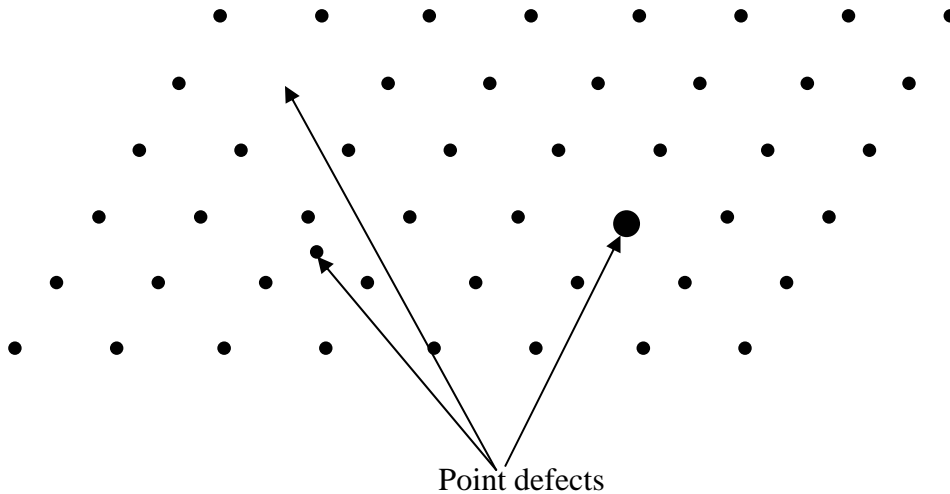


Chapter 4 Point defects and dislocations

I. Lattice impurities and vacancies

1. A point defect in a crystal is (i) the occupancy of a lattice sites by impurity atoms/ions or a voids (i.e. vacancy); or (ii) extra atoms/ions not in regular lattice positions.



2. Defects modify the properties of a sample from that of a perfect crystal.
3. Defects are unavoidable. Even if you can prepare the sample with the purest materials, vacancy defects will occur because disorder will increase the entropy of the system.
4. Historically, point defects in crystals were first considered in ionic crystals, not in the much simpler metal crystals. The reason was that some known properties of ionic crystals (e.g. conduction by ion migration at high temperatures) could be understood for the first time in terms of point defects, while no special properties of metals (in the twenties) were in desperate need of an explanation.

II. Schottky and Frenkel defects

1. Imperfection due to vacancy is also called a *Schottky defect*. It is created by transferring an atom/ion from the original correct site to the surface of the sample.
2. If E_v = energy to move an atom from its site to the surface. Probability of finding site in vacant is given by

$$P = \frac{1}{1 + e^{E_v / k_B T}}$$

Note that if E_v is large, $P \rightarrow 0$. $P = 1/2$ if $E_v=0$ (no difference between occupancy and vacancy).

3. If there are N sites and n vacancies in a sample, then $P=n/N$

$$\frac{n}{N} = \frac{1}{1 + e^{E_v/k_B T}}$$

$$\Rightarrow N = (1 + e^{E_v/k_B T})n$$

$$\Rightarrow \frac{n}{N - n} = \frac{1}{(1 + e^{E_v/k_B T}) - 1} = e^{-E_v/k_B T}$$

This is the ratio of the vacant sites to occupied sites.

4. At higher temperatures, the number of vacant sites will increase. The actual concentration of vacancies can be higher if the sample is grown at a higher temperature and then cooled suddenly (quench).

5. At low temperatures, $n \ll N - n$,

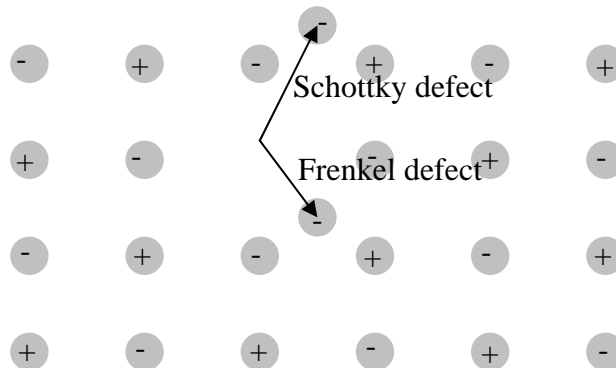
$$\frac{n}{N} \approx \frac{n}{N - n} = e^{-E_v/k_B T}$$

For example, if $E_v=1$ eV and $T=1000$ K (note that $1\text{K} \approx 0.08$ meV, therefore $1\text{eV}/1000\text{K} = 1/0.08 = 12.5$)

$$\frac{n}{N} \approx e^{-12} \approx 10^{-5}$$

6. In ionic crystal, vacancies are formed in pair to maintain local neutrality.

7. If the atom is transferred to an *interstitial* position instead of surface, the defect is known as *Frenkel* defect.



8. If N = number of possible normal lattice sites, N' = number of possible interstitial site. ($N=N'$ for most of the cases), and n = number of Frenkel defects.

$$\text{Number of ways to arrange the interstitial atoms} = {}^{N'}C_n = \frac{N'!}{(N'-n)!n!}$$

$$\text{Number of ways to arrange the vacancies} = {}^NC_n = \frac{N!}{(N-n)!n!}$$

$$\text{Total number of possible ways} = \frac{N'!}{(N'-n)!n!} \frac{N!}{(N-n)!n!}$$

$$\therefore S = k_B \ln \Omega = k_B \ln \frac{N'!}{(N'-n)!n!} \frac{N!}{(N-n)!n!}$$

Stirling's approximation : $\ln(x!) \approx x \ln x - x$

$$S \approx k_B [(N' \ln N' - N') + (N \ln N - N) - (N'-n) \ln(N'-n) - (N-n) \ln(N-n) - 2n \ln n]$$

If E_I = energy required to form one defect

$$\therefore F = U - ST = nE_I - k_B T [(N' \ln N' - N') + (N \ln N - N) - (N'-n) \ln(N'-n) - (N-n) \ln(N-n) - 2n \ln n]$$

n is determined by minimizing the free energy :

$$\frac{\partial F}{\partial n} = 0 \Rightarrow E_I - k_B T [(\ln(N'-n) + 1) + (\ln(N-n) + 1) - 2 - 2 \ln n] = 0$$

$$\Rightarrow E_I - k_B T \left[\ln \frac{N'-n}{n} + \ln \frac{N-n}{n} \right] = 0$$

$$\Rightarrow E_I = k_B T \left[\ln \frac{(N'-n)(N-n)}{n^2} \right]$$

For $n \ll N, N'$,

$$E_I \approx k_B T \left[\ln \frac{N'N}{n^2} \right] \Rightarrow n = \sqrt{N'N} e^{-E_I/2k_B T}$$

III. Diffusion of point defects

1. Frenkel defects is important in explaining conductivity in some ionic salts, like many alkali halides. Electric conductivity in these ionic salts is caused by Frenkel defects (i.e. ions), *not* by electrons. This can be demonstrated by comparing the transport of charge to the transport of mass.

2. More precisely, the conductivity in an alkali halide can be modeled by the *diffusion* of Frenkel defects through the crystal. The current is driven by maintaining a concentration gradient and the diffusion current density follows the Fick's Law:

$$\bar{J}_N = -D \nabla N$$

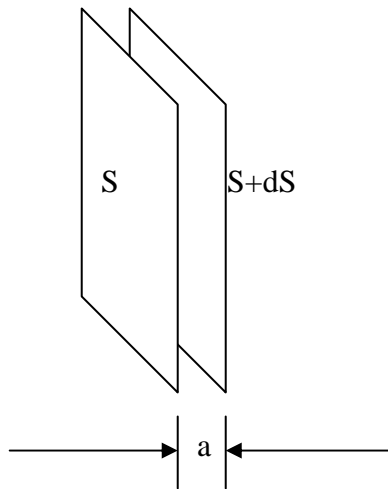
\bar{J}_N is the current density (ions per area per time) and N is the *concentration* of the current carrying ions (ions per volume) and hence the diffusion current has a unit of area per time

3. To diffuse, an ion must overcome the potential barrier presented by its neighbor. The barrier height is called the *activation energy* E (or more accurately we can define

activation energy E_+ for the positive ion and E_- for the negative ions). We should distinguish the difference between the energy of defect formation E_f (energy to produce one defect ion) and the activation energy E (energy to make the ions to move).

4. There are two mechanisms to make the ions to overcome the potential barrier: (i) by thermal excitation, and (ii) by quantum tunneling. In general quantum tunneling is important only for light ions, so we will consider only the thermal excitation here. For thermal excitation, if the ion makes ν passes (per unit time) at the barrier, there will be a probability of $\exp(-E/k_B T)$ in surmounting the barrier in each try. Hence, a fraction of $p = \nu \exp(-E/k_B T)$ ions will be excited to move in every second.

5. Diffusion constant is a function of temperature. Consider two planes separated by a lattice constant a , and let S (ions per area) be the ion concentration at the planes so that $S = Na$. Both N and S are function of the plane position:



$$dS = \frac{dS}{dx} a \Rightarrow \bar{J}_N = \text{Number of ions crossing the plane (per unit time)} = -pdS = -pa \frac{dS}{dx}$$

$$\Rightarrow \bar{J}_N = -pa^2 \frac{dN}{dx}$$

Compare with $\bar{J}_N = -D \frac{dN}{dx}$ (Fick's Law in 1D)

$$\therefore D = pa^2 = \nu a^2 e^{-\frac{E}{k_B T}}$$

6. The drifting (diffusion) velocity of the ions is proportional to the applied electric field \mathbf{E} . The proportional constant is known as the *mobility* of the ions:

$$\mathbf{v} = \mu \mathbf{E}$$

Since $\mathbf{j} = nq\mathbf{v}$ where q is the charge of the carrier. $\therefore \mathbf{j} = \mu nq\mathbf{E}$. Ohm's Law $\Rightarrow \mathbf{j} = \sigma\mathbf{E}$ where σ is the conductivity.

$$\therefore \sigma = \mu nq$$

According to Drude's model,

$$\sigma = nq^2\tau/m$$

where τ is the relaxation time. $\therefore \mu nq = nq^2\tau/m \Rightarrow \tau = m\mu/q$

μ is related to D by the Einstein's relation. Assuming Maxwell-Boltzmann distribution, $v_{rms}^2 = 3k_B T/m$ and from statistical mechanics:

$$D = v_{rms}^2\tau/3 \Rightarrow D = k_B T\tau/m$$

$$\Rightarrow D = k_B T\mu/q \quad (\text{Einstein relation})$$

7. Since σ depends on D , and D depends on T , so now we can figure out how σ depends on T :

$$D = k_B T\mu/q \Rightarrow D = k_B T\sigma/nq^2$$

$$\Rightarrow \sigma = Dnq^2/k_B T$$

$$\Rightarrow \sigma = (nq^2 v_a^2 / k_B T) e^{-\frac{E}{k_B T}}$$

IV. Color Centers

1. Color centers are imperfections in crystals that cause color (defects that cause color by absorption of light). Electrons in defect region only absorb light at certain range of wavelength. The color seen is due to lights not absorbed.

2. This phenomenon is common in many transparent insulators (example: diamond). Many metal oxides fall in this category.

3. Examples of color centers:

(i) A diamond with C vacancies (missing carbon atoms) absorbs light, and these centers give green color.



(ii) Replacement of Al^{3+} for Si^{4+} in quartz gives rise to the color of smoky quartz.

(iii) A ruby (Al_2O_3) may contain < 1% Cr and it will look pink or red, but the same material without Cr will be completely colorless.

3. There are different mechanisms for the light absorption.

4. F center has been identified by electron spin resonance as an electron bound at a negative ion vacancy. When excess alkali atoms are added to an alkali halide crystal, a corresponding number of *negative vacancies* are created. In other words, there is a surplus of electrons. These electrons will migrate and bound to a vacant negative ion

site. The distribution of the excess electron is largely on the positive metal ions adjacent to the vacant site. Optical absorption arises from an electric dipole transition to a bound excited state of the center. F center is the simplest trapped-electron center in alkali halide crystals. Absorption wavelength increases (~from 4000 angstrom to 6000 angstrom) with the size of the alkali ion (from Li to Cs) because the electron at the vacant site are less bound to the larger alkali ions.

5. Other centers.

F_A center: One of the nearest positive neighbors which bind an F center is replaced with another type of alkali ion.

M center: An M center consists of two adjacent F centers.

R center: An R center consists of three adjacent F centers.