Defects in Crystalline Solids (Part-1)

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Lecture - 06
Schottky Defects + Extrinsic Defects

So, come let us come back to where we left.

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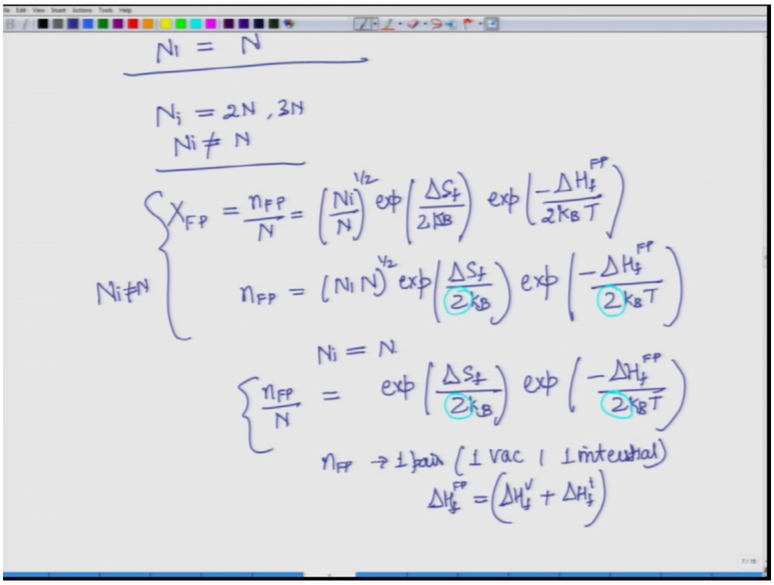

$N_i = N$

$N_i = 2N, 3N$

$N_i \neq N$

$$N_i \neq N \begin{cases} X_{FP} = \dfrac{n_{FP}}{N} = \left(\dfrac{N_i}{N}\right)^{1/2} \exp\left(\dfrac{\Delta S_f}{2k_B}\right) \exp\left(\dfrac{-\Delta H_f^{FP}}{2k_B T}\right) \\ n_{FP} = (N_i N)^{1/2} \exp\left(\dfrac{\Delta S_f}{\textcircled{2}k_B}\right) \exp\left(\dfrac{-\Delta H_f^{FP}}{\textcircled{2}k_B T}\right) \end{cases}$$

$N_i = N$

$$\begin{cases} \dfrac{n_{FP}}{N} = \exp\left(\dfrac{\Delta S_f}{\textcircled{2}k_B}\right) \exp\left(\dfrac{-\Delta H_f^{FP}}{\textcircled{2}k_B T}\right) \end{cases}$$

$n_{FP} \rightarrow 1$ pair (1 vac 1 1 interstitial)

$$\Delta H_f^{FP} = \left(\Delta H_f^v + \Delta H_f^i\right)$$

Now, there are two possibilities like I said where N i is equal to N or when N i is not equal to N. So, let us first look at when N i is not equal to N. You would see that x Frenkel pair, which is the fraction of Frenkel pair which is equal to n f p by N, it will come out to be N i by N 1 by 2 there is a factor 2 over here, will come to that why. So this is minus delta H f formation of Frenkel pair by k B T. Actually the more general form of this equation would be something like this where n F p is equal to N i times N to the power 1 by 2 oh sorry I have missed up the Frenkel 2 here, it is 2 over here. And I will come to that in a moment first let me complete this equation.

So, this is showing you the number of Frenkel pairs, the relation for number of Frenkel pairs, which is related to N i and N. Actually will derive this relation letter on also, so I am not going into the details right now. We will we will be able to see when we come to this equation from defect equilibria, as I using treating defect as a reaction. Over there you would be able to directly see, how the how it is how this comes to when an N i is not equal to N. Now, in this particular case if you make N i equal to N, so far we have assumed N i is not equal to N. Now, if you make N i equal to N, this will become n F P by N equal to e x p.

So, you have see what is the difference when you have N i not equal to N, these are the two relations for that. And when N i is equal to N, then this is how the relation looks like. There is a N i term when N i is not equal to N, which is obvious. But what is another thing that you need to see that is apart from N i relation between N i and N is this factor 2. So, we see a factor 2 over here and why does this factor 2 arise over here, this factor arises, because when we are saying n F p, we mean 1 pair which means 1 vacancy plus 1 interstitial.

So, delta H f actually represents here, the formation of vacancy plus delta H f formation of interstitial not directly in this relation, but this is just to show that this is delta H Frenkel pair is the formation of 1 vacancy plus 1 interstitial, so this is the average of those two values, which is represented by delta H f Frenkel pair by 2. And that that is where this factor 2 is arising from. So, you have 2 defects being generated 1 pair being generated, and which is represented by this equation.

Earlier we had only one defect arising or the relation was describing about one relation one defect. And again like I said when we go to defect reaction from there, we will again derive this relation. And you will see you will see more meaning to these terms. So, this was Frenkel defect.

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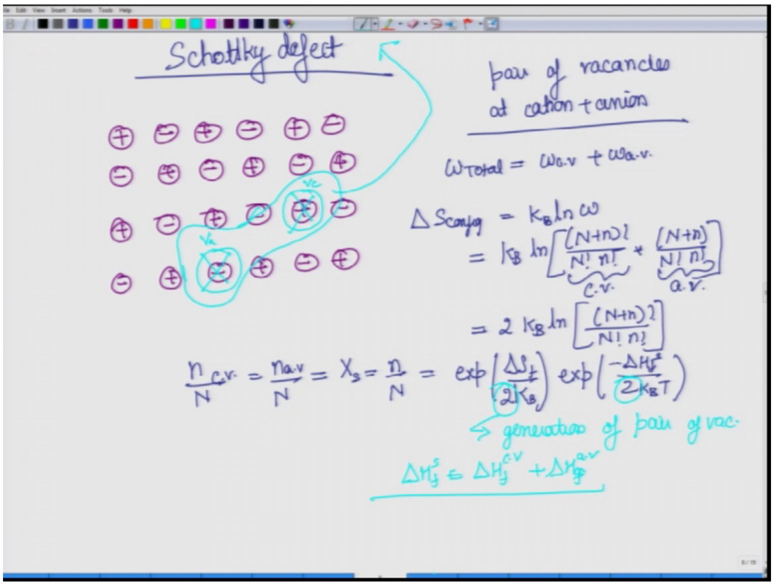

pair of vacancies at cation + anion

$$\omega_{Total} = \omega_{c.v} + \omega_{a.v.}$$

$$\Delta S_{config} = k_B \ln \omega$$

$$= k_B \ln \left[\underbrace{\frac{(N+n)!}{N!\,n!}}_{c.v.} * \underbrace{\frac{(N+n)}{N!\,n!}}_{a.v.} \right]$$

$$= 2\,k_B \ln \left[\frac{(N+n)!}{N!\,n!} \right]$$

$$\frac{n_{c.v.}}{N} = \frac{n_{a.v}}{N} = X_s = \frac{n}{N} = \exp\left(\frac{\Delta S_f}{\boxed{2}k_B}\right) \exp\left(\frac{-\Delta H_f^s}{\boxed{2}k_B T}\right)$$

→ generation of pair of vac.

$$\Delta H_f^s = \Delta H_f^{c.v} + \Delta H_f^{a.v}$$

Now, let us move onto another kind of ionic defect, which is Schottky defect. Again let us start with a simple schematic. So, what is the Schottky defect? Even before I go to the schematic, it is Schottky defect is when you have a pair of vacancies, pair of vacancies not at just any place, but at cation and anion sites. So, the there should be missing pair of atoms, one atom missing from cation site another pair missing from anion site.

So, for example, again let since we are talking about ionics solids, so we will have something like this and again like I said I will have to draw equal number of cations and anions. Now, let us take away 1 atom from over here, 1 cation from somewhere over here. So, let us say I have take, I will take away this cation and this becomes a vacancy. Now, let us take away another anion from somewhere, and this becomes a vacancy. So, this is a vacancy at this is a vacancy at minus or anion site; this is vacancy at cation site. Now, this pair is termed as Schottky defect. So, you have to have a vacancy at cation and vacancy at anion.

So, now, now that we know what is the Schottky defect, we can very easily formulate the relation the equilibrium concentration for this. Again like in the Frenkel defect, we know that w total is equal to w cation vacancy plus w anion vacancy. So, there is a subscript c v, and there is a subscript a v. And this would imply the delta S configuration, which is equal to k B l n w's. So, that derivations are very similar the only thing is what is what are will be the exact values of w over here. Since, both of them have a vacancies, so you would see that this is, in fact a little bit simpler compared to Frenkel defect and you will get.

So, like I said you can either multiplied. So, inside this log term these are both multiplied and there is meaning to it, because they are currently they are exactly same relation, but in the Frenkel defect these two terms were different here. So, one of them is representing cation vacancy, this another one is representing anion vacancy. Over there one of them was representing cation vacancy, and other was representing cation interstitial.

So, with the instead of N, we had N a number of interstitial sites. And over here, so this part becomes 2, so this becomes 2 k B l n. And therefore, if we look at the number of cation vacancies by N which will be equal to anion vacancies will divide, which will be divided by N with will be equal to X Schottky, it will be equal to or we can call it as n by N it can be written like e x p delta s f by K B exp. So, there is a 2 over here minus delta H f Schottky by 2 k B T.

So, just like in the previous Frenkel defect when we were describing the Frenkel defect, there is again a factor 2 over here, and that factor 2 represents generation of pair of vacancies. So, delta H f can be looked at as delta H f cation vacancies plus delta H f anion anion vacancies and therefore this is nothing but average of these 2 quantities. And therefore, you get this term delta by 2. So, in all other ways, this relation is similar to the one that we derived for Frenkel over there we had N as an interstitial, but here we do not have the problem N interstitial. So, in that sense it becomes much more simpler.

And again you would see that these derivations would be become much more meaningful, when we look at them from the point of view of defect reaction. Now, so far all the defects that we have talked about are intrinsic meaning, they are for pure materials, whether they are a compound, whether they are pure material. But they are if the defects are being created by those elements from themselves, so those are called intrinsic defects.

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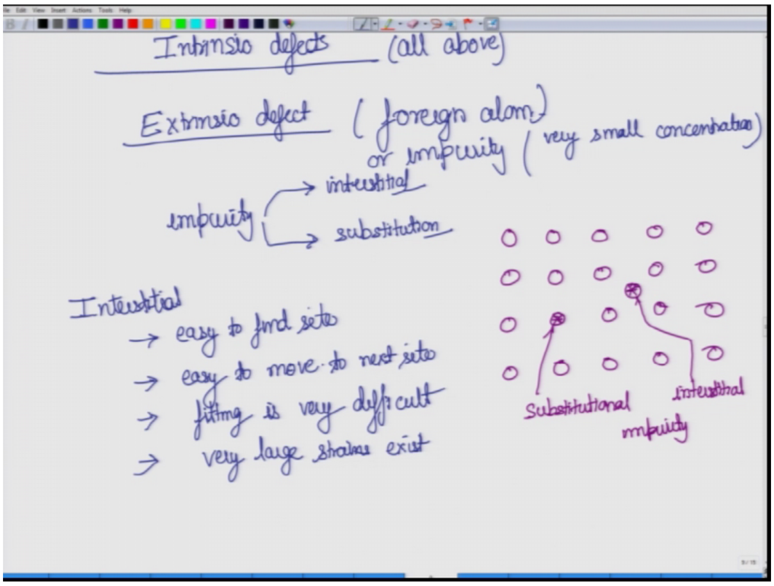

Intrinsic defects (all above)

Extrinsic defect (foreign atom)
or impurity (very small concentration)

impurity → interstitial
→ substitution

Interstitial
→ easy to find sites
→ easy to move to next sites
→ fitting is very difficult
→ very large strains exist

So far we have discussed only intrinsic defects all above defects. Now, what we are what we need to go where is where remove on is to extrinsic defects. What extrinsic defect, when you have some foreign atom involved in it or impurity. Now, impurity can be in the form again the when we have we are talking about impurity, there are few things to note. We are talking about very small concentration ok. We are not increasing this concentration to the extent that we have to discuss about solid solubility. We are much below that limit and that is something that we have to remember whenever we are talking about impurity.

So, for example, carbon in a Fe will not be really an impurity, because it is forming and (Refer Time: 11:57), it is a solution, it is in a much larger quantity. We are talking about something let us say at if you are talking about a very small fraction, like in copper in nickel. Even carbon in a Fe, carbon in a iron can be considered, if you are talking about a very very small fraction of carbon in iron ok. So, now, here this foreign atom or impurity can be in two different forms. This impurity can be classified into different ways basically there are two different ways. This impurity can get embedded; one is by forming interstitial or it goes into a interstitial site; other it substitutes one of the original atoms. So, this will be called a interstitial defect; this will be called a substitutional defect.

So, again now that we have talked about it let me show you what the schematic of it would look like. So, let us say this is one particular type of matrix the original material, and an impurity gets embedded into it. So, this is the impurity, so this is another kind of atom. Now, this is sitting at as you can see in the lattice side. So, this will be called substitutional impurity, what will be the other kind like we said interstitial. So, for example, let us say another this b atom, which is not the host atom is sitting somewhere over here. So, this is not a lattice site. So, in this case it will be called a interstitial impurity.

So, these are the two different kinds of defects, that you can see when you have foreign atom, it can either is being the interstitial site or it can be in the substitutional site. So, let us look at some of the characteristics for interstitial the although the way I have drawn it, it looks like there is sufficient space, but as you know in reality the atoms would be much much closer while. And therefore, the interstitial sites there are several kind of interstitial sites like tetrahedral sites, octahedral sites, and the and the position at the size available over there is very very small compared to the atom sites. So, that is why these are not the regular position or these are not the places where actually you find the atoms. But some of the atoms, which are smaller in size can go in and they like to stay in those places that they prefer the interstitial site.

So, in terms of number of sites where the interstitial can go since it is all empty, so easy to find site. So, that is an if an advantage, if your look, if you are interstitial atom looking for a site, then you know that there are several, because all of them are almost open so, easy to find site. If you want to migrate from one place to another, so you say that is the place where there is less energy, then you know that all the other for migration you need to jump, and you need vacancies around. So, in a in affect all other sites are vacant for you so, easy to glide or easy to move.

However, like I said this the position over here, the size over here is very very small. Therefore, fitting is very difficult, and whenever there will be atom over here in the interstitial the atoms around it the host atoms they will get displaced from the position. And because of this and this displacement would be really very large in value something like 10 percent 20 percent some very large strains, so very large strains exist, when we are talking about interstitial impurity. Will come back to interstitial.

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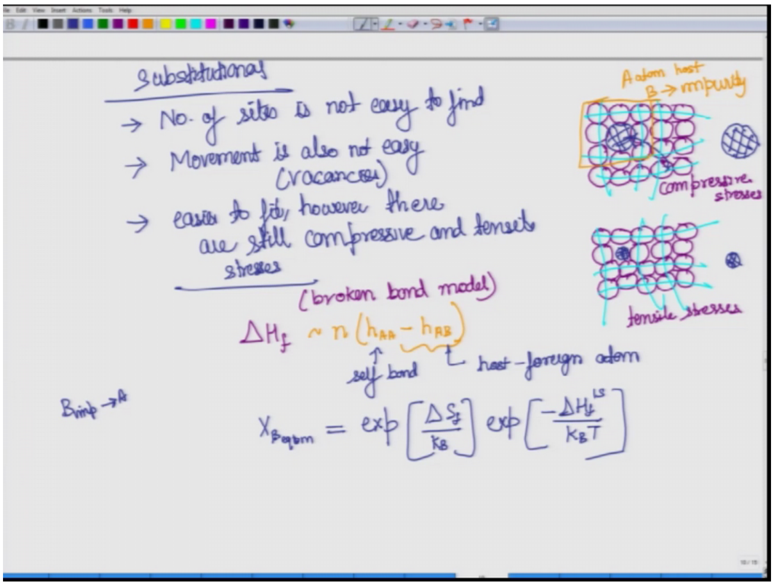

Substitutional

→ No. of sites is not easy to find

→ Movement is also not easy (vacancies)

→ easier to fit, however there are still compressive and tensile stresses

(broken bond model)

$\Delta H_f \sim n\,(h_{AA} - h_{AB})$

self bond

host-foreign atom

$B_{imp} \rightarrow A$

$$X_{B_{eqbm}} = \exp\left[\frac{\Delta S_f}{k_B}\right] \exp\left[\frac{-\Delta H_f^{IS}}{k_B T}\right]$$

Now, let us go to another defect that we called substitutional. So, what is the substitutional that we have we have already seen that. But let me show you how this will also lead to strength, now lead to strain in the system. But before that let us look at some of the characteristics like we compared for the interstitial. So, here number of sites is not easy to find compared to the interstitial, in fact it will be much better. If I re draw one of these with the more realistic system, so you have I have left this place because, I want to add a different atom. Let us say this is large atom, so this is when you have a larger substitutional atom, the other case can be it is not that only larger atoms will create a strain even the smaller one can create strain.

So, let us say we have a smaller atom over here something like this., so this will in force other atoms to relax not relax basically movement take that extra space. And this itself will also cause strain in the matrix what you are seeing in here, there are strains like this, which are compressive in nature. So, it is compressing all the atoms around it. Over here, the strains are tensile in nature the atoms are getting pulled apart. Solve there over here we have tensile stresses over here we have compressive stresses is one thing the other thing that we need to look over here is that how these atoms find site for them. So, now, like I said this is one of the substitutional atom.

So, let us say there is still another atom on the edge, which wants to move over inside the system or over here. Now, as you can see that one of these atoms will have to be displaced. So, it has it is not, so easy for it to find a site and that is what I have written over here that it is not easy to find sites. So, number of sites is not easy to find where these atoms can substitute. Once they are in let us say by one way or other they are able to find a site. Now it let us say wants to move to somewhere over here. Again that is not, so easy for that it wants vacancies. So, movement is also not easy what you need are vacancies, and vacancies are not and vacancies are very small fraction.

So, the probability of finding a vacancy is very small. The only thing advantage compared to interstitial is that easier to fit ok. It is easier to fit, however there are still compressive and tensile stresses. So, this is the direct comparison of substitutional impurity compared to the interstitial. So, the first two factors that we discussed in interstitial it was easier.

Now, finding the site is easier all the sites of a vacant in a way movement is easier because all the sites are vacancies. On the other hand for substitutional finding site is not easy all the sites are occupied by the host atom. Movement is not easy, because by for movement it needs vacancies, and vacancy concentration are very small almost always.

The on the other hand the third factors, which is fitting. So, for interstitial fitting is very problematic, because we are talking very very small volume or space inside the lattice. So, over there fitting is much more difficult and there are very very larger strains. Over here, fitting is not that big a problem it is much easier to fit. However, it does not mean that it will not create stresses in the matrix. It will still create compressive stresses and tensile stresses depending on whether you are substituting with a larger atom or a smaller atom.

Now, when we are, now that we have looked at substitutional. Now let us look at how this equilibrium concentration would look like. So, again what I will need to do is to first try to find what will be the form or how this formation energy will be related to the atoms and the bonds. Again well go back to our broken bond models. Remember we have used broken bond model. So, what you see over here is that, so let us just zoom into this region.

So, let us say we have this extra atom, which is the B atom. And the other the host is the A atom. So, A atom is host, and the B is the impurity. Now, what will be the formation energy of this would be directly related to how many bonds have been broken for the original atom if where it where there. And how many new bonds have been formed when this impurity B atom has been put there. So, it will be equal to whatever is the depending on the crystal structure there will be n number of nearest neighbors.

So, there let say this is the n this n will be n times what will the difference between h A A, which is the bonding energy between seven type of atom, which were originally present minus the bond the energy that has been released by formation of impurity atom. So, h A A minus h A B. So, this delta h formation would be related to the difference in the bonding energy between these two. If you remember that for vacancy also we said, that the formation energy would be related to the number of broken bonds. Here the bonds of broken, but there also being getting replaced by another substitute atom, so that is represented by this h A B.

So, what is h A A, it is self bonds meaning between A A atoms A B is between host and foreign bond host and foreign atom. So, B impurity in A how will be find the equilibrium concentration. So, X B equilibrium using our same old formulation we can write it like this delta S f. So, it will not be very different again it is something similar only how you how you find delta H f.

And then the entropy, and other terms would remain similar, because just like in vacancies this is substitutional atom will also be able to provide or different ways of arrangement. So, in that term configurational entropy equation would be similar all though the values might be different. And therefore, the final form of the equation as you can see is very similar to that what we found for vacancies.

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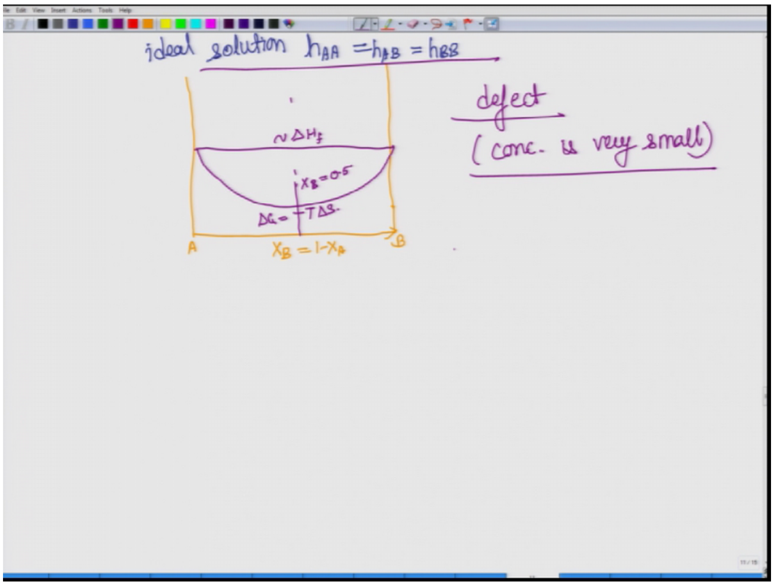

Now, here, so there can be some interesting information that we can obtain. Let us say we are talking about an ideal solution, where ideal solution where h A A is equal to h A B equal to h B B. Then how would this plot look like the delta g delta h and t delta s term. So, let us say on the n x and the x axis we have X B which is equal to 1 minus X A. So, you are going from pure A to pure B. So, initially we are talking about impurity in B. So, we are somewhere over here, now since h A A is equal to h A B.

If you go back what you see is that, when h A is equal to h A B. Then delta h formation would be equal to approximately 0. And therefore, the delta H term would be equal to delta this will be the delta H formation, which is almost 0. So, it remains constant. Now, the other term which is the minus T delta S, which will dominate the g term it would look something like this. So, we have a relation our we have the plot for minus T delta S. And this will be if you are assuming h A A equal to h A B, then this will be equal this will be minima at X B equal to 0.5.

And this will also be the real equation or a plot for delta G. So, this is how delta G would look like for in the condition of ideal solution. However, like we said we should not extrapolate these two very large concentration. We remember we are talking about defect and for that we have already made an assumption that concentration is very small. So, we must keep this value very small and not considered the larger values. So, we will come back to this and we will also look for another we look at other situations particularly non-ideal situation. In fact, I would suggest that you look at it, and see how it will vary. So, I will leave you at that and we will come back in the next lecture.