3. Point Defects and Diffusion

3.1 Diffusion Primer

3.1.1 Diffusion and Point Defects

Point defects generally are mobile - at least at high temperatures. They are the vehicles that make the atoms of the crystal mobile - point defects are the cause of **solid state diffusion**.

Many products of modern technology depend on solid state diffusion and thus on point defects. Some examples are:

- **Microelectronics** and **Optoelectronics**.
- Solid state *Sensors*, e.g. the oxygen sensor regulating the emissions of your car.
- Solid state *batteries*,*accumulators* and *fuel cells*.
- *High strength materials*.

The concentration of point defects, their specific kind (including impurity atoms), their migration parameters, equilibrium or non-equilibrium conditions and the atomic mechanisms of diffusion determine what you get in a specific solid state experiment involving diffusion.

- Small wonder that many diffusion phenomena are not yet totally clear!

If we use the term "diffusion", we always and exclusively mean that *something* moves around in a random fashion,. i.e. does a **random walk**.

- The "*something*" in the context of this lecture is an *atom* moving around randomly in a crystal. Generally, it can be *any* particle or even quasi-particle we like - atoms, molecules, electrons, positrons, photons, phonond, excitons, ...

3.1.2 Recapitulation of Ficks Laws and Random Walk

Lets quickly go over the basic laws of diffusion which were discovered by Adolf **Fick** on a phenomenological base long before point defects were known. The starting point is **Ficks 1. Law**, stating:

- The **flux** *j* of diffusing *particles* (not necessarily atoms) is proportional to the *gradient* of their *concentration*, or

$$j_i \ = \ - \ D \cdot \nabla c_i$$

- The index **i** refers to the particular particle with number **i** observed; *D* is the diffusion coefficient of that particle.

Note that even this purely phenomenological description applies to everything - e.g. liquids - as long as we discuss *diffusion* and not, e.g., some kind of flow.

- This means that the underlying dynamics of the particles on an atomic scale is essentially random walk.
- The derivation of the simple continuum equation above from the primary events of random scattering (causing random walk) of many discrete particles takes a lot of averaging. If you don't know how it's done (or forgot), do consult the proper (english) modul of "Introduction to Materials Science II" (and the links from this modul).

If there are several interacting particles, the formulation of Ficks **1.** law must be more general, we have

$$j_i \ = \ - \ M \cdot \nabla \mu_i$$

- With μ = chem. potential; *M* = mechanical mobility.
- Since the gradient of the chemical potential may be different from zero even for constant concentrations, special effects as, e.g., **uphill diffusion** are contained within this formulation.

The next basic equation is the **continuity equation**. It states:

- *Changes* of the particle concentration within a volume element must express the *difference* of what goes in to what goes out - we have *conservation of the particle number* here. In mathematical terms this means

$$\frac{\partial c}{\partial t} \ = \ - \ \text{div} \ j$$

● This is if course only true as long as no particles are generated or annihilated (as, e.g., in the case of electrons or holes in an illuminated semiconductor).

▸ Combining the two equations from above we obtain **Ficks 2. law**:

● The *temporal change* in concentration at a given point is proportional to the *2nd derivative of the concentration*, or

$$\frac{\partial c}{\partial t} = \text{div} (D \cdot \nabla c) = D \cdot \Delta c$$

● With the final equation being valid only for $D =$ **const.**

▸ Ficks equations look innocent enough, but solutions of the rather simple differential equations forming Ficks laws are, in general not all that simple! They do follow some general rules, however:

● They involve almost always statistical functions, as well they should, considering that diffusion is a totally statistical process at the atomic level.

● The solutions to heat conducting problems are quite similar, as well they should, because the conduction of heat can be treated as a diffusion phenomena. (it actually *is* a diffusion phenomena).

● This link gives some more information about Fick's laws and standard solutions.

▸ Many diffusion phenomena can be dealt with on the phenomenological base of Ficks laws. All that is required, is to know the diffusion coefficient and its dependence on temperature and possibly other variables - you do not have to know anything about the *atomic mechanisms* involving point defects to solve diffusion problems.

● It turns out, however, that complex diffusion problems - e.g. the simultaneous diffusion of **B** and **P** in **Si** can not be modeled adequately without knowing the atomic mechanisms and their interaction. This explains the impetus behind major efforts to unravel the precise mechanisms of diffusion in **Si** and other semiconductors.

▸ All we have to know about **random walk** is the general relation between the average distance $\langle r^2 \rangle$ covered by a randomly "walking" object (which we often also call **diffusion length L**) , the number N of steps made, and the (average) distance r_0 covered in one step.

● For three-dimensional random walk we have quite generally

$$\langle r^2 \rangle = L^2 = r_0^2 \cdot 3N$$

3.1.3 Coupling Phenomenological Laws to Single Atomic Jumps

▸ We now must link the phenomenological description of diffusion (that only works on averages and thus only if many particles are considered) with the basic diffusion event, the single jump of a single atom or defect.

▸ We describe the *net flux* of particles as the difference in the number of particle jumps to the left and to the right. With the jump frequency ν we obtain Ficks **1.** law with an expression for the diffusion coefficient (for cubic crystals), a detailed derivation is given in the link.

$$D = g \cdot a^2 \cdot \nu$$

● With $a =$ lattice constant, $\nu =$ jump frequency, i.e. the number of *jumps per second* from one position to a neighboring one .

● g is the **geometry factor** of the lattice type considered. It takes into account that considering all jumps that are possible in the given lattice, only some have a component in the x-direction. Its definition is

$$g = \frac{1}{2} \cdot \Sigma_i \frac{\Delta x_i}{a}$$

● g is always about **1** as you will find out doing the exercise, so we will not consider it any more.

▸ The jump frequency $\nu = N/t$ (= number of jumps N per second) is given by

$$\nu = \nu_0 \cdot \exp - \frac{G_m}{kT}$$

- with G_m = free enthalpy for the jump or for the migration of the atom or defect. ν_0 is the frequency of "attempts" to overcome the enthalpy barrier for a jump; it is, of course, the vibration frequency of the lattice atoms, i.e. around **10^{13} Hz**.

This gives us the second important parameter set describing a property of a point defect, namely its **migration energy** and **entropy**

- All we have to do is to express $G_m = H_M - TS_M$, with H_M = migration enthalpy (or -energy), and S_M = migration entropy.

- The magnitude of the migration entropy will be comparable to the formation entropy because it has the same roots. It is thus around **1 k** for "normal" crystals.

Combining everything, we obtain an expression for the diffusion coefficient **D** in terms of the migration energy:

$$D = D_0 \cdot \exp - \frac{H_M}{kT}$$

- Where all constant (or nearly constant) factors have been included in D_0. Some numerical values are given in the link.

These formulas relate the atomic properties of defects to the diffusion coefficient from Ficks laws.

There is one more expression of prime importance when it comes to diffusion. It brings together statistical considerations from looking at random walk (which is exactly what a vacancy does) as given above with the diffusion coefficient. All we have to do is to express **N** by the diffusion coefficient.

- What we get is the famous **Einstein** - **Smoluchowski** relation (for **3**-dimensional diffusion).

$$D = \frac{L^2}{6\tau}$$

- With **L** = mean square displacement or **diffusion length**, τ = time since start of the diffusion (or, if the particle "dies", e.g. by recombination in the case of minority carriers in semiconductors, its **lifetime**).

Einstein derived this in **1905** in a slightly more general form:

$$D = \frac{\langle r^2 \rangle}{g^* \cdot \tau}$$

- With **r** = vector between "start" and "stop" of the diffusing particle for the time τ; $\langle r^2 \rangle$ is thus the average of the square of the mean displacement (this is something different from the square of the average!), and **g*** is some factor "in the order of **1**", i.e. **2**, or **6**, depending if the diffusion is **1 -**, **2 -** or **3 -**dimensional and what kind of symmetry (cubic, etc.) is involved.

Now let's do an exercises:

Exercise 3.1-1
Calculate geometry factors

Exercise 3.3-1
Quick Questions to 3.