2 + l^2}} \qquad (4)$$

whence, using equation 2,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.$$

Check: Consider the (110) planes: there is one through the origin, one diagonally across the middle of the cube, and so on. The perpendicular spacing is one half the diagonal of the cube face, $\sqrt{2}/2 = 1/\sqrt{2} = 1/\sqrt{1^2 + 1^2 + 0^2}$.

1.7.5 Angles between planes

For cubic crystals only.

The unit vector normal to (hkl) **is**

$$\hat{\mathbf{n}} = \frac{h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}}}{\sqrt{h^2 + k^2 + l^2}}$$

and if we want to find the angle θ **between this plane and the plane** $(h'k'l')$ **we use**
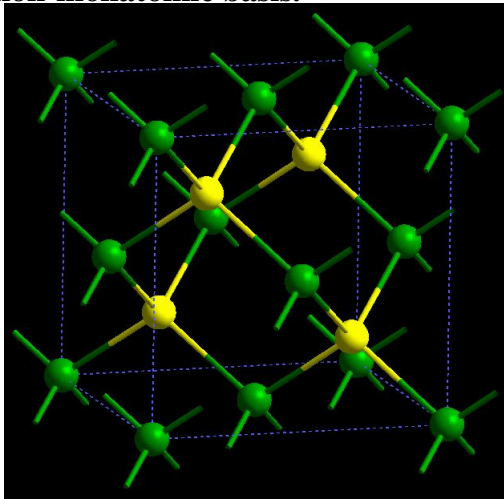
$$\hat{\mathbf{n}}.\hat{\mathbf{n}}' = \cos\theta$$

so

$$\cos\theta = \frac{hh' + kk' + ll'}{\sqrt{h'^2 + k'^2 + l'^2}\sqrt{h^2 + k^2 + l^2}}.$$

1.7.6 More Examples

Lattices with a non-monatomic basis.

FCC, with basis of Ga at (000)**, As at** $(\frac{1}{4}, \frac{1}{4}\frac{1}{4})$**.**

Diamond or Silicon
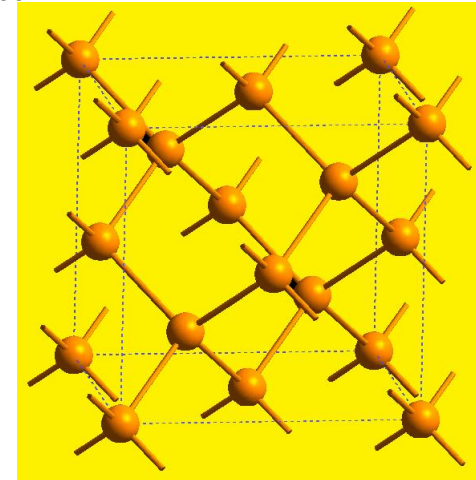
FCC, with basis of Si at (000)**, Si at** $(\frac{1}{4}, \frac{1}{4}\frac{1}{4})$ **–** *inequivalent* **atoms (look at bonding).**

Hexagonal close packing
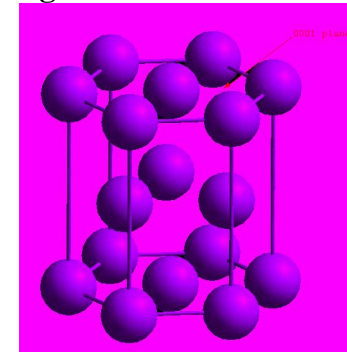
Hexagonal: basis of one atom at $(0,0,0)$ **and one at** $\frac{1}{3}(\mathbf{a}+\mathbf{b})+\frac{1}{2}\mathbf{c}$**. For perfect packing,** $c = \sqrt{8/3}a$**.**
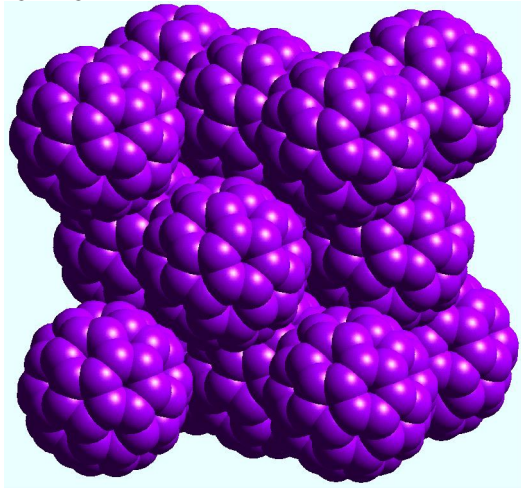
Hexagonal close packing and face-centred cubic (cubic close-packing) are similar – in each case we stack up planes of closely-packed atoms, but the sequence is different.

In cubic, the close-packed planes are (111)**.**

Buckminsterfullerine

FCC, with basis of one C_{60} molecule at (000) – really orientations of molecules will differ.

1.8 Packing Fractions

For monatomic cubic crystals, it is easy to work out the *packing fraction*, that is, the fraction of space that is filled if we place a sphere on each lattice site and expand the spheres until they touch.

1.8.1 Simple cubic

The spheres touch along the $[100]$ directions, so if the lattice parameter is a the sphere radius is $a/2$ so the packing fraction is

$$\frac{sphere\ \ volume}{cell\ \ volume} = \frac{\frac{4}{3}\pi(a/2)^3}{a^3} = 0.52$$

1.8.2 Body-centred cubic

The spheres touch along the $[111]$ directions, so if the lattice parameter is a the sphere radius is $a\sqrt{3}/4$ so the packing fraction is

$$\frac{twice\ \ sphere\ \ volume}{cell\ \ volume} = 2\frac{\frac{4}{3}\pi(a\sqrt{3}/4)^3}{a^3} = 0.68$$

1.8.3 Face-centred cubic

Packing fraction is 0.74.

1.8.4 Hexagonal close-packed

Packing fraction is 0.74.

1.9 Defects

Nothing in Nature is perfect, and crystals are no exception. Any real crystal contains defects, and these affect its properties in various ways.

- Defects in diamond alter the colour;
- defects in semiconductors (of the right kind) allow them to be used to make devices;
- defects in metals alter their mechanical properties;
- defects affect thermal and electrical conductivity.

1.9.1 Point defects

Missing atoms, atoms in positions where an atom would not normally be (interstitials), impurities. Schottky defect: an atom is transferred from a site in the crystal to a site on the surface. If this costs energy E_v, the number of vacancies in equilibrium is

$$n = N \exp(-E_v/k_B T),$$

where N is the total number of atoms in the crystal (see 2B28 notes). Remember that crystals are often formed by cooling quite quickly from the melt, and atoms move quite slowly in solids, so a high-temperature number of defects can be 'frozen in'. In ionic crystals, to keep the crystal neutral we form positive and negative defects in charge-compensating pairs.
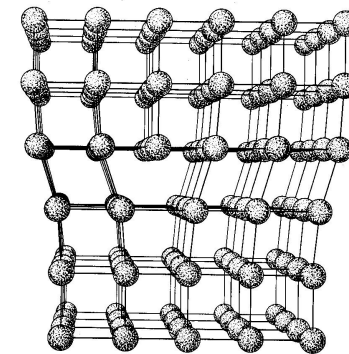
Frenkel defect: an atom is moved from a normal atomic position to an interstitial position. Solid-state diffusion is affected by defects.

1.9.2 Dislocations

Dislocations are *line defects*. Simplest to visualize is an *edge dislocation* – think of an extra half-plane of atoms.
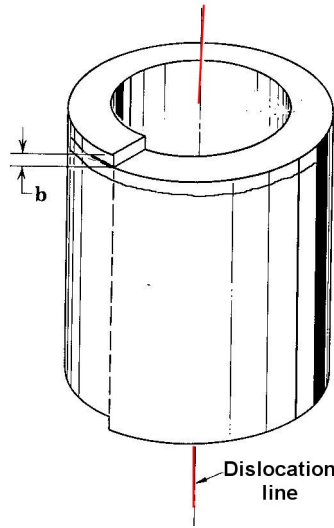

Affects deformation properties – to slide upper block over lower now only requires a *line* of bonds to break at a time, not a whole *plane* – process of *slip*. Explains low yield strength of solids.

Screw dislocations give a helical structure to the planes.
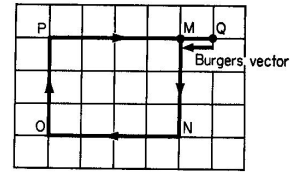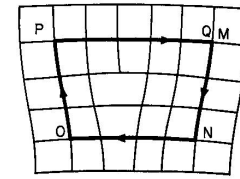

Screw dislocations often show up in crystal growth

A growth spiral on a silicon carbide crystal, originating from the point of emergence of a screw dislocation (courtesy Prof. S. Amelinckx).

Dislocations are characterised by their *Burgers vectors* – the mismatch in position between going round a path in the perfect crystal or round the dislocation.
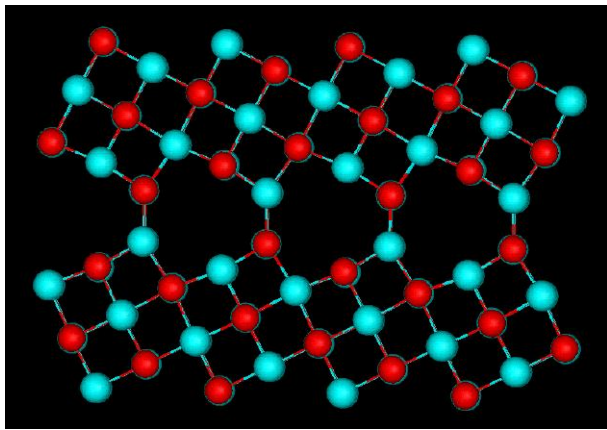

Edge: b perpendicular to line of dislocation. Screw: b parallel to line of dislocation.

1.9.3 Planar defects

In a sense, the surface of a crystal is a planar defect! If two crystals grow together with a mismatch in orientation, we have a *grain boundary*.
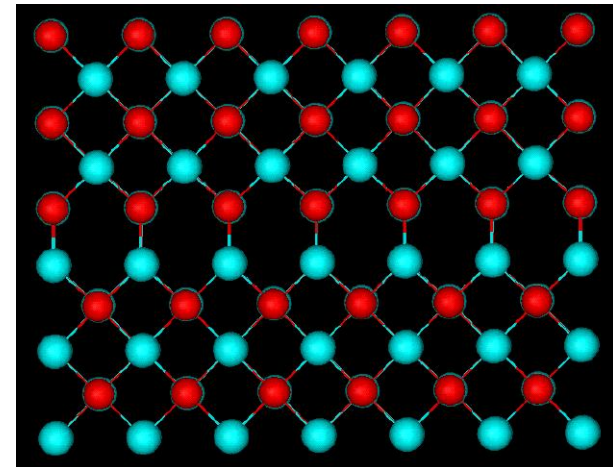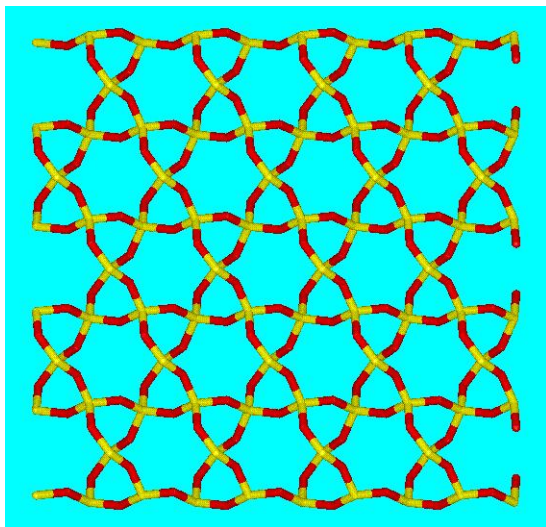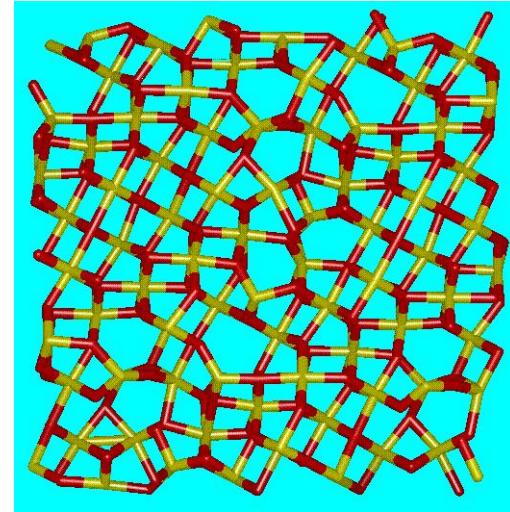
Can sometimes represent a grain boundary as a line of edge dislocations.

1.9.4   Amorphous Solids

Not all solids are crystalline: if a crystalline material is represented by:

then an amorphous structure would be

The *local* structure is similar to that in the crystal, but *long-range order* is lost.