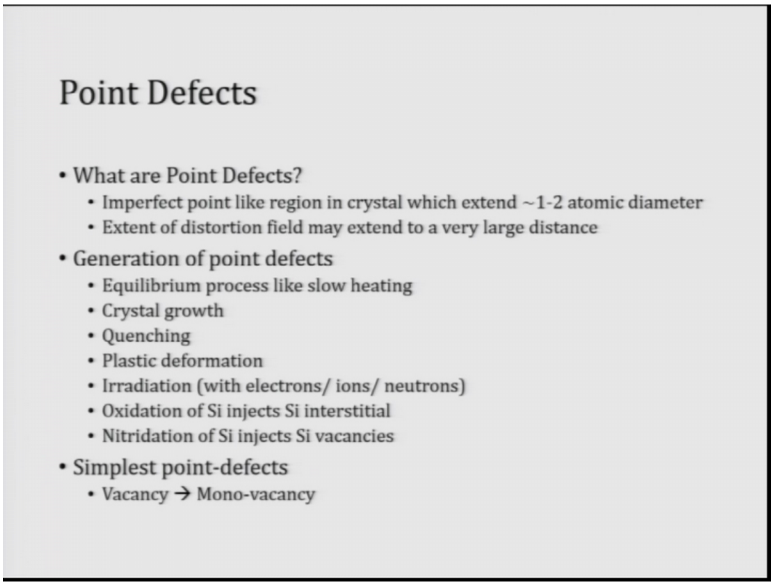
Defects in Crystalline Solids (Part-I)

Prof. Shashank Shekhar
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 02
Equilibrium Point Defects

So welcome back. So, last lecture was about introduction introducing you to various kinds of defects, now we move on to one particular type of defect. Let us start with the 0 dimension point defects and what is the simplest point defect that we can have? It is the vacancy or the mono vacancy. So, to begin with let us ask the question what are point defects ok.

(Refer Slide Time: 00:44)



Point Defects

- What are Point Defects?
  - Imperfect point like region in crystal which extend ~1-2 atomic diameter
  - Extent of distortion field may extend to a very large distance
- Generation of point defects
  - Equilibrium process like slow heating
  - Crystal growth
  - Quenching
  - Plastic deformation
  - Irradiation (with electrons/ ions/ neutrons)
  - Oxidation of Si injects Si interstitial
  - Nitridation of Si injects Si vacancies
- Simplest point-defects
  - Vacancy → Mono-vacancy

So, I said discontinuity in crystalline system is defect, but what is point defect how would you define point defect. So, point defect is defined as imperfect point like region in crystal. So, it is very much like a point which extends up to approximately 1-2 atomic diameter.

So, in a crystalline material you would be seeing some defect which is extending only 1-2 atomic diameter, then you can call it point defect. Because point if you go by mathematical definition is no dimension and therefore, it should be it should not exist at all for that matter.

But in terms of this subject, we define point defects when they are extending to 1-2 atomic diameter. However, it may be just point a very small dimension 1-2 atomic diameter; however, there distortion field and their effect stresses and forces can be felt up to a very very large extent. So, that is something that we must keep in mind that defects are not look very localized they always have effect on a very broad or larger scale.

Next we need to understand how these defects are generated. Now in there can be equilibrium for processes or there can be non equilibrium process. Equilibrium processes are simple like slow heating, if you start a material which is already at equilibrium with equilibrium concentration of point effects and if you keep heating it at a very slow rate, then with increase in temperature, there will be some generation of point effects which will be at equilibrium with that temperature.

However there are other non equilibrium processes which lead to generation of point defects and that point effects may not be in thermal equilibrium, meaning that is the density of the defects may not be equal to what is expected, it may be higher or lower in such cases most of the time it will be higher. So, what are these methods for example, crystal growth?

Growing interphase does not have to produce equilibrium amount of defects. So, for example, you are growing a crystal let us say in a single crystal method or a poly crystal method, now there will be a liquid solid interface. Now that interface does not have to produce that equilibrium amount of defect it can produce more than that it can produce less than that most of the time like I said it is higher temperature. So, it will produce higher number of defects and therefore, this will also lead to point defects.

Quenching. So, you are let say at higher temperature obviously, if because of higher kinetics or higher mobility, the defects may whatever the larger fraction of defects that are supposed to exist at that temperature would be generated and they will attain equilibrium. So, there will be large fraction of defects, now you suddenly cool it. Now the defects do not have enough mobility to anneal out and therefore, all those defects have been quenched in. So, they will remain in the material.

Plastic deformation; when you do plastic deformation there will be dislocation claims and whenever dislocations claim they leave behind vacancies. So, this is again generation of point defects and when we are doing plastic deformation we have density dislocation density of the order of 10 to the power 14 per meter square, the unit is per meter square because as we dream as we remember from the descriptors dislocations have length per unit volume. So, it will boil down to per meter square. So, it is of the order of 10 to the power 14 per meter square.

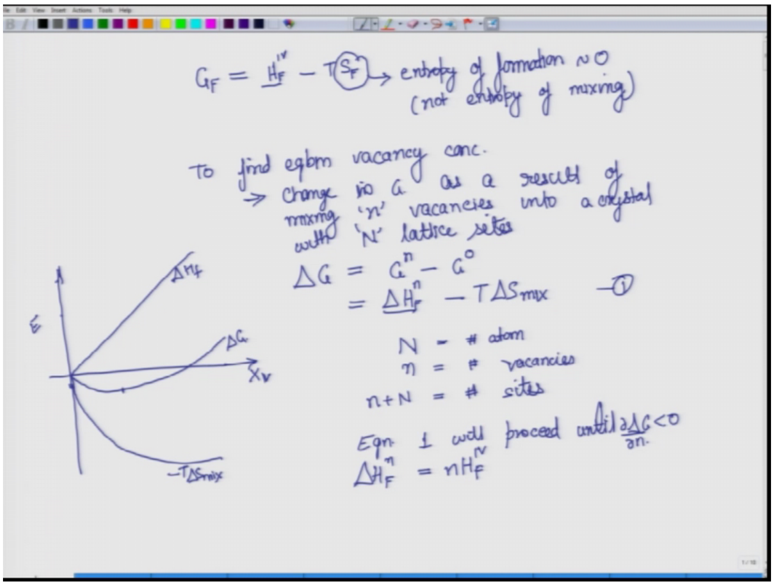
Now, the plus these defects can also be generated because of irradiation, irradiation of electrons, irradiation of ions, irradiation of neutrons for example, in at atomic reactors they produce large very very large number of point defects. In fact, irradiation with neutrons leads to increase in volume. So, that is one place we are you can actually see change in density because of presence of point defects.

Another source for generation of point defects is oxidation of silicon. So, whenever oxidation of silicon takes place then some amount of silicon gets injected into interstitial sites. Similarly whenever nitridation of silicon takes place then some amount of silicon vacancies are injected. So, all these are processes by which defects are generated.

To begin with to, in order to understand to be to extend our course, we will start with one of the simplest point defects and what is one of the simplest point defects let say we are in a single pure material and to be even simpler we will talk about metals then we are talking about vacancies. And even vacancies can be mono vacancies, dye vacancies, there can be cluster vacancies, but we will not get up to begin with we will just start with mono vacancies. So, we are talking about unit point defects or unit missing atoms which are mono vacancies.

So, now let us look at to begin with what we will do is, we will try to understand what is the enthalpy of formation.

(Refer Slide Time: 06:22)



$G_F = \underline{H_F^{1V}} - T\boxed{S_F^{*}} \rightarrow$ entropy of formation ~ 0 (not entropy of mixing)

To find eqbm vacancy conc.

→ Change in G as a result of mixing 'n' vacancies into a crystal with 'N' lattice sites

$$\Delta G = G^n - G^0$$
$$= \underline{\Delta H_F^n} - T\Delta S_{mix} \quad -①$$

N - # atom

n = # vacancies

n+N = # sites

Eqn 1 will proceed until $\frac{\partial \Delta G}{\partial n} < 0$

$\Delta H_F^n = nH_F^{V}$

So, let say it has given that the enthalpy or the Gibbs free energy of formation. So, I will say subscript F is and the superscript is 1V to denote one vacancy minus T S again F. So, this is entropy, now this entropy you must be careful this is entropy of formation.

Now, later on we will deal with entropy of mixing. So, this is not the same entropy we are talking about, this is the entropy of formation and this is usually 0. To begin with and again to make it simpler, our calculation will take this as 0 and this is not entropy of mixing.

Now our next step is that since there is energy reduction with the formation of vacancy. So, there will be more and more vacancies getting formed. So, what is that equilibrium concentration? Because as you keep increasing the vacancy there will be change in the entropy of the overall system, where is that change in the entropy? Because when you do the mixing then there is a configurational entropy or how many ways you can mix it, reduces the overall energy of the system. So, that way the total energy reduces and, but at the same time the H factor the H term keeps increasing. So, there would be our you can say counterbalance to H by this entropy term and therefore, there will be a minima in the G which is what we want to find at what fraction of vacancies in the system that minima occurs.

So, let us say that as a result we what we need to find is, to find equilibrium vacancy concentration. So, what we need to do is find change in G as a result of. So, let us define some numbers as a result of mixing n vacancies. So, we want this is a unknown number n into a crystal with N lattice sites ok. So, what we are assuming here is that, there is a system where there are N lattice sites and we will be introducing n number of vacancies into it.

Now, what will be the change in this? So, this change can be denoted by delta G which will be G n minus G naught. So, G naught is when you have 0 vacancies, N is when you have n number of vacancies and since you have since you are mixing it in the lattice sites the vacancies are being mixed in the lattice sites. So, this can be related as delta H formation n. Here I am putting the superscript n meaning this is the formation enthalpy of formation for n number of vacancies and this time the delta is that I am using is the delta S mix.

So, let us call it equation one for the timing. So, this is the change in delta G. Approximately what we are saying is that something like this will occur, where delta HF is increasing like this and we are assuming that delta S which is the entropy is leading to the lowering because there is a minus term over there. So, this is minus T delta S mix and as a sum of these two the delta G is varying like this.

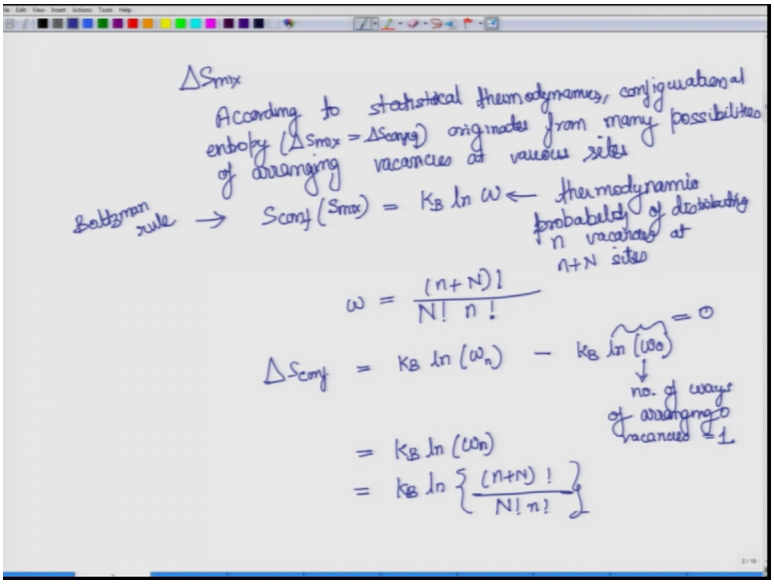
So, somewhere delta G is minimum and the. So, here let us define this is fraction of vacancies. So, let us call it X V and this is energy, which can be Gibbs free energy, enthalpy energy or anything. So, this is delta G minus T delta S is also in the energy units. So, all these are energy and one is increasing the other is decreasing, and because of that the there will be a counter balancing act on the delta G and we should get some minima is what we are saying.

Now, here again let me clarify what we have said earlier that it is N is equal to number of atom sites n is equal to number of vacancies. Now if we are already incorporating let us say in the final state the number of vacancies have been incorporated therefore, n plus N would be the total number of sites. So, now, this is another quantity that we have to remember which is n plus N.

Now, like I said this reaction which is equation 1 will proceed until delta G is less than 0, delta G meaning change in the. So, here we are talking about del delta G by del n. So, this will keep on in we can keep adding vacancy is as long as delta G change in the delta G with respect to n is less than 0.

Now, for that what we need to find here is what is what will be delta HFN we have already defined delta HF 1v, but we do not know yet what will be delta HFN for that we can take an approximation that delta HFN is nothing, but n H 1v. So, the change in enthalpy in the formation of n number of vacancies is equal to change in the enthalpy of one vacancy times n vacancies. So, since we had n vacancies this becomes n times HF. Actually it should be an delta HF, but since we have already we are talking with respect to initial and final. So, this will become delta HF, but for the sake of simplicity we will let it be as it is right now. Next what we need to find is this term T delta S.

(Refer Slide Time: 13:32)



ΔS_{mix}

According to statistical thermodynamics, configurational entropy ($\Delta S_{mix} = \Delta S_{config}$) originates from many possibilities of arranging vacancies at various sites

Boltzman rule → $S_{conf}\,(S_{mix}) = K_B \ln \omega \leftarrow$ thermodynamic probability of distributing n vacancies at n+N sites

$$\omega = \frac{(n+N)!}{N!\; n!}$$

$$\Delta S_{conf} = K_B \ln(\omega_n) - K_B \overbrace{\ln(\omega_0)}^{=0}$$

$\downarrow$ no. of ways of arranging 0 vacancies = 1

$$= K_B \ln(\omega_n)$$

$$= K_B \ln\left\{\frac{(n+N)!}{N!\, n!}\right\}$$

Now, this is delta S mix what is delta S mix? According to statistical thermodynamics, this configurational entropy which is also which is the other name for mixing this configurational entropy which is delta which is also delta S mix equal to delta S configurational originates from many possibilities of arranging these vacancies.

So, now let us take example of just 0 vacancy how many ways can 0 vacancies be distributed or arranged in a N lattice system. So, that will be only 1 ok. So, in that case it would mean that delta X is equal to 0 that we will see. So, let say now. So, what is this statistical thermodynamics saying that according to this statistical thermodynamics, configurational entropy originates from many possibilities of arranging vacancies among sites.

So, now let us move on to what will be the definition of this S configurational which is also the S mix. then according to the Boltzmann rule this can be given as KB ln W now again this new term is with KB is the Boltzmann constant. So, this is from Boltzmann law.

So, now again a new term is being defined. So, we started with the understanding delta s mix, but now we have come up with another term which is W what is this W? This W is thermodynamic probability which represents number of different ways of distributing n vacancies of distributing n vacancies at n plus N sites and again this is simple combinatorics and if you have n vacancies and n plus N sites, it can be easily shown that this W is equal to n plus N factorial divided by N factorial divided by small n factorial.

So, now we have this W, but now this W is which was earlier unknown, but the way it has been defined now we are able to find a relation for it find a value for it. So, if we find value for it we already know Boltzmann constant. So, we will be able to find entropy. So, the change in entropy which is from the state where there is no the vacancy to the state where there is a vacancy will be given like this KB ln W n minus KB ln W 0.

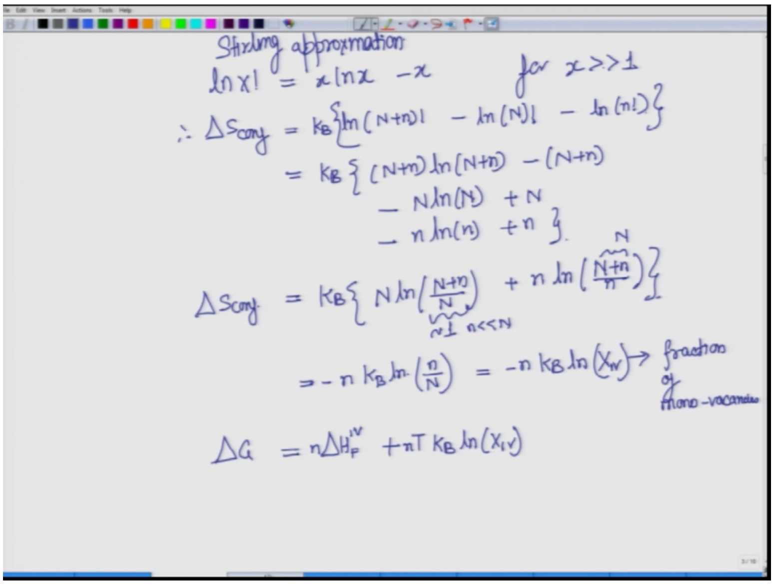
What is this W 0, W 0 is number of ways of arranging vacancies even if we talked about 1 vacancy it would become lot more ways, but we are talking about 0 vacancies. So, now, just imagine that there is a perfect crystal and you want to add 0 vacancy meaning no vacancy into it meaning the overall site remains as it is. So, there is only one way and therefore, this W naught becomes equal to 1 and therefore, this ln W naught becomes equal to 0 ln W ln one is equal to 0.

Therefore delta S configuration is now defined as ln W n now we need to find this ln W n which is already given here. So, it is KB ln n plus N factorial by N factorial by n factor by small n factorial. So, this is our delta S configuration.

So, now we have seen that to find what is the change in the energy with respect to adding of vacancies there are two terms delta H formation, which we have for n vacancies which have you have equated as n times delta H formation of one vacancy and the other term which was the entropy term we have now defined it in these terms.

So, now we have both the relations. So, now, we should be in a position to simplify it ok. So, because what we have right now is delta S configuration in a factorial term, log inside the log we have a factorial term and for this.

(Refer Slide Time: 19:14)



Stirling approximation

$$\ln x! = x \ln x - x \qquad \text{for } x >> 1$$

$$\therefore \Delta S_{conf} = K_B \{ \ln (N+n)! - \ln (N)! - \ln (n!) \}$$

$$= K_B \{ (N+n) \ln (N+n) - (N+n) - N \ln (N) + N - n \ln (n) + n \}$$

$$\Delta S_{conf} = K_B \{ N \ln \underbrace{\left(\frac{N+n}{N}\right)}_{\sim 1 \; n << N} + n \ln \left(\frac{\overset{N}{\widetilde{N+n}}}{n}\right) \}$$

$$\Rightarrow - n K_B \ln \left(\frac{n}{N}\right) = - n K_B \ln (X_{iv}) \rightarrow \text{fraction of mono-vacancies}$$

$$\Delta G = n \Delta H_F^{iv} + n T K_B \ln (X_{iv})$$

The well known Stirling approximation is used. So, using Stirling what is this Stirling approximation this is ln times X factorial is equal to x ln x minus x, this is true only when x is much much greater than one much larger than 1 and therefore, our relation which said that delta S configuration is equal to KB ln and you can say this is the denominator can be put as negative of log. So, minus ln N factorial the upper case N and then also the smaller case n.

So, now we will have to apply the stirling approximation on all the three terms and it is not very difficult it will become something like this minus. So, this is for now for the second term we will expand the second term using stirling approximation minus of minus becomes plus therefore, delta S configuration is equal to KB. Now we will put the terms with log in one place. So, this is the full form of delta S configuration which can be easily evaluated now we do not have any factorials over here. In fact, now with what we have we can even for a simplified further.

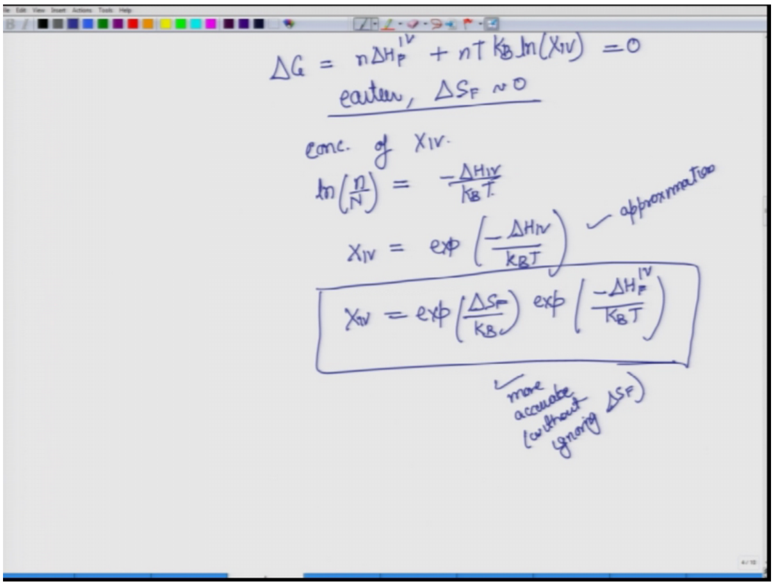
For example as you can see that this n plus N over here number of vacancies would always be very very smaller compared to number of atomic sites. So, therefore, this will quantity n plus N by N this can become can be approximated as N because N is much smaller than N now here n plus N can be approximated as N and therefore, this is since ln 1 where this becomes 0. So, we have only two terms and KN ln and if we reverse this why will reverse this is I will tell you say moment is n by N.

Now, why did we reverse it because this quantity this represents nothing, but fraction of vacancies. So, this becomes minus n KB ln X 1v or v, but I think we have used earlier v. So, I was put it as v and what is this X v, this is fraction of mono vacancies. It is important to keep this word mono vacancies mono because we will see that similarly you can also calculate for dye vacancies or tri vacancies or higher fractions or higher orders and simultaneously you would be able to show that their fractions are much much smaller.

So, now this is the relation and if you put delta G delta G will be equal to delta n delta H formation 1v plus now because this is minus term. So, this will become T although this quantity itself will be negative. So, the this term will itself still remain negative and this becomes nT KB ln X 1v actually let me use this 1v in all these places because to differentiate it with respect to mono vacancies.

Now, earlier we have, when we were deriving these relations now let me go to the next page.

(Refer Slide Time: 24:32)



$$\Delta G = n\Delta H_F^{1V} + nT K_B \ln(X_{1V}) = 0$$

earlier, $\Delta S_F \sim 0$

conc. of X_{1V}.

$$\ln\left(\frac{n}{N}\right) = \frac{-\Delta H_{1V}}{K_B T}$$

$$X_{1V} = \exp\left(-\frac{\Delta H_{1V}}{K_B T}\right)$$ ✓ approximation

$$\boxed{X_{1V} = \exp\left(\frac{\Delta S_F}{K_B}\right)\exp\left(\frac{-\Delta H_F^{1V}}{K_B T}\right)}$$

✓ more accurate (without ignoring ΔS_F)

So, let me write it again here the relation, now earlier when we were deriving if you remember we said that the S or the delta S if we are looking with respect to difference delta S formation is approximately 0.

Now, if we do not ignore that then we will have some more terms over here. So, we will have another delta SF coming over here, but before that let us get to what we need here what we want to what we started with was to find out what is the concentration of X 1v right.

Now, when we have what we said that when you keep increasing the concentration of mono vacancies, there will come up point where the energy will not reduce any further which means this will become 0 or something like this you will get a relation that we will derive next time, we will get a relation something like this and this n by N is nothing, but our fraction of single mono vacancies, this will be given by and like I said that if you had not ignored if you had not ignored the SF delta SF formation term, then this would be further accurately represented by this relation. So, this is a approximation this is more accurate because here we are not ignoring. So, this we have using this derivation we have been able to obtain the value of the fraction of mono vacancies. So, this is the relation that gives it.

And next time what we will do is try to understand, what is the effect of addition of these mono vacancies on delta G; how does a delta G and delta S change when we keep increasing mono vacancies particularly when in the initial period when we have almost no vacancies too small number of vacancies? So, well end here and we will come back and extend what we understood today.

Thanks.