Electroceramics

Prof. Ashish Garg
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture – 13

So, welcome to this new lecture. So, what we will do is that we will just review the pervious lecture and before before we start the new lecture.

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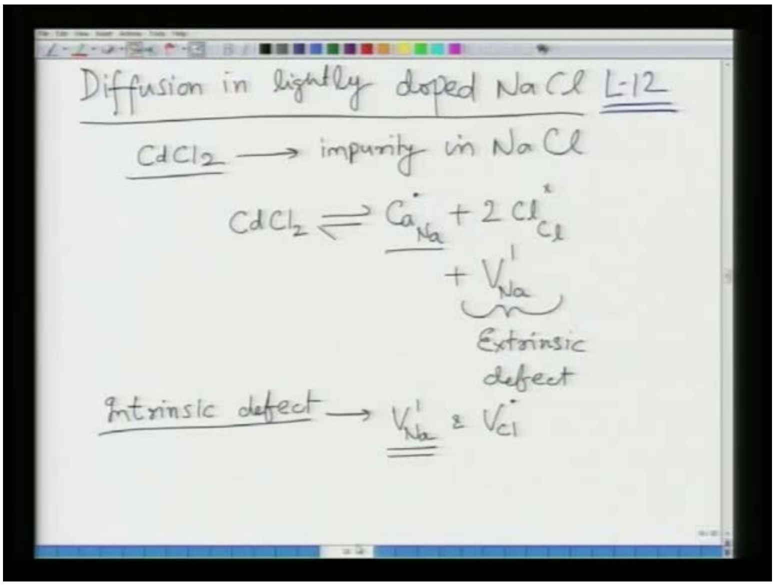

Diffusion in lightly doped NaCl L-12

CdCl2 → impurity in NaCl

$$CdCl_2 \rightleftharpoons \underline{Ca^{\bullet}_{Na}} + 2Cl^{x}_{Cl} + \underbrace{V'_{Na}}_{\text{Extrinsic defect}}$$

Intrinsic defect → V'_{Na} & $V^{\bullet}_{Cl}$

So, this is where we started the last lecture, in this lecture we discussed the case of diffusion in a lightly doped N a C l, this was done to differentiate between intrinsic diffusion and extrinsic diffusion. This is because you know that as you know that sodium chloride is a material which predominantly has shot key defects in the pure state, which means it has sodium and chlorine vacancies and sodium vacancies being more mobile are the defects which diffused.

At the same time sodium chloride in most practical applications tends to contain some impurities like cadmium chloride and these impurities give rise to again sodium vacancies. So, there is a competition between the sodium vacancies which are created thermally by means of shot key defects formation and there are and there are some sodium vacancies which are created by impurity concentration.

So, impurity concentration determines that whether you will have sodium vacancies created by the impurity or by thermal means. As we know that in impurity concentration is independent of temperature, so the vacancy concentration which is which is governed by impurity concentration is temperature independent thing.

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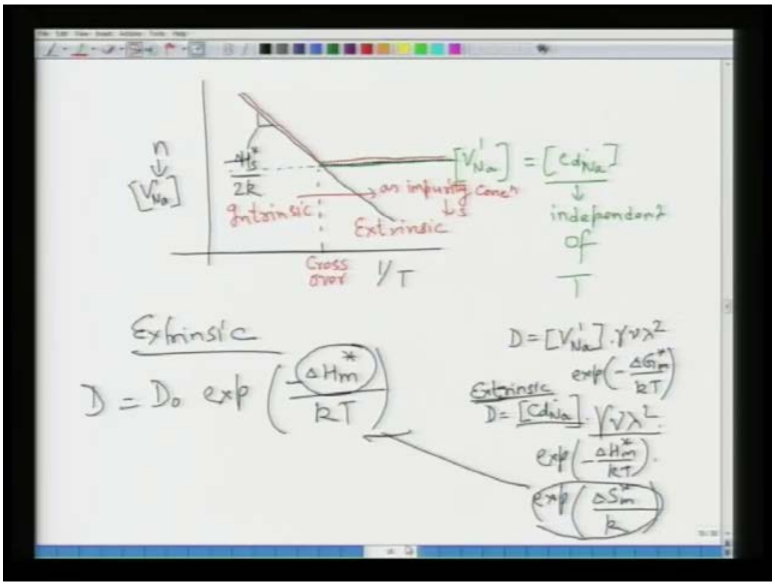

Extrinsic

$$D = D_0 \exp\left(-\frac{\Delta H_m^*}{kT}\right)$$

$$D = [V'_{Na}] \cdot \gamma \nu \lambda^2 \exp\left(-\frac{\Delta G_m^*}{kT}\right)$$

Extrinsic

$$D = [Cd^{\cdot}_{Na}] \cdot \gamma \nu \lambda^2 \cdot \exp\left(-\frac{\Delta H_m^*}{kT}\right) \cdot \exp\left(\frac{\Delta S_m^*}{k}\right)$$

So, as a result what we have here is, we have a region in which the vacancy concentration is a constant, which is determined by the a impurity concentration and when the thermally generated vacancies start increasing in number, then those vacancies dominate. So, as a result you have two regions, you have extrinsic region, which is dominated by vacancy created by the impurities. And then you have intrinsic region, which is due to vacancies created by thermal shot key defect formation or thermal means, and as a result this is also reflected in diffusivity.

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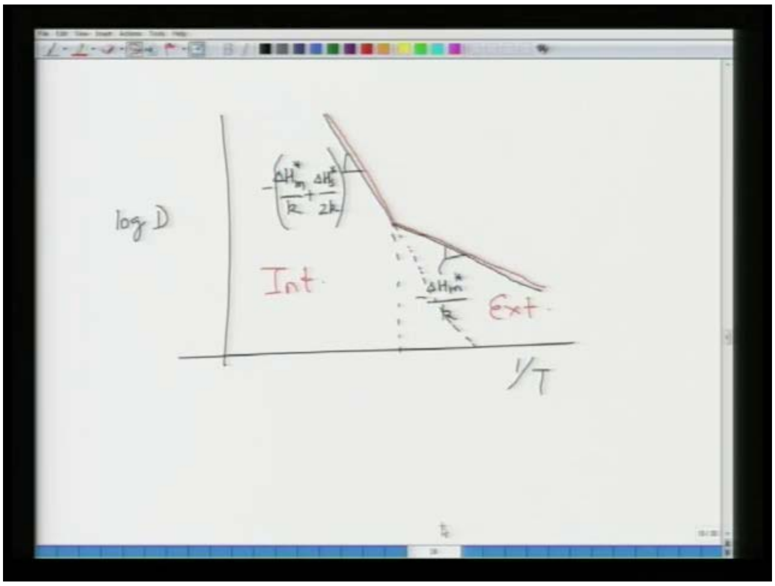

So, you have two regions of diffusivity in the extrinsic region, since the vacancy concentration a vacancy is already generated by impurities and their concentration is much larger as compared to a intrinsic or thermally created vacancies. So, the only energy barrier that needs to your overcome is the migration energy. So, in the extrinsic region slop of log D verses 1 by t curve will give you migration energy. On the other hand if you if you look at the plot on the left side.

So, there is a cross over from extrinsic to intrinsic and at the cross over the concentration of vacancy is due to thermal and impurity means are equal. In the left hand side region which is also called as intrinsic region. Now, you need to spend two energies, one energy first energy is the energy which needs to be spent in creating the vacancies and then second energy is the energy which is needs to be spent in moving these vacancies, so as a result the activation energy goes up. So, this has to be taken into consideration and as we will see subsequently this has its manifestation in the in the conductive as well.

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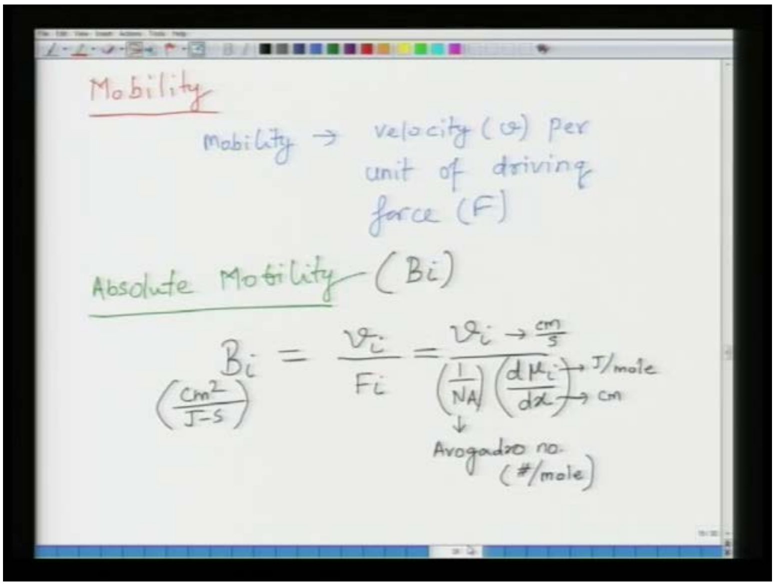

Mobility

Mobility → velocity (v) per unit of driving force (F)

Absolute Mobility (B_i)

$$B_i = \frac{v_i}{F_i} = \frac{v_i \rightarrow \frac{cm}{s}}{\underbrace{\left(\frac{1}{N_A}\right)}_{\text{Avogadro no. } (\#/mole)}\left(\frac{d\mu_i}{dx}\right)\begin{matrix}\rightarrow J/mole\\ \rightarrow cm\end{matrix}}$$

$$\left(\frac{cm^2}{J\text{-}s}\right)$$

So, and then we looked at, then we moved on to talking about properties, such as mobility which we will soon relate to electrical mobility and mobility is defined as nothing but velocity per unit of force.

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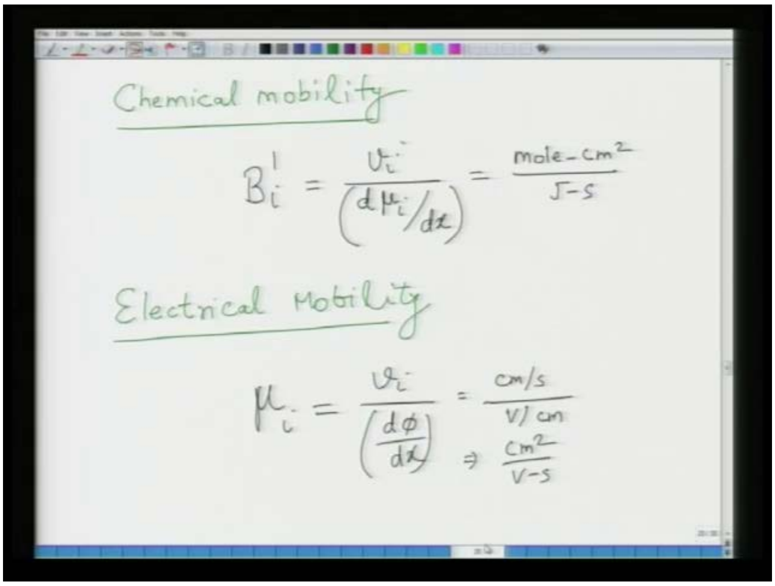

Chemical mobility

$$B_i^1 = \frac{v_i}{\left(d\mu_i/dx\right)} = \frac{mole\text{-}cm^2}{J\text{-}s}$$

Electrical Mobility

$$\mu_i = \frac{v_i}{\left(\frac{d\phi}{dx}\right)} = \frac{cm/s}{V/cm} \Rightarrow \frac{cm^2}{V\text{-}s}$$

So, there are there could be various different kinds of mobility’s in our context.

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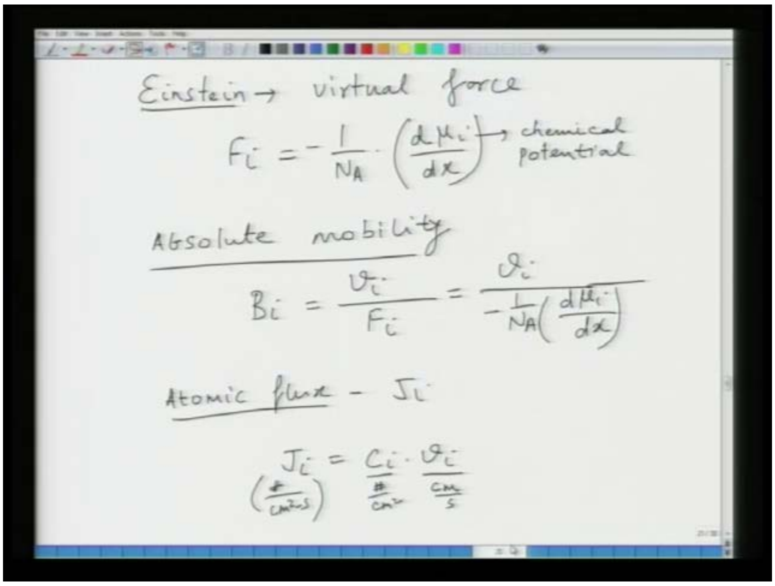

Einstein → virtual force

$$F_i = -\frac{1}{N_A}\cdot\left(\frac{d\mu_i}{dx}\right) \rightarrow \text{chemical potential}$$

Absolute mobility

$$B_i = \frac{v_i}{F_i} = \frac{v_i}{-\frac{1}{N_A}\left(\frac{d\mu_i}{dx}\right)}$$

Atomic flux - J_i

$$\underset{\left(\frac{\#}{cm^2 s}\right)}{J_i} = \underset{\frac{\#}{cm^3}}{C_i}\cdot\underset{\frac{cm}{s}}{v_i}$$

We took the hypotheses of Einstein, who said that when you have diffusion in a system as a result of chemical potential gradient, there is a force which is exerted on the spices. And this force gives rise to a mobility called as absolute mobility and from, this we can work out what is the flux.

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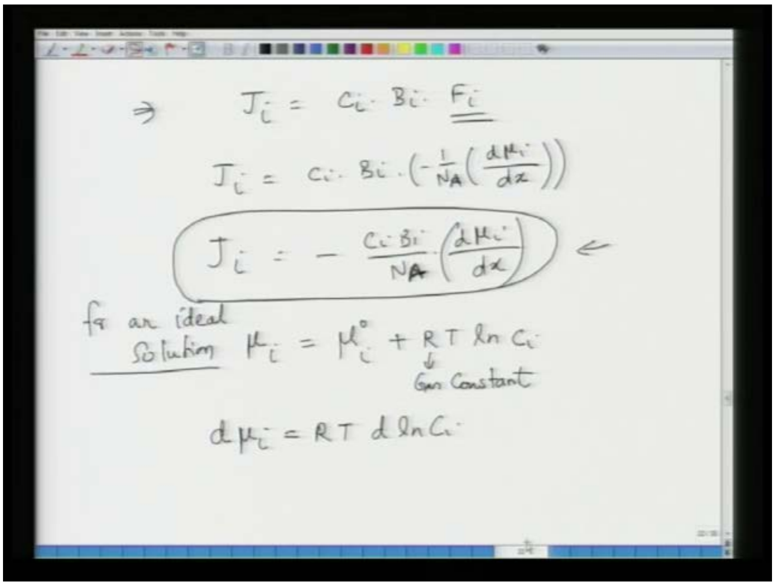

$$\Rightarrow \quad J_i = C_i\cdot B_i\cdot \underline{\underline{F_i}}$$

$$J_i = C_i\cdot B_i\cdot\left(-\frac{1}{N_A}\left(\frac{d\mu_i}{dx}\right)\right)$$

$$\boxed{J_i = -\frac{C_i B_i}{N_A}\cdot\left(\frac{d\mu_i}{dx}\right)} \leftarrow$$

for an ideal solution $\mu_i = \mu_i^0 + \underset{\substack{\downarrow \\ \text{Gas Constant}}}{R}T\ln C_i$

$$d\mu_i = RT\, d\ln C_i$$

Then we can relate this flux, in terms of chemical potential gradient which can then be converted into concentration gradient.

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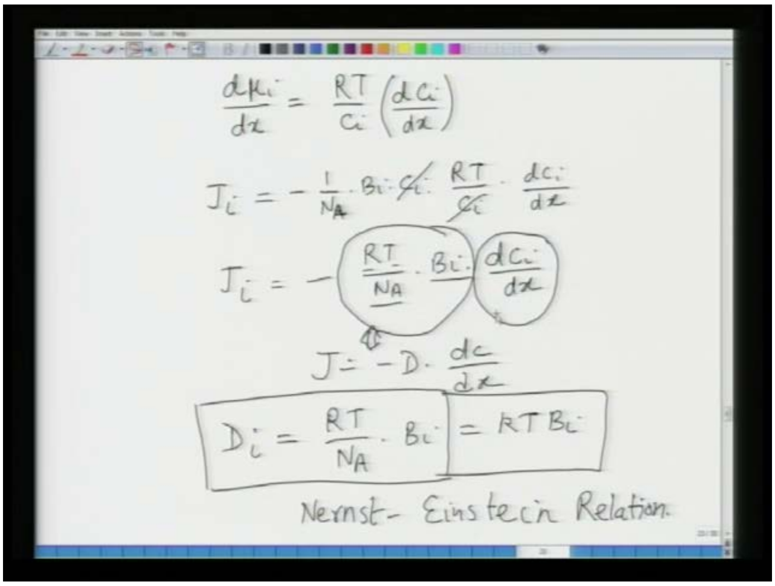

$$\frac{d\mu_i}{dx} = \frac{RT}{c_i}\left(\frac{dc_i}{dx}\right)$$

$$J_i = -\frac{1}{N_A}\cdot B_i \cancel{c_i}\cdot\frac{RT}{\cancel{c_i}}\cdot\frac{dc_i}{dx}$$

$$J_i = -\left(\frac{RT}{N_A}\cdot B_i\right)\left(\frac{dc_i}{dx}\right)$$

$$J = -D\cdot\frac{dc}{dx}$$

$$\boxed{D_i = \frac{RT}{N_A}\cdot B_i}\boxed{= RT B_i}$$

Nernst- Einstein Relation.

What we get is a relation between the diffusivity which is given from Fick’s first law, which is J is equal to minus d c by d x and this comparison between the expression which is worked out using this mobility model, or Einstein’s model is a compared with the Fick’s first law. Then you get the value of diffusivity as D i or diffusivity of species i is equal to R T, R is the gas constant, T is the temperature and N A is the absolute number, R T by N A into B i, where B i is the absolute mobility of a species i or alternatively it is equal to k T by B i. This is called as Nernst-Einstein relation; it is a very important relation because it has its own importance in the ionic conduction.

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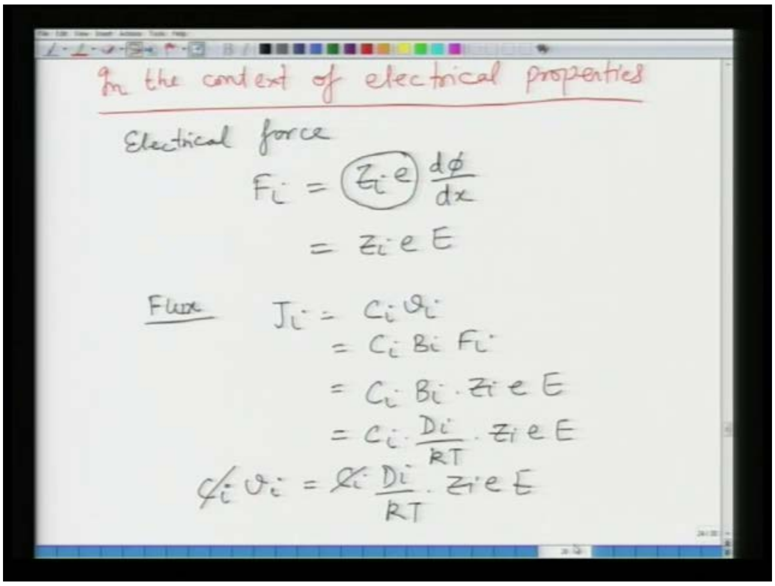

In the context of electrical properties

Electrical force

$$F_i = \boxed{z_i e}\frac{d\phi}{dx}$$
$$= z_i e E$$

Flux

$$J_i = c_i v_i$$
$$= c_i B_i F_i$$
$$= c_i B_i\cdot z_i e E$$
$$= c_i\cdot\frac{D_i}{RT}\cdot z_i e E$$

$$\cancel{c_i} v_i = \cancel{c_i}\frac{D_i}{RT}\cdot z_i e E$$

Actually in any kind of conduction, because you can do the same exercise for electronic conduction as well. Now, in the context of electrical properties, we can calculate what electrical force is, the electrical force is nothing but as you know in a electronic system like metals F is equal to e E. Now, in this ionic system it becomes F is equal to Z i e into d phi by d x which is nothing but E and then we know what flux is, flux is nothing but C i V i. So, now what we do is that we substitute for B i and F i in this expression, so we get the J i expression in terms of C i D i and E and we equated to the original expression C i V i. So, what we get from here is an expression for V i which is D i Z i E into capital E which is the field divided by k T.

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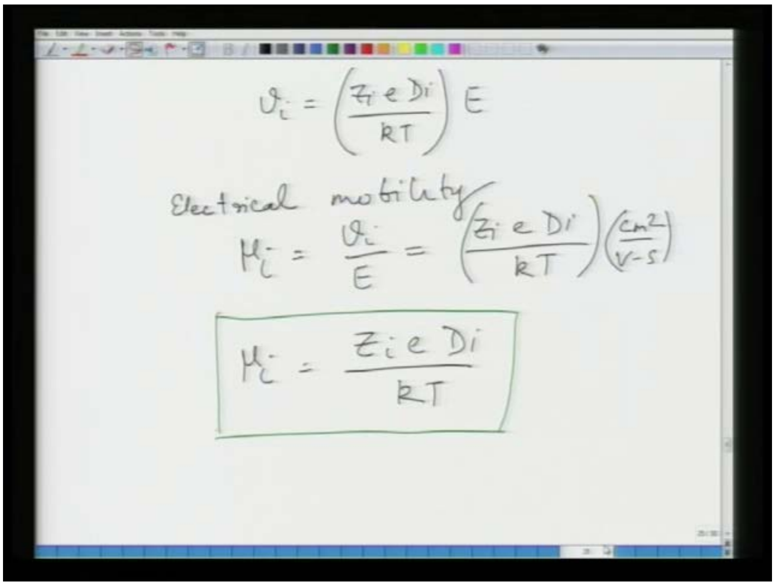

$$\vartheta_i = \left(\frac{Z_i e D_i}{kT}\right) E$$

Electrical mobility

$$\mu_i = \frac{\vartheta_i}{E} = \left(\frac{Z_i e D_i}{kT}\right)\left(\frac{cm^2}{V\text{-}s}\right)$$

$$\boxed{\mu_i = \frac{Z_i e D_i}{kT}}$$

From this what we get is the mobility, this is called as ionic mobility, this is not electronic mobility, and this is ionic electrical mobility. So, this is mu i is equal to Z i e D i by k T, because we know that in case of electrons mu i does not depend upon diffusivity, I will just come to that in a minute. Here so you have this dependence on temperature and diffusivity, so this is your mu i for ionic systems, in case of ionic defects.

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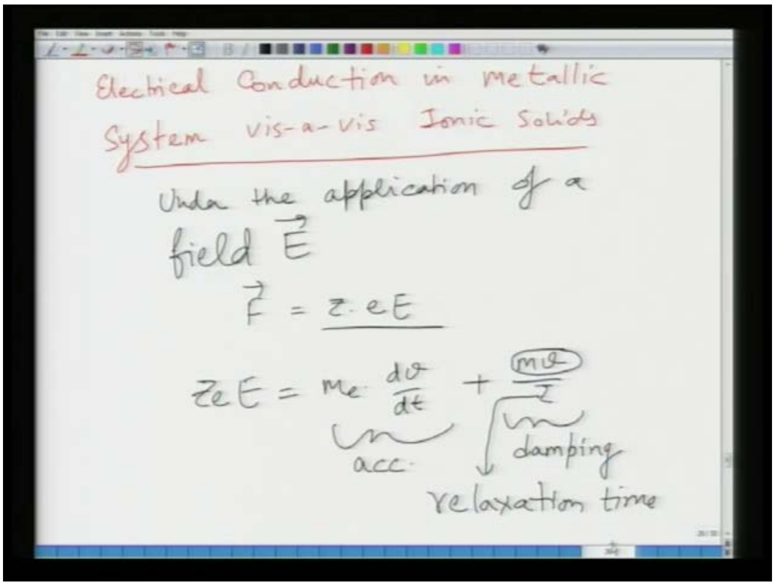

Electrical Conduction in metallic System vis-a-vis Ionic Solids

Under the application of a field $\vec{E}$

$\vec{F} = z \cdot eE$

$$zeE = m_e \underbrace{\frac{dv}{dt}}_{acc.} + \underbrace{\frac{mv}{\tau}}_{damping}$$

relaxation time

So, we just went on to compare this ionic conduction with conduction and metals.

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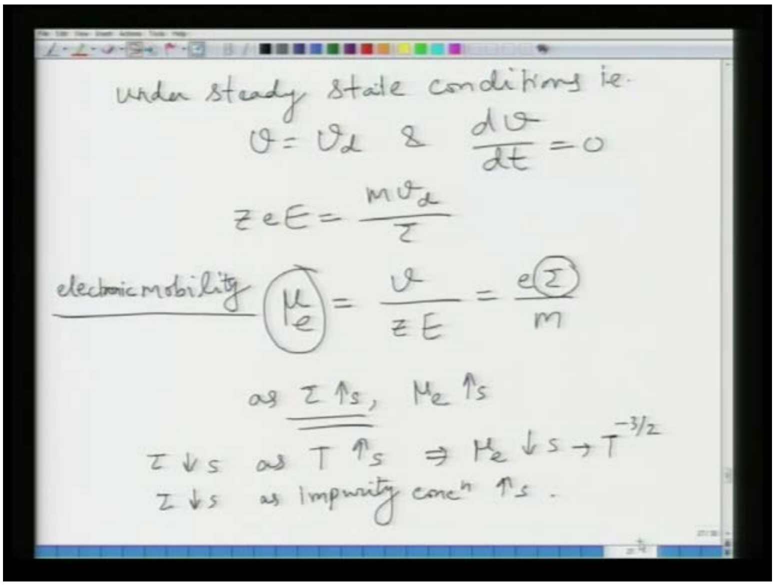

Under steady state conditions ie.

$v = v_d$ & $\frac{dv}{dt} = 0$

$$zeE = \frac{mv_d}{\tau}$$

electronic mobility $\mu_e = \frac{v}{zE} = \frac{e\tau}{m}$

as τ ↑s, μ_e ↑s

τ ↓s as T ↑s $\Rightarrow \mu_e$ ↓s $\rightarrow T^{-3/2}$

τ ↓s as Impurity concn ↑s.

In case of metals, we saw that this mu which is called as electronic mobility is again you can relate it to V divided by Z E or basically velocity by force or e E in this case. So, this becomes e Tau by m and this e Tau by m is nothing but your electronic mobility and where Tau is the relaxation time and which is the average time spent between two successful collegians. As you can see now, whatever factors increased Tau they have also result in increase in mobility.

So, typically tau decreases as temperature increases because electron phonon its scattering increases, because atoms vibrate more and more as you increase the temperature as you know. As a result electrons scatters more and this relationship goes as T to the power minus 3 by 2 and this tau also decreases as the impurity concentration increases. But as you can see there is no, there is no relation like dependence on d explicitly.

So, there is no diffusivity dependence there is there is a temperature dependence which is implicit you cannot see it here, but Tau depends upon T. So, as a result, this is the difference between electronic and ionic. Another difference between metals and ionic solids is, in metals in metals and semi-conductor a transport takes place in the bands, so it is a band transport. So, whether it is a metal or semiconductor, although the relationship of conductivity with temperature is different, because in semiconductors what happen is, as you increase the temperature the carrier concentration goes up.

However, mechanism of transport is similar in both these materials; it is called as band transport. Within band transport the electrons moves between the energy levels. Now, in case of ionic solids, the transport is called as polaronic transport and this happens by hopping and hopping is basically. So, I will come to now polaronic transport in much more detail, in contrast to metals. So, we will start this new lecture by discussion on ionic conduction.

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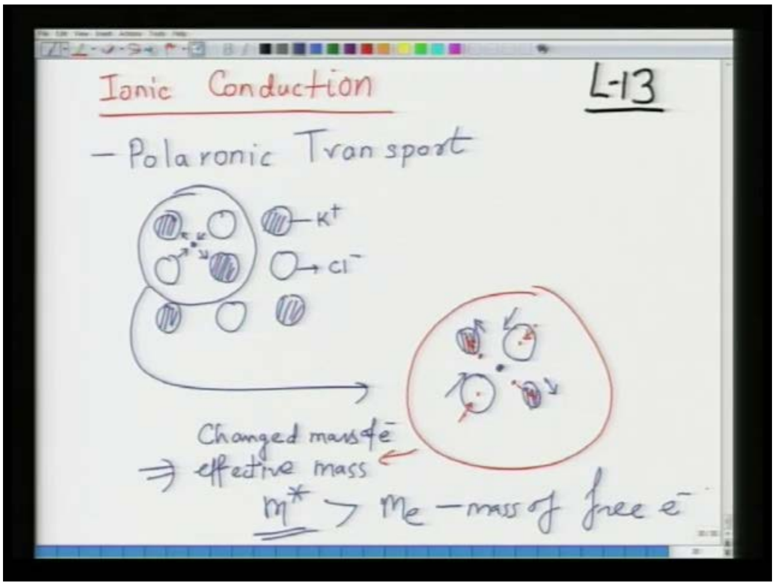

Ionic Conduction

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- Polaronic Transport

Changed mass of e^-

$\Rightarrow$ effective mass

$m^* > m_e$ - mass of free e^-

So, we are saying that this is polaronic transport. Now, what happens in these solids is, in ionic solids is, electrons is in closed proximity of the lattice, it is not free unlike in metals. So, what happens is that the moment it is in, the fact that is in the closed approximately of the lattice, it tends to polarize the lattice, now how? So, you suppose you have a lattice like this, so suppose this is your one type of ion and this is another type of ion, so let us say this is your, let us say K plus and this is let us say your C l minus.

Now, suppose you have a electron somewhere here, now when you have a electron which is localized to the lattice what happens is, this electron it pulls these ions towards it and it pushes these ions which are the positively charged away from it. So, what happens in the end is you have a distortion, so if you if you if you just zoom this area and look at it now, so what it becomes is you have electron here, so these two positive guys, negative guys sorry, they come close to this electron, so they are pushed towards as a result of coulombic attraction.

As a result of coulombic repulsion I should make them smaller they are cat-ions actually. So, these excuse me let me just redraw this picture taking the size little bigger, so this is your electron, I am saying as that these K plus ions which are the shaded ions go away, so what you have is K plus ions they go away.

So, suppose this was the equilibrium position, so both of them have moved out. On the other hand, the the chlorine ions they have come closer, so they have moved this way. So, what you have is a distortion, so this distortion results in the region which is called as a, so this this association of electron or carrier with the lattice, results in the polarization. As you know polarization is nothing but shifting of charges, charge centers away from each other.

So, for example, this center which was here earlier, now it has moved to this direction and this center which is here now it was somewhere here, so it has moved to this direction. So, this as result this has resulted in polarization of the lattice as it is called in scientific language and this whole entity is called as polaron. So, now naturally, more the polarization of the lattice, which means more closely the electron, is associated with the lattice.

So, as a result size of the polaron determines how closely, how loosely bound the electron is with the lattice. So, smaller the polaron is which means more is the interaction of electron with the lattice and larger the polaron field is, if polaron field is larger then this a small group of atoms then it is called as a weakly interacting or weakly connected, weakly weak polaron. Now, this polarization also results in changed effective mass of changed mass of electron and which is called as effective mass.

So, it is given as m star, so typically it is it is larger than mass of free electron. So, basically it has electrons in the form of polaron, carriers in the form of polaron have become heavier as compared to free electrons. So, naturally one of the repercussions of this is going to be, that is going to be difficult to move this electron now. So, it does not move and moreover, since this electron is now associated with the lattice, it does not move freely, it does not move freely in the band.

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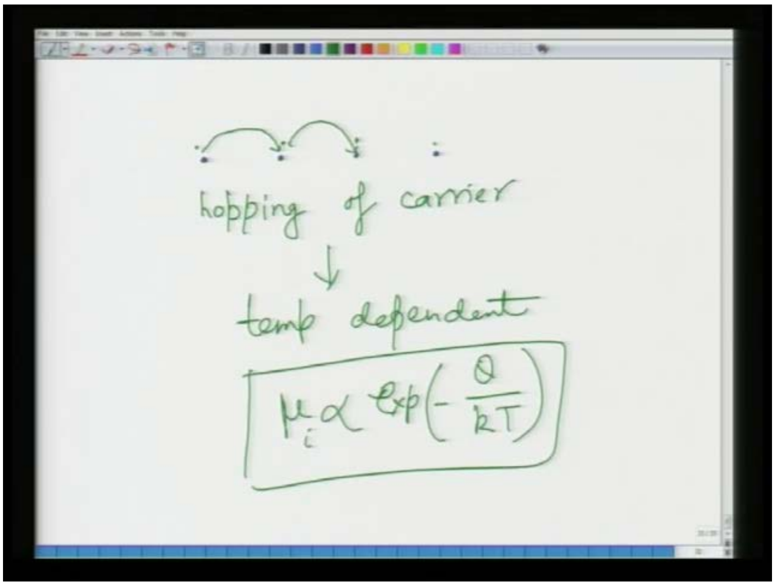

So, rather if it has to move how it moves is, so now suppose this is one site, this is another site, this is another site, this is another site and suppose the electron was associated with this site. So, what happens is it goes from this state to that state by the hopping and from this to by hopping, so basically it hops between different atomic states and this is called as you know polaronic conduction and this is what ionic conduction is basically.

So, now as you can see this since this a hopping related phenomena, so hopping of carrier and this hopping tends to be temperature dependent, just like you know diffusion. So, as a result in these systems, the mobility which you see is dependent upon temperature in the form of exponential minus some energy Q divided by k T and so this mu i would be of this form in ionic systems, as a result of this thermally activated hopping phenomena.

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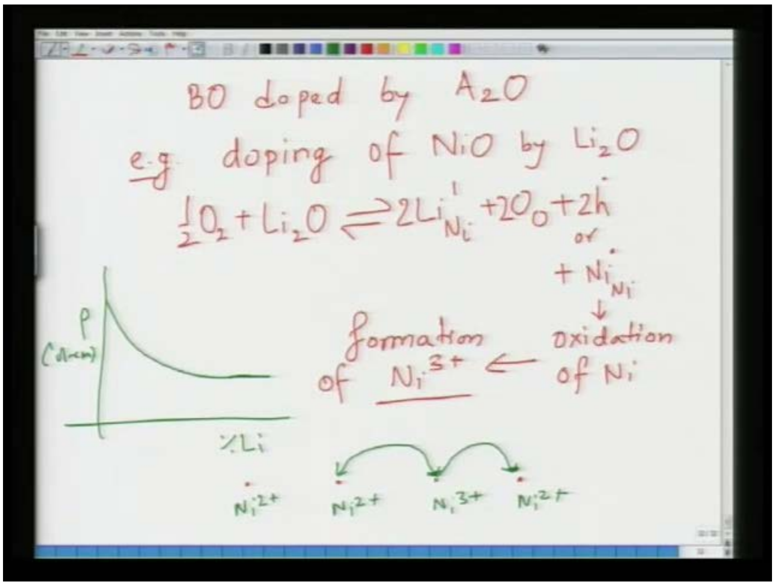

BO doped by A_2O

e.g. doping of NiO by Li_2O

$$\frac{1}{2}O_2 + Li_2O \rightleftharpoons 2Li_{Ni}^{'} + 2O_O + 2h^{\bullet}$$

or

$+ Ni_{Ni}^{\bullet}$

$\downarrow$

oxidation of Ni

formation of Ni^{3+} $\leftarrow$

So, for now this can be interpreted in various different ways. For example, you take the example of an oxide B O and this is doped by let us say A 2 O and the example in our case could be doping of N i O nickel oxide by L i 2 O. Now, when you when you dope nickel oxide by Li 2 O, what are you going to get? L i 2 O will result in L i at N i site, so when a L i goes to N i site it is going to have 1 negative charge on it and let us say you have oxygen going to oxygen site and if you have. Now, in order to maintain the site transport if you have both the L i's going to oxygen site, then you are going to form oxygen vacancy or let us say you bring in the oxygen from outside, so both the oxygen's are occupied.

In this case, what it can result in? Either the formation of a hole or you can represent this by N i at N i site, so this is nothing but oxidation of nickel, so what it means is that formation of N i 3 plus. So, what now you have is lattice sites will be like this, so some of these will be N i, most of these will be N i 2 plus and some of these will be N i 3 plus.

So, what happens is this extra electron or extra charge associated, in this case not electron, but hole. So, in this case this extra charge associated with this N i 3 plus site can be.

So, what happens is, the electron will carrier will move like this or in this case rather it will move like this, so or if the electron moves, you can imagine in whatever way, hole moving to this side or electron moving to this side. The result is when you have this movement taking place, so each of these N i 3 plus will be converted into N i2 plus and N i 2 plus will be converted into N i 3 plus. So, this will be subsequent movement from one side to another and this is why it is a hopping related, hopping kind of transport.

Now, what happens when you dope it? So, conductivity you can say, resistivity versus percentage lithium, so as you can see, as you introduce more and more lithium into it you are going to introduce more and more holes or more and more oxidation of nickel. So, what happens is, as a result you have the connectivity of this material it goes down. Straight line not a curved line, so this resistivity goes down, resistivity you can write in n centimeter. This is because of there is increase in the carriers which can move between the nickel sites. So, this is one example, you can have many example you can have formation of vacancies.

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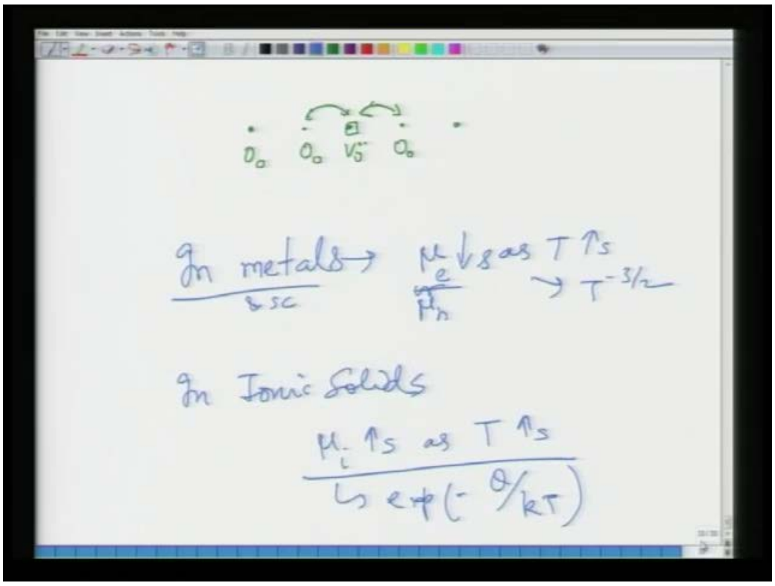

So, if you have for example, formation of vacancies then, so you have this o o sites and then you have this vacant V o site, so you will have now charge transport between these two sites or these two sites. So, charge will again move in this row of oxygen atoms giving rise to hopping kind of conduction. So, this is another, so this is basically this kind of transport is thermally activated phenomena which is which is which depends very strongly upon temperature.

So, as a result mobility is exponentially dependent upon temperature having activation energy let us say Q. Conduction in such cases is also determined by things like, what is the concentration of impurities, especially those impurities which introduce extra defects or extra carriers into the system, of course within the appropriate limits. So, typically you will find as you introduce impurities which gives rise to defects, the conductivity tends to go up, on the other hand, if you look at metals and semiconductors, semiconductors well I mean you you can increase the conductivity by doping. But if you look at the pure semiconductor.

For example in the metal as a semiconductor where band band transport is the mechanism of transport, mobility is mobility is affected by only temperature. So, this is what it is, so basically in in in to summarize this part in metals in metals and semiconductors mu decreases as temperature increases, so this is mu electronic or mu hole.

In ionic solids and this is typically T to power minus 3 by 2 relation, in case of ionic solids mu i in this case, mu i increases as temperature increases and this is because of this relation of exponential minus Q by k T. so, this basically you can imagine as if you know you have counter movement of vacancies, because as charge is associated with the vacancies. In the previous case you can say it is the movement of N i 3 plus ions, in this case it would be movement of vacancies, so instead of charge transport you must consider this rather as a ionic transport. So, that is why conductivity in ionic systems is a hopping kind of system, because here the defects move and movements of defects is nothing but diffusion.

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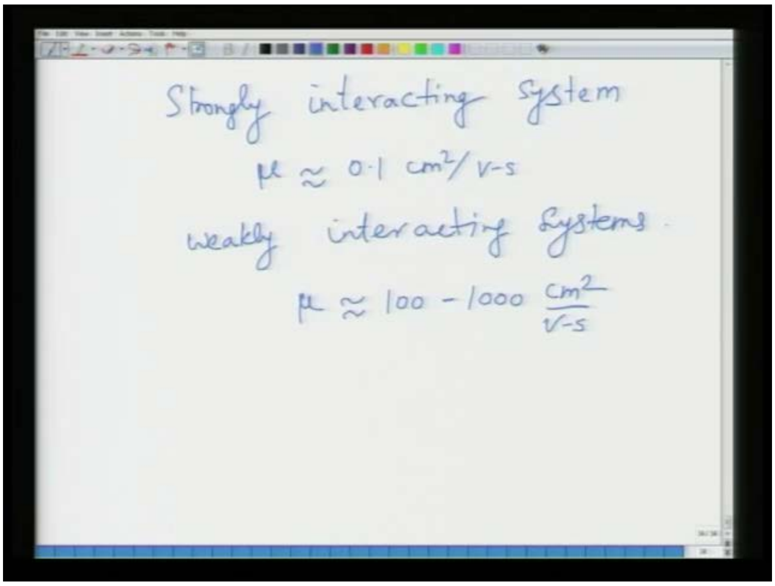

Strongly interacting system

$\mu \approx 0.1\ cm^2/V\text{-}s$

weakly interacting systems.

$\mu \approx 100 - 1000\ \frac{cm^2}{V\text{-}s}$

So, the typical typical values for mobility is, so strongly interacting systems, system where the polaron are smaller size, mu's are of the order of 0.1 centimeter square per volt second and these are about. In case of weakly interacting systems, where polaron interaction is weaker the mu's can be of the order of a 100 to 1000 centimeter square per volt seconds. So, I will give you some values of mobility's which you can just have a look and analyze them yourself.

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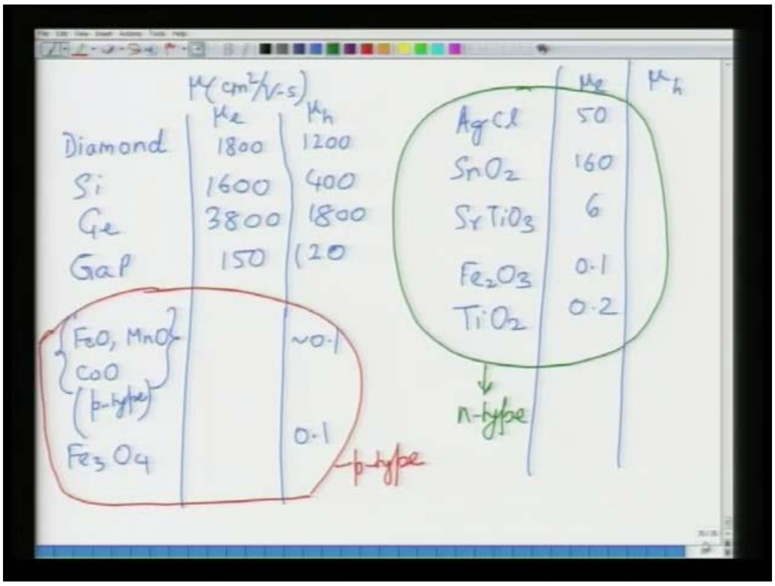

$\mu\ (cm^2/V\text{-}s)$

	μ_e	μ_h
Diamond	1800	1200
Si	1600	400
Ge	3800	1800
GaP	150	120
FeO, MnO, CoO (p-type)		~0.1
Fe_3O_4		0.1

p-type

	μ_e	μ_h
AgCl	50	
SnO_2	160	
$SrTiO_3$	6	
Fe_2O_3	0.1	
TiO_2	0.2	

n-type

So, for example, I will start with some of the ionic and non-ionic systems as well, so mu here is in the units centimeter square per volt seconds. So, for example, for diamond mu e and mu h, both electrons and holes, so this is 1800 and this is 1200. So, diamond has actually very good mobility of electrons and holes, it is just that it has a very large band gap, so as a result it is a very good insulator. Silicon on the other hand has about 1600 and 400, so silicon has more mobile electrons as compared to holes.

Germanium which is also very good semiconductor 3800, 1800 and so these are your, non-ionic covalently bonded solids. If you look at compound semiconductor like Gallium phosphide it has much smaller numbers. So, these are approximate numbers, they are not absolute numbers, they are approximate numbers depend upon various factors and now if you look at. For example, oxides like F e o, M n o or c o o these are typically metal deficient oxides. Metal deficient oxides means, you will have holes so they are typically p type conducting oxides

So these are all p-type this is already we have learnt so here the mobility is of the order of 0.1 very small. As you can see it is a very small number and these are all these are these are typically very strongly interacting systems. And if you look at things like silver chloride, silver chloride again silver chloride is more electron transport system and here mu e is about 50, units are always same in all the cases. In case of for instance tin oxide S n O 2, S n O 2 is used as a conductor in verity of applications, specially in electronic applications as a electrode layer conducting electrode layer.

If you look at strontium titanate, strontium titanate has about 6 and F e 2 O 3 has about 0.1, T i O 2 as about 0.2. In the case of p type again F e 3 O 4 tends to be p type as well this has 0.1. And so there are basically you have p type ionic solids and so these are all p type ionic solids because here whole mobility dominates over the electronic mobility. These are your, so I can write p type and these are your other one’s are your electronic predominantly electronic transport materials. And this is where your electronic mobility dominates.

So, this is these are the values as you can see the values compared very poorly with the other systems. So, these mobilities are extremely low, as compared to other materials and since, and the moment. So, we said the strongly interacting systems and we weakly interacting systems. Typically strongly interacting systems are ionic solids and weakly interacting systems would be your semi-conductors or even metals, metals there is no interaction at all they are free electrons.

So, this is the picture which emerges of when we see when we look at the difference between the ionic and metallic conduction. So, again to summarize the metallic condition is basically you have free electros in the metals, and those free electros are free to move between the energy bands. So, it is so the mobility there is purely electronic mobility and that mobility is affected only by temperature.

In case of semiconductor also although the concentration changes as a function of a temperature, again the transport is band transport and again the mobility is dependent predominant only on temperature. In case of ionic solids, in case of ionic solids the situation is different the concentration of carriers is dependent on both impurity concentration as well as temperature, but the mobility is a strong function of temperature and it depends exponentially. So, and this mobility is more like diffusivity because here that transport of charge is similar to transport of defects in the system, which is nothing but diffusion. So, that is why if you remember the previous expression in the previous lecture here somewhere here.

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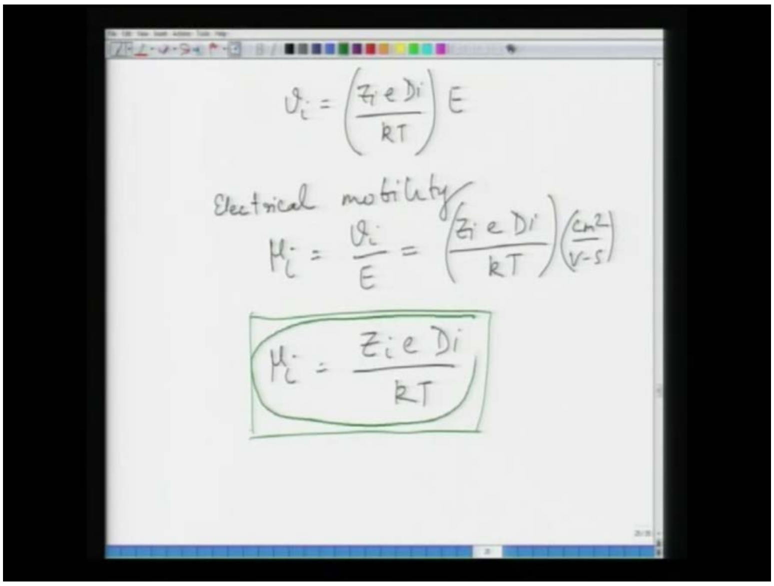

$$\vartheta_i = \left(\frac{Z_i e D_i}{kT}\right) E$$

Electrical mobility

$$\mu_i = \frac{\vartheta_i}{E} = \left(\frac{Z_i e D_i}{kT}\right)\left(\frac{cm^2}{V\text{-}s}\right)$$

$$\boxed{\mu_i = \frac{Z_i e D_i}{kT}}$$

So, here now you now you appreciate this expression more so that mu i is equal to z i e D i by k t. So, this mu i is the function of D i and this D i is a very strongly temperature dependent. So, this is the difference between metals and again, and another thing is that ionic systems are polaronic transport because here the electron is not electron is confined to the lattice sites. As a result this confinement results in polarization of the lattice and this thing whole entity is called as polaron.

So, now we will what we will do is that, we will look at the expression of the conductivity what the conductivity is like. So, we know what the conductivity is conductivity is nothing but you know charge flux per unit area flow of charge per, per unit area per unit electric field. And this has a unit of per ohm centimeter or per meter and this can conductivity is expressed as. So, what we are going to do now here is.

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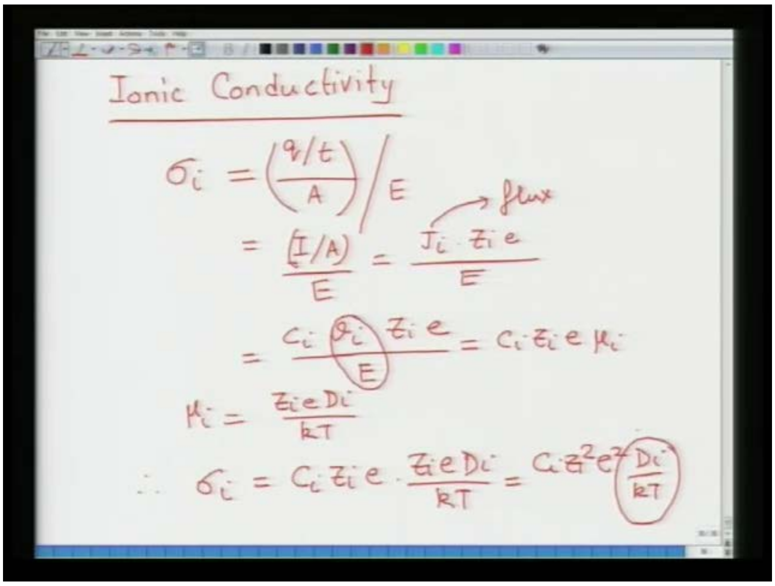

Ionic Conductivity

$$\sigma_i = \left(\frac{q/t}{A}\right) \Big/ E$$

$$= \frac{(I/A)}{E} = \frac{\overset{\text{flux}}{J_i} \cdot z_i e}{E}$$

$$= \frac{c_i \boxed{\frac{v_i}{E}} z_i e}{} = c_i z_i e \mu_i$$

$$\mu_i = \frac{z_i e D_i}{kT}$$

$$\therefore \sigma_i = c_i z_i e \cdot \frac{z_i e D_i}{kT} = c_i z^2 e^2 \boxed{\frac{D_i}{kT}}$$

So, conductivity is it is expressed as sigma i which is nothing but connectivity of i, i specie let us say and this is nothing but given as q by t which is charge per second divided by area. So, this is flux per unit area divided by your electric field e. So, this I can write as I by A into E and I by A as you know is current density. So, this would be your flux multiplied by z i e and this would be divided by E, which is the electric field. Now, if you write the expression for j i which is the flux which is nothing but c i v i. So, c i is the concentration, v i is the velocity multiplied by z i e divided by capital E which is electric field. So, this j is nothing but flux there is not current density it is flux now again for ionic systems we can use the Nernst Einstein Nernst Einstein equation.

And from this equation we saw that earlier, we saw that mu i was equal to z i e D i divided by k T. So, that is why this sigma i becomes equal to c i, so you can change this a little bit what you can do here is this becomes c i z i e into mu i because this v i by e will become mu i this is velocity per unit electric force, which is the field. So, this becomes c i z i e into mu i is z i e D i divided by k T. And this becomes equal to c i z i square e square D i by k T. So, conductivity in ionic system it depends upon concentration of course, concentration of carriers is important or defects is important, but it depends very strongly up on temperature, and temperature because this D i is a very strong function of temperature.

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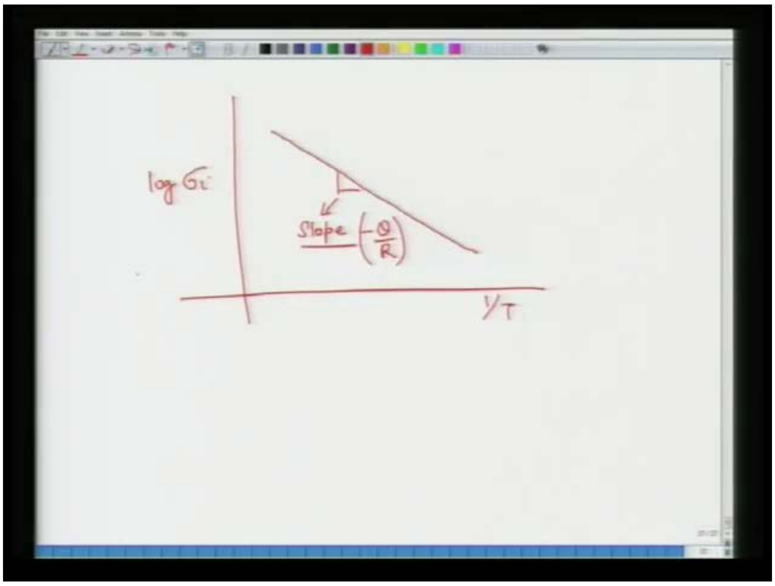

So, now when you plot this log D i verses 1 by T log sorry log sigma i and distance vary like this and this is nothing but your slope which is nothing but minus Q by R minus q by k. So, similar to now in case of if you have impured solids similar to diffusivity, you will have two regions.

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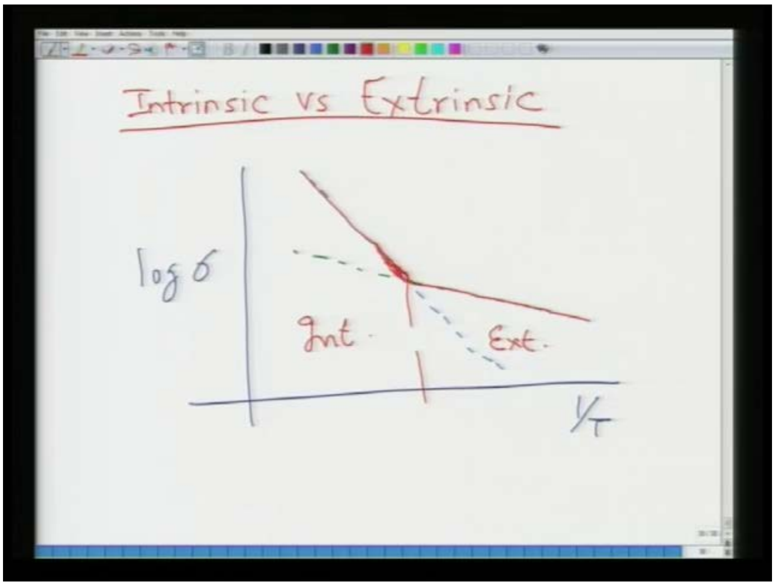

So, intrinsic verses extrinsic, so in case of systems having impurities whether intentional or unintentional it does not matter. So, you have you when you plot log D log sigma verses 1 by T you will again have. Of course, if I plot both of them separately, so this will be your intrinsic part and this will be your extrinsic part. The overall behavior would be like this is basically a straight line, my hand is not very stable. So, this is your extrinsic region this is your intrinsic region. So, again the reasons are similar as as as in case of diffusivity the only difference is that instead of diffusivity you have connectivity.

So, now what we will do is that we will now look at the so this electron and now this ionic systems they have of course, electronic ionic conductivity. As we have seen now they also have electronic conductivity the fact that they have a band gap, and they have a certain number of electrons and holes in conduction and valence band, as a result of intrinsic ionization.

So, there will always be component of electrons in whole intrinsic electron and hole concentration, which will give rise to your intrinsic conduction. So, just like in any other material. So, there will be, so the conductivity will be sum of this electronic conductivity, which is due to intrinsic electron and hole creation and some of you and your ionic conductivity you just do the defect formation. So, the total conductivity now…

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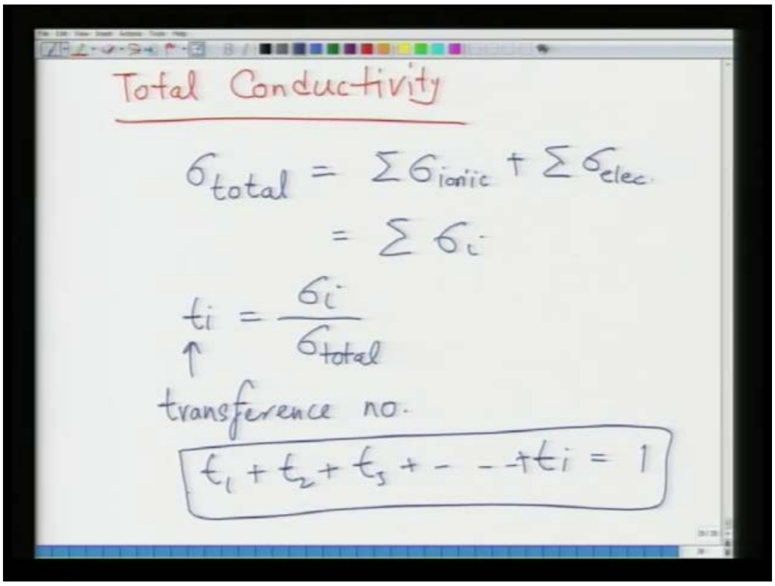

Total Conductivity

$$\sigma_{total} = \sum \sigma_{ionic} + \sum \sigma_{elec}$$

$$= \sum \sigma_i$$

$$t_i = \frac{\sigma_i}{\sigma_{total}}$$

↑

transference no.

$$\boxed{t_1 + t_2 + t_3 + - - - + t_i = 1}$$

So, the total conductivity sigma, sigma total will be basically sigma ionic so whatever ionic species are present and sigma electronic. And this will be nothing but equal to sigma i any kind of various species. Fraction of the conductivity carried by each of these species is called as fraction of this conductivity of each species to with respect to the total conductivity is called as a number which is called as a transference number. So, t i is equal to sum sigma i divided by sigma total and this is called as your transference number. Now, you can see that if this is the case then t 1 plus t 2 plus t 3 plus t i will be always equal to 1. So, this is your, so naturally when you have electronic conduction.

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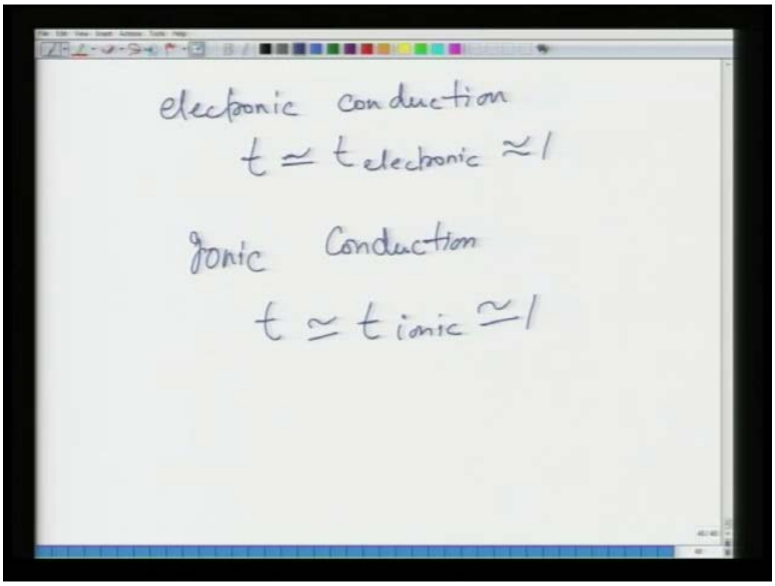

electronic conduction

$$t \simeq t_{electronic} \simeq 1$$

ionic Conduction

$$t \simeq t_{ionic} \simeq 1$$

Then so in case of electronic conduction t is almost equal to t electronic, and this will be equal to 1. In case of ionic conduction t will be equal to t ionic and this would be equal to 1, so and when you have mixed conduction then of course, t is a composition of both electrons and electronic and ionic conductivity. Now, what we will do is that I will give you some values of conductive transference numbers for various ionic systems, and that the thing to which note is that in case of in case of metals and metals their conductivities are very high. In case of ionic conductors the conductivities vary within the range 10 to the power minus 5 to at the most hundred siemens per meter.

If you look at semi-conductors and metals, these are orders of magnitude higher than what you see in metallic conductors. Atleast 3 to 5, atleast 3 to 5 orders of magnitude and in fact it could be much higher, so and the oxides are also of different types the range is massive because some oxides are easily reducible, some oxides are easily oxidizable, some oxides except impurities are much more readily as compared to other oxides.

So, as a result depending up on the characteristics in terms of defect concentration and in carrier concentration their conductivity is also very significantly. Also it is dependent up on the diffusivity of species that are present in those systems. So, I will give some of the values and then we will move on to little bit more quantitative analysis of this ionic conductivity so in case of the t values.

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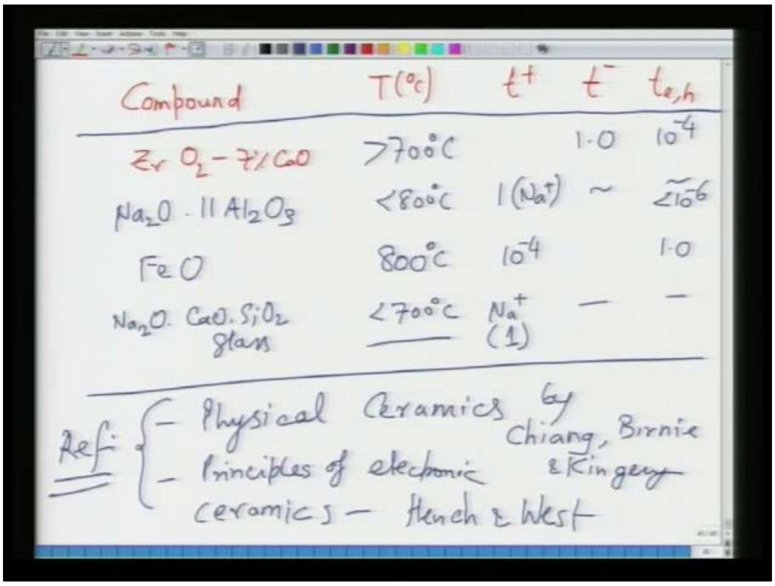

Compound	T(°c)	t^+	t^-	$t_{e,h}$
$ZrO_2 - 7\% CaO$	>700°C		1.0	10^{-4}
$Na_2O \cdot 11 Al_2O_3$	<800°C	1 (Na^+)	~	$\lesssim 10^{-6}$
FeO	800°C	10^{-4}		1.0
$Na_2O \cdot CaO \cdot SiO_2$ glass	<700°C	Na^+ (1)	—	—

Ref:
- Physical Ceramics by Chiang, Birnie & Kingery
- Principles of electronic ceramics – Hench & West

For example, I will give you so what we have is compound name or formula and this is since it is depended upon temperature, the temperature which I will range of temperature and then t plus or t minus or t electron, or hole t plus or t minus is dependent up on type of ion positively charged or negatively charged defect or ion.

So if you look at for example, zirconium oops so have done wrong Z r O 2 stabilized with 7 percent calcium oxide. And this gives you this is at a more than 700 degree centigrade and this gives you typically, hole ionic conductivity of almost ionic conductor and this t minus is because of oxygen ion conduction, defects are oxygen vacancies.

Since, vacancies move which means the oxygen ions also move that is why it is noted as t minus and this is very small 10 to the power minus 4 negligible. In case of beta, beta eliminates N a 2 O dot 11 A l 2 O 3 these are called as beta eliminates or beta alumina. This is these operate at much lower temperature as compared to the previous one and here sodium ions are the most mobile, and this is almost equal to 1. These are almost nil much smaller than 10 to the power minus 6.

Similarly, if you look at the case of iron oxide iron oxide is 800 degree centigrade approximately, and this is again iron oxide happens to be a good electronic conductor. So, as a result you have almost excellent electronic conductivity, and very poor ionic conductivity of… So, here you have a oxygen iron vacancies and those iron vacancies mean you have iron movement of iron atoms, so that is why you have t plus.

Similarly, if you look at for example, N a 2 O, C a O, S i O 2 glass and here N a plus again and it is almost equal to 1 and these are very small. This is again much lower than 700 degree centigrade. So, these are some of the typical values on in these ionic systems, you can look at the books which I provided in the bibliography. Specially the books by books of physical ceramics that gives you some of these values. Also by Chiang Birnie and Kingery and then you have principles of electronic ceramics Hench and West. These two books will be, so these two books will give you the some of the values of transference numbers in these systems.

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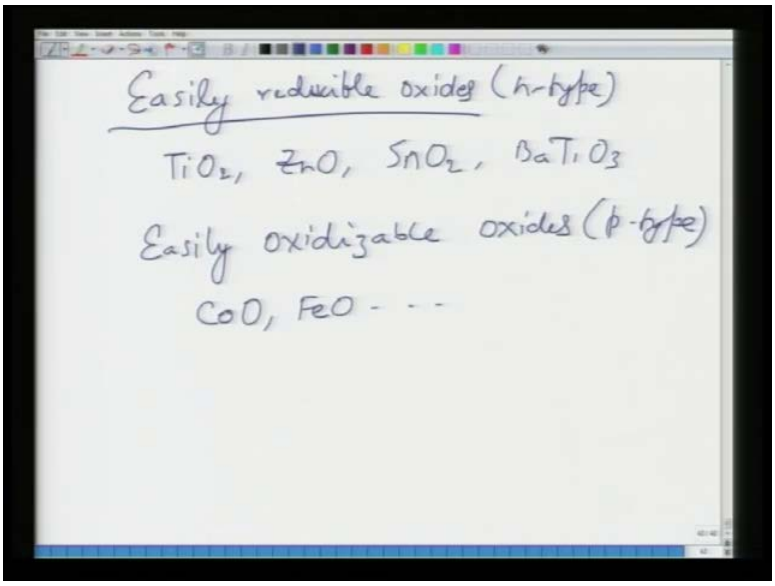

Easily reducible oxides (n-type)

TiO_2, ZnO, SnO_2, $BaTiO_3$

Easily oxidizable oxides (p-type)

CoO, FeO - - -

So, you have basically you have these in case of some of the examples of oxides, so you have easily reducible oxides and these easily reducible oxides are typically your titanium oxides or zinc oxide, which are typically your let us say n type oxides. And S n O 2 barium titanate all these are prone to having n type behavior due to creation of either oxygen vacancies, or which give rise to composite electrons are something else or you can have cation interstitial plus electrons. The easily oxidizable materials are, which are typically p type and here we look at mainly materials like cobalt oxide, iron oxide etcetera these are all p type and these are all metal deficient typically. So, these are some of the examples of these ionic conductors which are.

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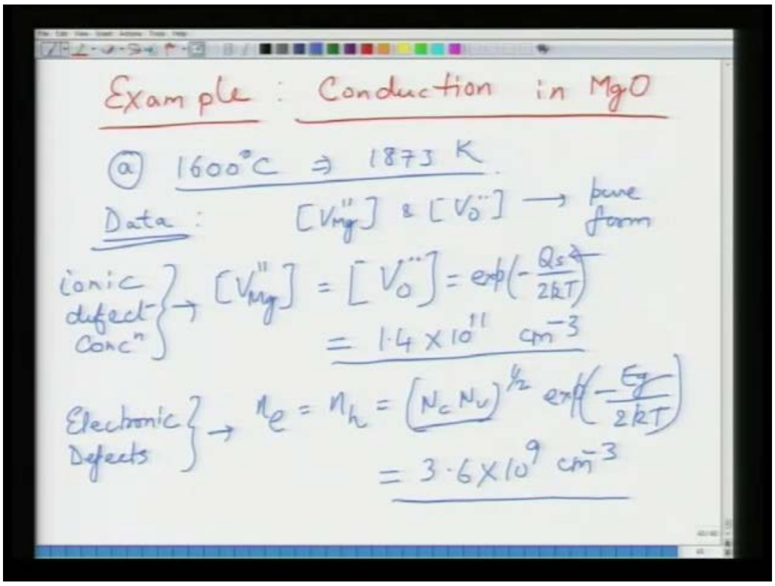

Example : Conduction in MgO

(a) 1600°C ⇒ 1873 K

Data : $[V_{Mg}'']$ & $[V_O^{\bullet\bullet}]$ → pure form

ionic defect conc^n } → $[V_{Mg}''] = [V_O^{\bullet\bullet}] = \exp\left(-\frac{Q_s}{2kT}\right)$

$= 1.4 \times 10^{11}\ cm^{-3}$

Electronic Defects } → $n_e = n_h = (N_c N_v)^{1/2} \exp\left(-\frac{E_g}{2kT}\right)$

$= 3.6 \times 10^{9}\ cm^{-3}$

So, I will we will take one example here, just to see what it means, so example we will take is conduction in magnesium oxide not that magnesium oxide is a very useful material from the conductivity point of view. We will just take this example just to illustrate our point. So, let us choose a temperature, so we choose a temperature at 1600 degree centigrade which is 1873 Kelvin. Now, the points, the data, which is given is the concentration of Schottky defects. So, this magnesium oxide will have Schottky defect which means, V m g and V o in the pure form.

So, V m g is equal to V o and this how will you calculate, you can calculate this using exponential minus Q s or h s delta h s divided by 2 k T. So, this for a given value of Q s we have looked at the values earlier and this works to be 1.4 into 10 to the power 11, 11 not 10 per centimeter cube. So, you can refer to previous lectures for the value of q and t as you know is 1873 Kelvin and this can be calculated as to be 1.4 into 10 to the power 11. So, this is your ionic defect, defect concentration.

And now your electron electronic defects concentration this is n e is equal to n h, and this is given as N c N v to the power half into exponential minus of E g by 2 k T. That you remember from the previous discussion and when we discussed the defects. You know what is N c N v that can be easily found out, and if you refer to previous lectures refer to the band gap of magnesium oxide. This value at this temperature works out to be 3.6 into

10 to the power 9 per centimeter cube. So, I know what is the intrinsic defect concentration and I know what is the intrinsic electrons and holes concentration.

Now of course, what we are looking at is we are looking at the calculation of conductivity in both the cases. And we will see what kind of conduction prevails in magnesium oxide now the diffusion co efficient. So, in order to work out the ionic diffuse ionic conductivity, you need to know that diffusivity. And diffusion in magnesium oxide takes place by movement of magnesium vacancies because magnesium, magnesium ions are smaller than oxygen ions and they tend to be more mobile.

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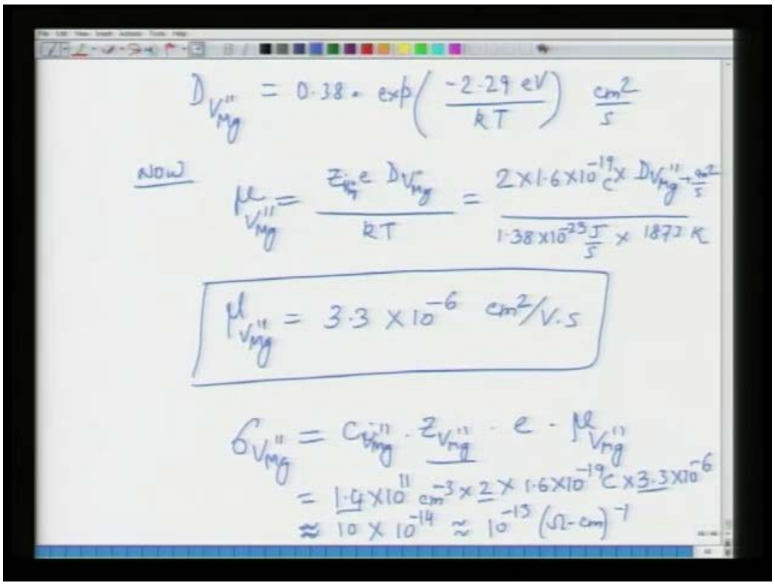

$$D_{V''_{Mg}} = 0.38 \cdot \exp\left(\frac{-2.29\ eV}{kT}\right) \frac{cm^2}{s}$$

Now

$$\mu_{V''_{Mg}} = \frac{z_{V''_{Mg}} e D_{V''_{Mg}}}{kT} = \frac{2 \times 1.6 \times 10^{-19} C \times D_{V''_{Mg}} \frac{cm^2}{s}}{1.38 \times 10^{-23} \frac{J}{s} \times 1873\ K}$$

$$\boxed{\mu_{V''_{Mg}} = 3.3 \times 10^{-6}\ cm^2/V.s}$$

$$\sigma_{V''_{Mg}} = C_{V''_{Mg}} \cdot z_{V''_{Mg}} \cdot e \cdot \mu_{V''_{Mg}}$$

$$= 1.4 \times 10^{11}\ cm^{-3} \times 2 \times 1.6 \times 10^{-19} C \times 3.3 \times 10^{-6}$$

$$\approx 10 \times 10^{-14} \approx 10^{-13}\ (\Omega\text{-}cm)^{-1}$$

As a result we take D v m g into account and D v m g is given as 0.38 into exponential of minus 2.29 electron volt divided by k t and this unit is centimeter square per second. So, this is the given value. Now you know what is the temperature so what is mobility now from the Einstein, Nernst Einstein relationship you know that mu V m g. What will this be? This will be now z e D v m g. So, this will be z v m g D v m g divided by k T and I know that for V m g z is equal to 2 into 1.6 into 10 to the power of minus 19 into D v m g divided by 1.38 10 to the power minus 23 joule per second into 1873 Kelvin and this will be in coulomb and this is in centimeter square per second.

So, if you now put in the value of temperature here and you work it out, this comes out to be 3.3 into 10 to the power minus 6 centimeter square per volt second, V m g can be calculated as C i or C v m g multiplied by z V m g multiplied by e into mu v m g. And C v m g is nothing but your defect concentration. So, this will be and z V m g is equal to 2. So, this will be 1.6 excuse me, let me just so C v m g from the previous slide, we can take this is 1.4 into 10 to power 11. So, I can see this 1.4 into 10 to the power 11 per centimeter cube multiplied by 2 multiplied by 1.6 into 10 to the power minus 19 coulomb multiplied by 3.3 into 10 to the power minus 6.

Now, if you just calculate these will be so 1.4 into 2 10 to the power 2.82, 2.8 into. So, this will be approximately 6.6 approximately 10 approximately 10 multiplied by 10 to the power minus 25 plus 11 10 to the power minus 14 approximately 10 to the power minus 13 Ohm's centimeter inverse. So, this is your ionic conductivity and now if you look at electronic conductivity.

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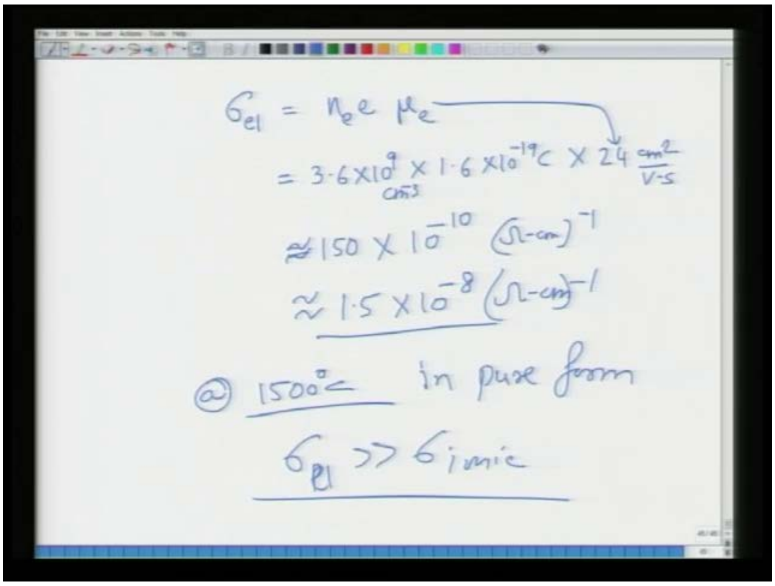

$$\sigma_{el} = n_e e \mu_e$$

$$= 3.6\times10^{9}\,\frac{}{cm^3} \times 1.6\times10^{-19}\,C \times 24\,\frac{cm^2}{V\text{-}s}$$

$$\approx 150 \times 10^{-10}\,(\Omega\text{-}cm)^{-1}$$

$$\approx 1.5\times10^{-8}\,(\Omega\text{-}cm)^{-1}$$

@ 1500°C in pure form

$$\sigma_{el} >> \sigma_{ionic}$$

Sigma electronic is so z i e, so you can say basically sigma this is equal to nothing but your n e mu e. So, n n e you know is equal to from this relation 3.6 into 10 to the power 9, 3.6 into 10 to the power 9 centimeter cube, per centimeter cube into 1.6 10 to the power minus 19 coulomb. We need mu e, mu e for these materials is approximately equal to 24 centimeter square per whole second. And if you now calculate this, this will be your approximately this will be 150 approximately, I am just doing the mental math's. So, 150 multiplied by 10 to the power minus 10 Ohm's centimeter inverse. So, this will be approximately 1.5 into 10 to the power minus 8 Ohm's centimeter inverse.

So, compare these forms so here you have sigma electronic of 1.5 10 to the power minus 8 per Ohm’s centimeter. And you have ionic conductivity of 10 to the power minus 13 per ohm’s centimeter. So, clearly in the pure form at this temperature, so at 1500 degree centigrade in pure form sigma of sigma electronic is much larger than sigma ionic. So, this is the thing in pure form. Now, what happens in the impure form, when we dope m g o with some impurity intentionally, or unintentionally that is the different issue, what happens that we will see in the next class.

Thank you.