Lecture 24

Ionic conductivity and Diffusion Mechanism

Recap: For ionic conductivity, transport of one or more types of ions across the material is necessary. In an ideal crystal all constituent ions are arranged in regular periodic fashion and are often stacked in a close-packed form. Thus there is little space for an ion to diffuse. However, at any non-zero temperature there exist defects. These could, for example, be positional disorder due to deviation from ideal stacking. Two types of defects important in the context of ion mobility in crystals are 'Schottky' and 'Frenkel' defect. These belong to the class of 'point defects' in crystals.

The key **difference between electronic and ionic conduction** is that **electronic conduction** is the movement of electrons from one place to another, whereas **ionic conduction** is the movement of **ions** from one place to another. The term **conduction** refers to the transfer of energy through a substance.

Ionic Conductivity, σ or λ, is defined the same as electrical conductivity:

$\lambda = nZe\mu$, where n is the number of charge carriers per unit volume, Ze is the charge (e= 1.602189×10^{-19}C), and μ is the mobility, which is a measure of the drift velocity in a constant electric field.

	Material	Conductivity / ($S\ m^{-1}$)
Ionic Conductors	Ionic crystals	$<10^{-16} - 10^{-2}$
	Solid electrolytes	$10^{-1} - 10^{3}$
	Strong (liquid) electrolytes	$10^{-1} - 10^{3}$
Electronic conductors	Metals	$10^{3} - 10^{7}$
	Semiconductors	$10^{-3} - 10^{4}$
	Insulators	$<10^{-10}$

The **ionic mobility** is described as the speed achieved by an **ion** moving through a gas under a unit electric field. It is denoted by (μ). The unit of **ionic mobility** is $m^2 s^{-1}$ $volt^{-1}$.

In ionic solids, while carrier concentration is independent of temperature (within extrinsic region), mobility is strongly affected by temperature as is also obvious from equation and is expressed as

$\mu \propto \left(\frac{-E_a}{kT}\right)$ where *Ea*, is the activation or migration energy.

Diffusion Mechanisms

Diffusion means atoms moving and changing places or It is mass transport by atomic motion. In atomic point of view diffusion is stepwise migration of atoms from lattice site to lattice site. Inhomogeneous materials can become homogeneous by diffusion. For an active diffusion to occur, the temperature should be high enough to overcome energy barriers to atomic motion

There are two main diffusion mechanisms in solids:

– Substitutional diffusion by vacancies

– Interstitial diffusion. Does not involve vacancies

In vacancy diffusion, an atom leaves its lattice site and fills the nearby vacancy, thereby creating a new vacancy at the original lattice site. In interstitial diffusion, a small interstitial atom or ion moves from one interstitial site to another interstitial site. ... No need of vacancies for this diffusion to occur. Interstitial diffusion is generally faster than vacancy diffusion because bonding of interstitials to the surrounding atoms is normally weaker and there are many more interstitial sites than vacancy sites to jump to. Requires small impurity atoms (e.g. C, H, O) to fit into interstices in host.

Factors affecting diffusion:

- Diffusing species: Different materials have different diffusion coefficient (D_o), which is also the indication of the diffusion rate.
- Crystal structure (BCC, FCC, ..)
- Imperfection (grain boundary, dislocation, vacancy, lattice)
- Temperature: Diffusion is thermally activated process

Temperature dependence can be expressed as follows:

$$\underline{D = D_o \exp(-\frac{Q_d}{k_B T})}$$

D_o : temperature independent preexponential (cm^2/s)
Q_d : activation energy for diffusion (eV/atom)
k_B : Boltzman's constant $= 8.617 \times 10^{-5}$ eV/K
T : absolute temperature (K)

Activation Energy for Diffusion

A high **energy** is required to squeeze atoms past one another during **diffusion**. This **energy** is the **activation energy**. Generally more **energy** is required for a substitutional atom than for an interstitial atom.When the temperature is high the thermal energy permits the atoms to overcome the potential barrier and more easily move to new lattice site. At high temperature the diffusion coefficient increases causing to larger flux of atoms. At low temperature (about 0.4 of T_m) the diffusion not significant.

Conditions for atom migration:

- empty adjacent site

- atom must have enough energy to break bonds and cause lattice distortion during displacement.

Diffusive motion influenced by atom vibrational energies (k_BT)