Crystalline Solids

Books

There are many good texts on crystalline solids which cover the defects we will be covering here, many of which will already be familiar to you from Solid State.

**e.g
Kittel
Ashcroft and Mermin
Rosenberg**

More specialist texts:

Hull and Bacon – Introduction to Dislocations

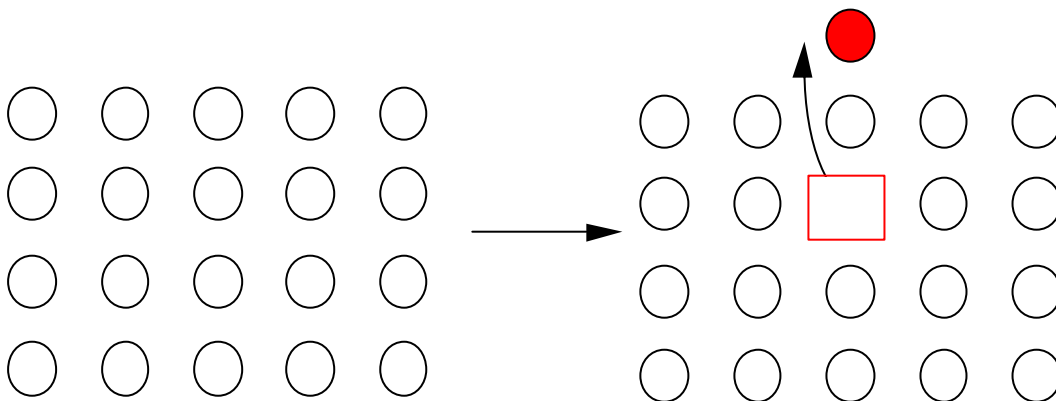**Ashby and Jones – Engineering Materials**

Defects

Three basic (geometric) types:
- **Point** – vacancy, interstitial, substitutional
- **Line** – dislocations
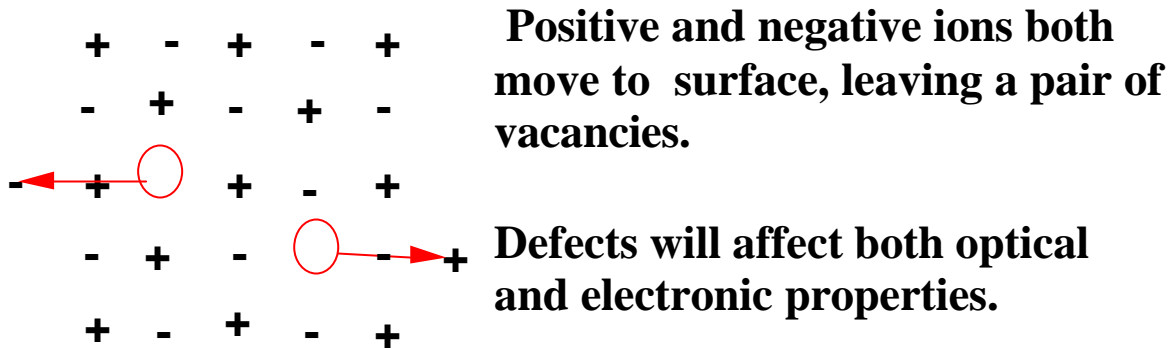- **Plane** – grain boundaries

Point Defects

1. Vacancy or Schottky Defect

Perfect Crystal
Free energy G_o

Defect Crystal
Free energy G

More complicated in ionic crystals, where still need to maintain charge neutrality in the bulk.

+ - + - +

- + - + -

← + ○ + - +

- + - ○ —→ +

+ - + - +

Positive and negative ions both move to surface, leaving a pair of vacancies.

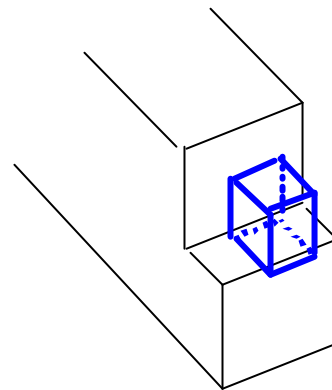**Defects will affect both optical and electronic properties.**

In general, the energy of formation E_v depends on site to which atom moved.
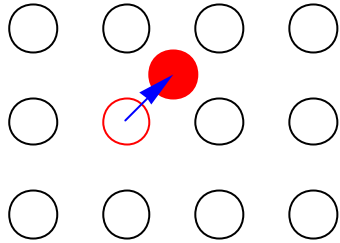
E_v lower if transferred to kink site (crystal ledge) than perfect surface.

On average E_v corresponds to net breaking of ~1/2 neighbouring bonds
~1/2 latent heat of sublimation/atom

$E_v \sim 1eV$

2) Interstitial vacancy – Frenkel defect

Ionic crystal – 2 types

**More likely since cations tend to be smaller than anions
þ lower associated strain energy.**

Energy due to strain (non-ionic case)

Strain energy = 1/2 elastic constant x strain^2 /vol

Define shear modulus G = $\dfrac{\text{stress}}{\text{strain}} = \dfrac{t}{g}$

Strain energy = 1/2 G g^2 (or equivalently 1/2 tg)

If b = lattice parameter
Volume ~ b^3
Strain ~1

⊳ Strain energy = 1/2 Gb^3

hence E$_{Frenkel}$ ~ 5-6ev

Much larger than E$_{Schottky}$ and also E$_{Frenkel}$ > k$_B$T

In general not thermodynamically stable, and won't be discussed further.

Equilibrium number of vacancies in monatomic crystal

(For complete discussion see Waldram, Theory of Thermodynamics)

Compute F for crystal with N atoms, n vacanices on $N+n$ sites.

3 contributions to toal entropy
- S_c determined by density of states etc for given configuration of atoms.
- S_bμ number of bulk configurations
- S_sμ number of surface arrangements

And
$$S_c = k_B \ln g_c(E)$$
$$S_b = k_B \ln W_b$$
$$S_s = k_B \ln W_s$$

At equilibrium
$$dF = dF_c - TdS_b - TdS_{S=0}$$

where $dF_c = dE\text{-}TdS_c\text{-}TdS_s$, the change in free energy when we move an atom from a particular bulk site to a particular surface site, without allowing lattice rearrangements to occur.

DF$_c$ ~ 6 nearest neighbour bond energies (since break on average 1/2 the bonds in the surface)

Now $W_b = \dfrac{(N+n)!}{N!\,n!}$

If 1 vacancy added W_b multiplied by

$$\frac{N+n+1}{n+1} \sim \frac{N+n}{n}$$

$$\searrow\, dS_b = k_B \ln\left(\frac{N+n}{n}\right)$$

For large crystals $dS_s \ll dS_b$

$$\searrow\, dF \sim dF_c - k_B T \ln\left(\frac{N+n}{n}\right) = 0$$

$$\searrow\, n \sim N \exp -dF_c/k_B T$$

This is generally quite small, but can become appreciable towards the melting point.

We will see later how vacancies are important for creep and diffusion

Dislocations – Line Defects

Dislocations were originally invoked to explain the discrepancy between theoretical shear stress and that experimentally determined, lo ng before a dislocation was directly seen.

Theoretical Shear Stress

As two atom planes move past one another, the stress must increase and then decrease.

Assume a sinusoidal form for the variation of shear stress _t_ with displacement _x_.
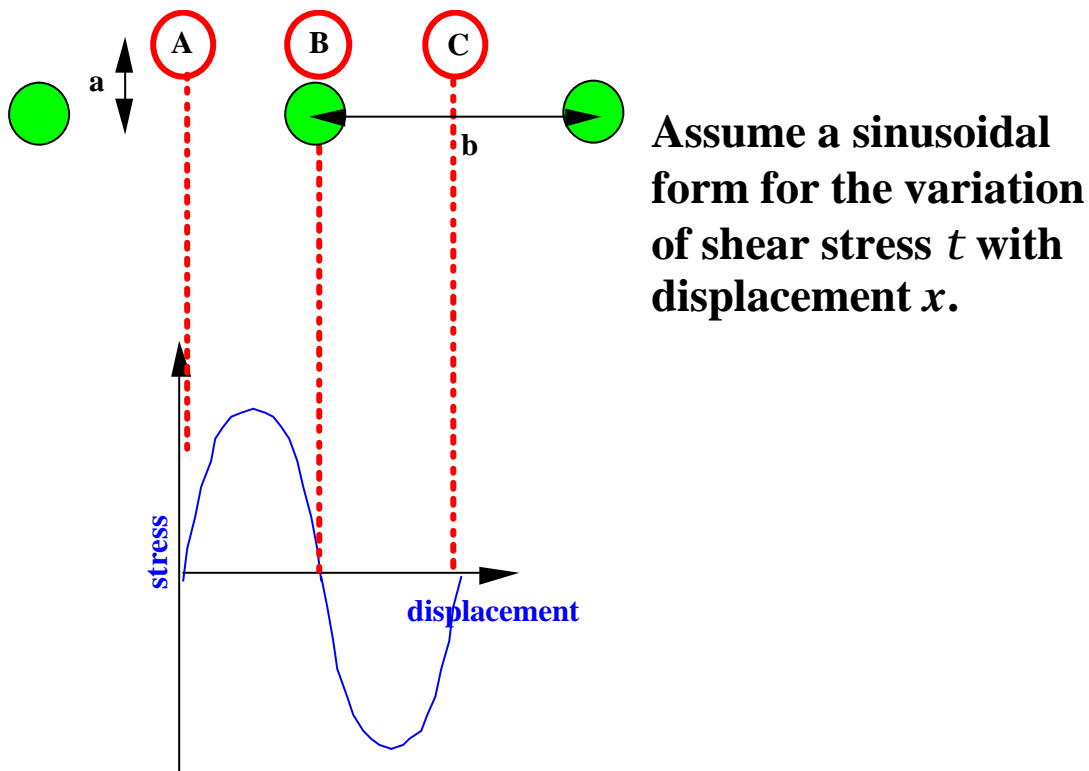
Shear stress $t = k \sin \dfrac{2px}{b}$ **with k = const**

Near origin, slope is measure of elastic shear modulus G.

Hence, within this linear regime $dt = G \dfrac{dx}{a}$ **and**

$$dt]_{x=0} = \frac{2pk}{b} \cos\left(\frac{2px}{b}\right) dx]_{x=0} \sim \frac{2pk}{b} dx$$

$\mathbb{P}$ $\quad \dfrac{2pk}{b} = \dfrac{G}{a}$ **and therefore** $k = \dfrac{Gb}{2pa}$

$$\backslash t = \frac{Gb}{2pa} \sin\left(\frac{2px}{b}\right)$$

Maximum shear stress t_0 is given by

$$t_o = \frac{Gb}{2pa} \sim \frac{G}{2p}$$

Better models give $t_0 \sim$ G/30

Experiment shows this is far too high
e.g Copper $\quad$ **G=4.6 GN m^{-2}** $\mathbb{P}$ **t_0 = 0.72 GN m^{-2}**

Experimentally a good single crystal gives τ_o 100 kN m^{-2}

Dislocations

The origin of the discrepancy between theory and experiment lies in the existence of dislocations.

Dislocations are characterised by their Burger's vectors. These represent the 'failure closure' in a Burger's circuit in imperfect (top) and perfect (bottom) crystal.
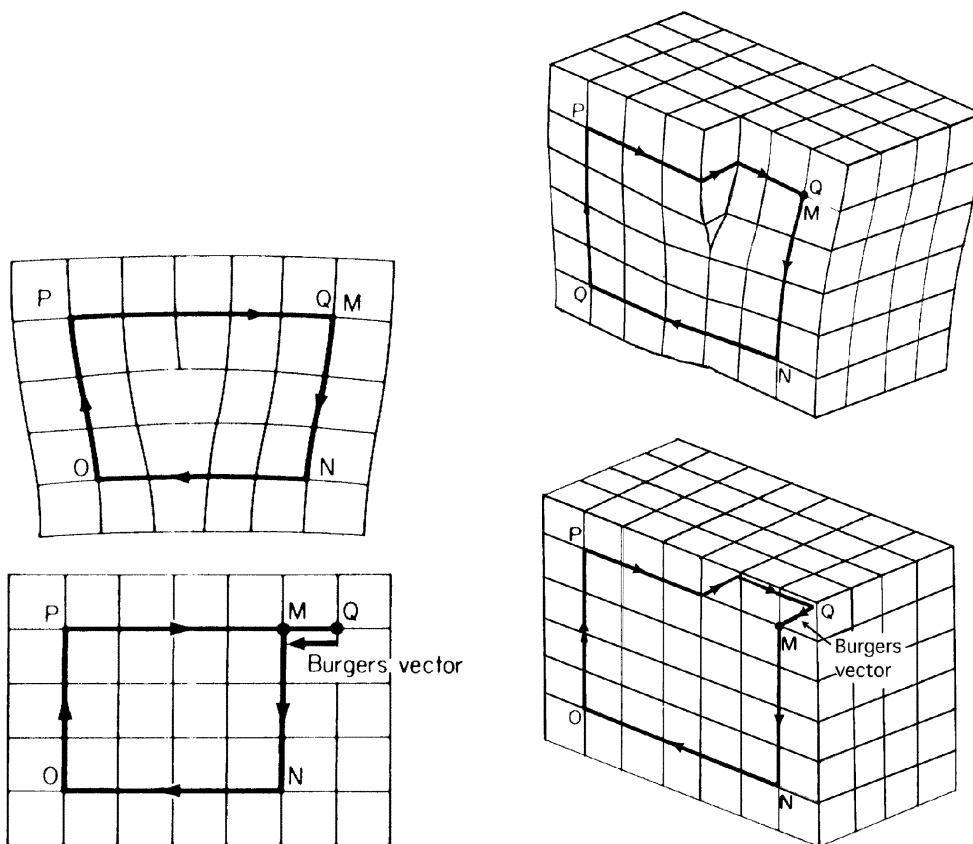
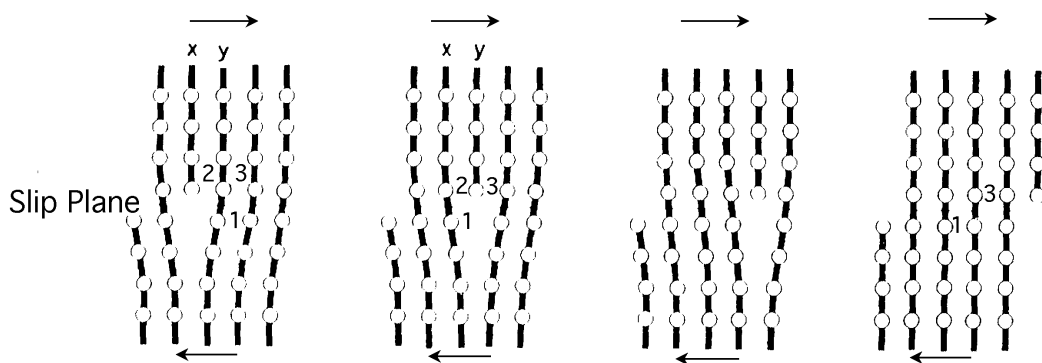**Edge**   **Screw**

Vectors describing dislocation line and Burger's vector are
Perpendicular   **Parallel**

Dislocation Motion

Dislocations make a material softer because they permit crystals to deform without moving one entire crystal plane over the one below.

e.g. movement of edge dislocations

The slip (also known as glide) plane is the plane on which the dislocation moves.

The glide plane is defined by the vectors b and l.

This means edge dislocations have a unique glide plane, but screw dislocations do not and can move on a whole family of planes.