Defects in Materials
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Lecture – 08
Types of Point Defects

Welcome you all to this course on Defects in Material. So far we have covered perfect crystals where no defects are present in the material, but we know all natural material when we look at it they do contain some type of the defect are the other we will talk about the various types of the defects. In the course of this lecture the question which arises is that why do defects form at all in the material that is one and another is all the defects bring down the free energy of the system or is it that some of the defects increase the free energy of the system this situation can also arise right some could be artificially created in the material some may be that naturally they will have.

In this one type of a defect which actually brings down the free energy of the system which will be talking about is your vacancies. So, what we will be talking about today or in a course of a three or four lectures on point defects in materials.

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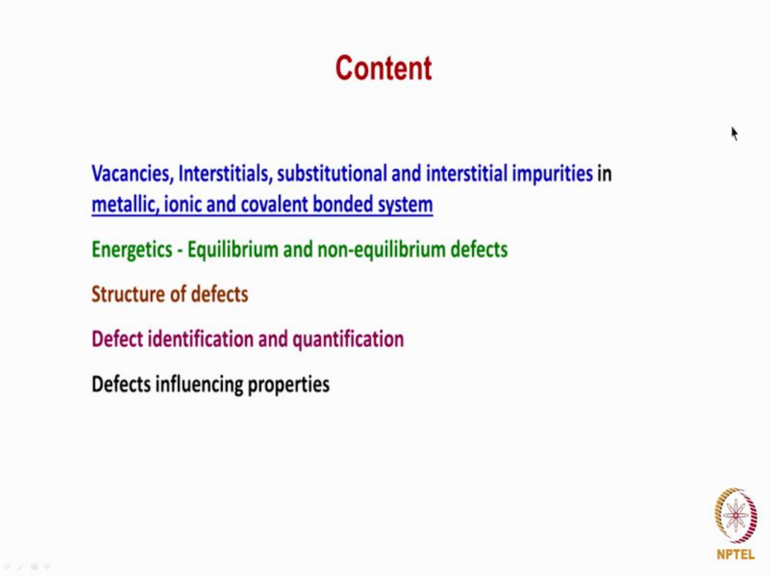

Content

Vacancies, Interstitials, substitutional and interstitial impurities in metallic, ionic and covalent bonded system

Energetics - Equilibrium and non-equilibrium defects

Structure of defects

Defect identification and quantification

Defects influencing properties

When we talk of point defects what are the type of point defects which we can have one they could be they can see interstitials then this could be substitutional and interstitial impurity atoms which could be there they are occupying isolated or atom positions in the crystal and the systems could be metallic covalent bonded or ionic materials are ordered alloy in all these type of materials point defects could occur.

Then the next question is that whether this point defects are energetically they bring down the free energy of the system we have to look at it from the energy point of view that depending upon that we will tell whether they are equilibrium defects or non equilibrium defects correct then what is the structure of this defect that is if a defect has been created some to bring down the strain energy some of the atoms will be add to maintain the charge balance atoms may be moving little bit forward or backward that will give raise to some distortion around the lattice site that is what it will bring this site what is going to be the structure of the defect.

Then what we have to know about the defect is that how much defects are present what is the equilibrium concentration of the defect which we can have. Then how to identify these various defects what are the techniques which are available not only identifying the defects. If you have to use it usefully in many of the design considerations of materials we should also be able to quantify how much the defects are present correct and towards.

Then possibly I will be talking about these defects influence property of the material a brief information I will talk about it, but what is essentially important is that of all these defects vacancies the one which is the most important defect, because the vacancies the which one which controls the entire phase transformation which are taking place in the material. And how the properties of the material changes during service as well as during, aging correct that is what is very important.

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Why study of vacancy is important / necessary ?

Vacancies control the diffusion of atoms which control the kinetics of phase transformation, deformation behaviour, annealing, recovery and recrystallisation and also life of components

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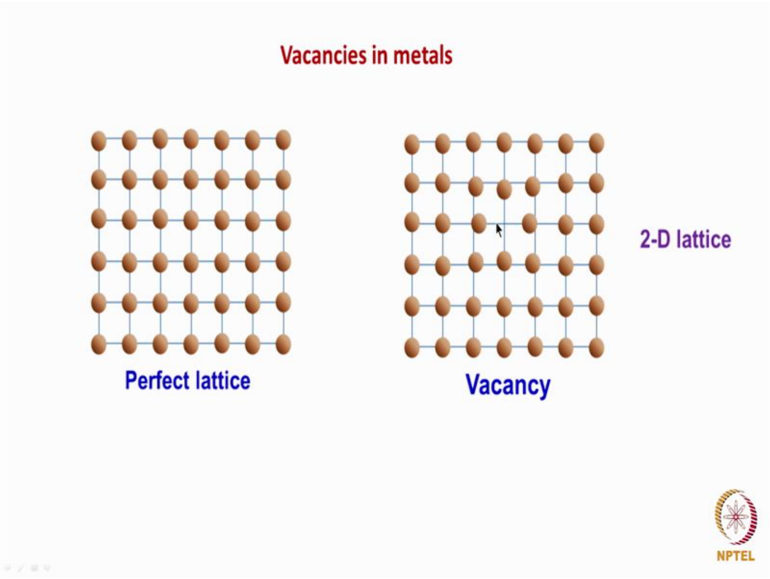

Vacancies in metals

Perfect lattice

Vacancy

2-D lattice

So, that is why the study of vacancy generation in the material and how the vacant kinetics of vacancy moment is very important before we go into these details let us just look at the different types of vacancies which are produced in materials. Let us take the case of a pure metals where the type of vacancy which we can produce if you take a perfect crystal in this one all atoms are occupying regular lattice positions correct all the lattice positions they are occupying if; for example, I remove a atoms from this particular site then it will generate a vacancy and here that black line shows the lattice lines. So, the absence of atom immediately one can see that when an atom has been removed the force balances between the atoms are keeping the atoms at particular positions.

Now, you can see that immediately the atoms which are at this lattice point that has moved closer the adjacent atoms these atoms also move close. So, there is a distortion which is created around each of the lattice positions correct that is closed it this is what we I am considering it is only a two dimensional simple cubic lattice square lattice.

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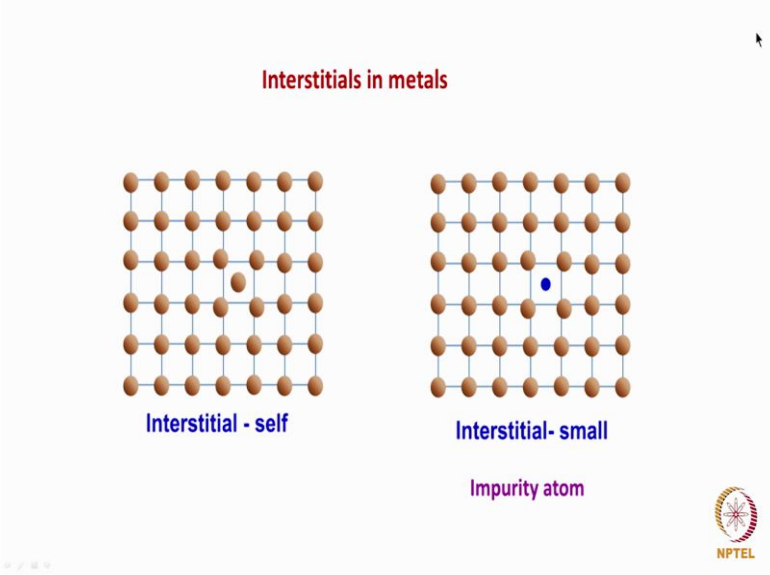

Interstitials in metals

Now, let us look at these are about vacancies suppose we are trying to insert an atom of the same material where can it go. So, all atom positions on the lattice sites are occupied then it has to go to a position which is an interstitials which is remaining in the crystal we which is there in the crystal the type of interstitials which could be there in different type of crystals that has been covered in the crystallographic class.

In this particular case when we consider the atom can occupy this center of this lattice other units cell correct randomly it can occupied when it comes to that center what is essentially is happening all other adjacent atoms this will be shifted away from the equilibrium position little bit away, because lot of strains are being introduced into that region locally.

So, this not only just strain we are bringing atoms which are at equilibrium distance. Now, put another atom which is closed by. So, the repulsive forces between the atoms also will increase that will also be responsible for movement of atoms away from each other that is how the distortion of the strain is generated we are on the defect position locally.

Now, let us consider the case where the case which we have considered just now when I talked about is about atom which is the same type of an atom which is introduced there are many cases where we have seen that interstitial many atoms which have like light elements like carbon oxygen nitrogen have small size they can also be introduced into the lattice. So, they would like to prefer to come into some interstitial position when they occupy the interstitial position we should understand that even they may create a small distortion around it because that distortion is, because depending upon the type of interaction which it has with the neighboring atoms that could be a repulsive force which may be moving atom away, but the extent to which atoms are moved from the lattice sites rippled maybe less.

So, this is essentially an impurity atom and this impurity atom is always externally added in the earlier case I have not mentioned how this atom is coming into this lattice site which we will talk about it later.

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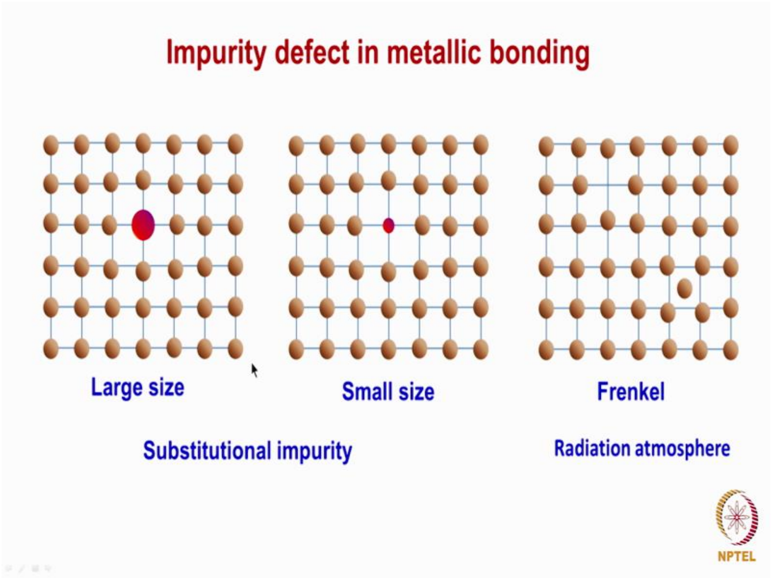

Impurity defect in metallic bonding

Large size

Small size

Frenkel

Substitutional impurity

Radiation atmosphere

NPTEL

Let us consider the case of a impurity which is added which is to a substitutional site if you add an impurity to a substitutional site that impurity could be either a larger than the atoms neighboring atoms or it could be smaller than that in these cases also they will be introducing distortions locally around the lattice site that is what easily what leads to strengthening of the material hardening of the material here one should be understand that when an substitutional impurity is added the position, which it can occupy in the lattice is already fixed it can replace only an atom position.

When an interstitial position and atom is occupying ones in a lattice one particular position is occupied by a particular type of an atom all other special positions which are there which are shown in the Wyckoff table all are potential positions where the interstitials can go and occupy. So, for the interstitial the number of positions which are available are very large and the energetic decide which position it will occupy the lattice.

The substitutional impurity could be smaller also either case there could be a distortion which will be generated around the lattice point, but there is another type of a defect which can be produced it because. So, far we talked about vacancies and interstitials right there are cases where both vacancy and interstitial could be produced simultaneously in the sample this happens during irradiation of a material with high energy ions where what happens is that atoms are knocked out from the lattice sites they.

So, a vacancy is created this knocked out atom comes and occupies some position it can only occupy an interstitial position. So, these type of defects are called as the Frenkel defects where we have an interstitial as well as the vacancy type of the defect is present simultaneously.

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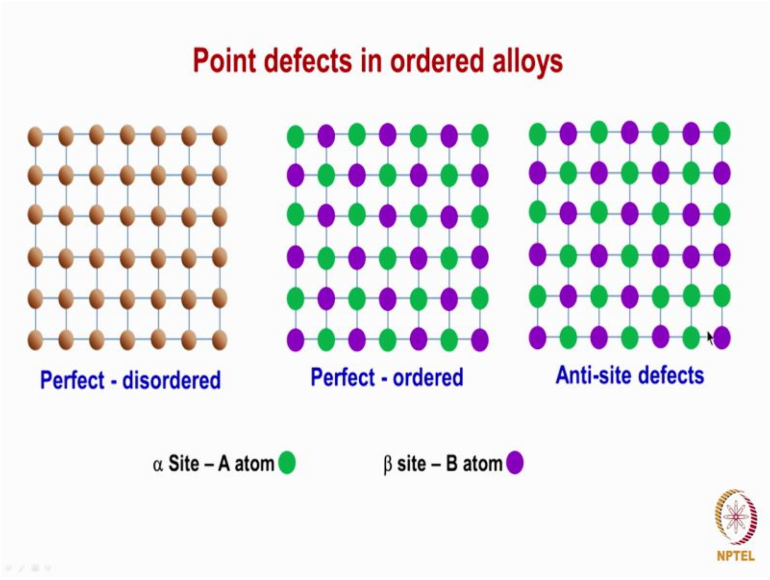

Point defects in ordered alloys

Perfect - disordered

Perfect - ordered

Anti-site defects

α Site – A atom ●

β site – B atom ●

Now, so far we considered this could whatever we have discussed. So, far is true for metallic systems or it is also true for a system which is a disordered alloy when I say that it is a disordered alloy what I mean that the position which the atoms can occupy in the lattice is not fixed, because other ways we know that the special positions which are there if one atom is a occupying a particular position in an ordered alloy another atom will occupy only as another specific position Wyckoff position in the lattice in a disordered alloy what happens is that especially in substitutional impurities when an element has been added this element has replaced some of the atom positions, but which position it is going to occupy will be essentially is random, but when we say disordered it does not mean that the alloys positionally disordered it is compositionally disorder that one should keep it in mind.

When this sort of a that is what this gray colour are the colour of the as earth which I am showing it for the atom to show that it is a disordered. So, what will be the probability of an atom occupying a position particular position that probability corresponds to the average composition are the concentration of the element which is present.

Now, I am showing an another case this is also a perfect lattice there is no defects we have considered now let us look at an another case where the same lattice, but now atoms occupy specific positions in the lattice sites here if we look at it the a atom occupies this alpha site b atom the pink coloured ones occupying the beta sites these sites they are occupying in a regular periodic arrangement.

Now, all our all our a atoms are occupying a site and b atoms are occupying only B sites in such a case what will be the order parameter or what is it going to be the order in this case it is a perfectly ordered alloy we will complete later shortly, because we define an order parameter also in this case, but even in this perfectly ordered alloy there are certain types of defects which could be produced it is not vacancies are interstitials.

You just now look at this third case which I am showing it here this is a alpha site where instead of an atom occupying A B atom is occupying this position and here it is a beta site where instead of A B atom A atom is occupying the position otherwise all the lattice sites are occupied, but if you look at the number of sites a atom is occupying and number of sites the B atom is occupying it is not 100 percentage there is a less one less here. So, when it is less the order parameter is defined in terms of the number of sites the lattices are occupying.

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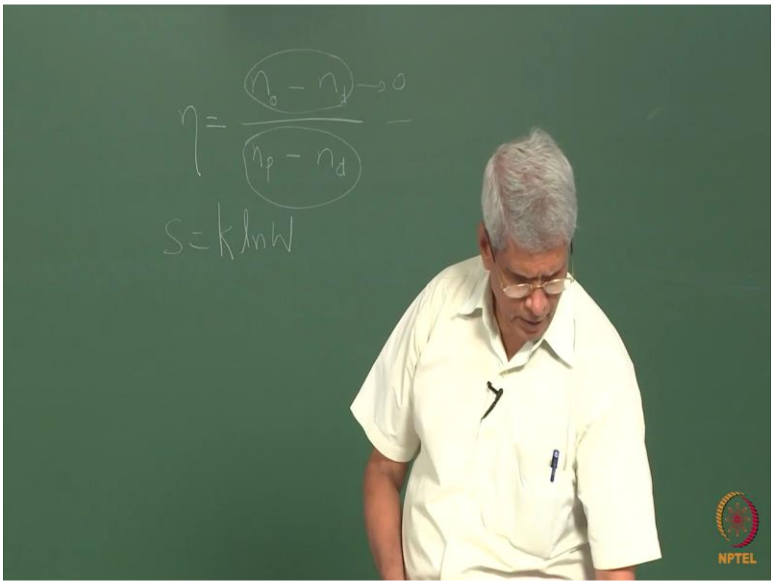

How exactly an order parameters are defined here N D is if this alloy having this specific composition is disordered then number of sites either A atom or A B atom will occupy is given by this value N D N P decides when there is a perfect order how many atoms sites are occupied how many B atom sites are occupied and this N O decides in the ordered alloy how many A atom sites or B atom sites are actually occupied, if it is perfectly ordered, then this N O will be equal to N P correct.

So, this ratio will turn out to be 1 then when the ratio is 1 we call it as a perfectly ordered alloy. Like that case which is being shown in this middle one here, if you not the middle 1 in the last case here you find that not all the atoms are occupying that site 1 atom is less right. But the perfect order position is N P and here the number which is occupying it is less in the disordered case if you see that this value will be this difference will be less than the denominator correct. So, then the order parameter will be less; yes.

Student: The defects these 3 majority defects are we will find only (Refer Time: 16:50) ordered alloy or.

No other defects will come; now just I am talking about is that the 1st type our defect even if point defects the type of point defect can be generated even in a perfectly ordered alloy ideal case alloy also this type of defects can occur.

Student: (Refer Time: 17:08) vacancies.

Vacancies will come.

Student: It should also (Refer Time: 17:10).

That I am coming to it later first I wanted to understand that this is the type of defect which can form because ordered alloys are the ones which quite often we deal with in metallurgy, but in ordered cases compared to disordered cases are compared to ionic cases there are types of defects which are being present before introducing it even in a perfectly ordered in an where there are no point defects are generated even then we can have a disorder in the material some defect could be there these defects are the anti site defects that is what I am trying to explain.

So, here suppose this value N 0 the number of positions in the perfect lattice it is occupying corresponds to that of the disordered number of atoms, then this will turn out to be 0 this will be some factors which remains constant. So, order parameter will become 0. So, order parameter this is how it is being defied and this is what we call it as a long range order parameter this clear how the long range order parameter is defined. So, these defects are called as anti site defects still we are now dealing with an ideal crystal only ordered crystal which we have considered now let us consider a crystal system ordered system where the defects are introduced into the lattice.

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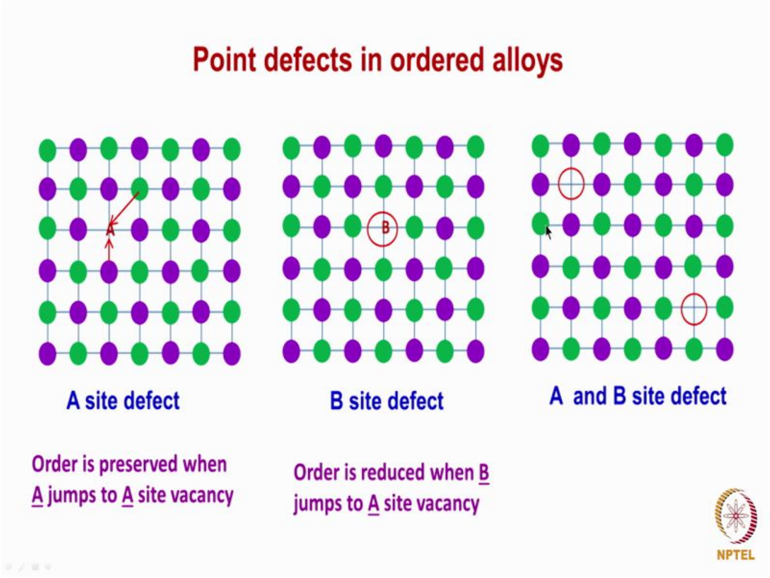

Point defects in ordered alloys

A site defect

B site defect

A and B site defect

Order is preserved when A jumps to A site vacancy

Order is reduced when B jumps to A site vacancy

So, let us consider the case where on the a site we have a vacancy which has been created that is one of the A atom is missing from that alpha site that I had just put it as an a atom which is missing there.

What are the possibilities now, if a vacancy has to move which of the type of atoms which can jump into this site one possibility is that this B atom is closest to a it can jump to this site correct or the a atom which is slightly far away that can also jump to that site these are all the two possibilities are there so that the defect moves right for diffusion to occur the defect has to move. So, these two possibilities exist then which is the one which will take place.

Similarly, we can look here this is A B atom site in which also similar process can take place either an a atom can jump to that site or A B atom can jump to that beta site both the possibilities are there you think of the case what will happen if there to an A site alpha site B atom jumps what are changes which can happen to this sample then the order will get reduced; that means, that that is in going to increase the energy of the system correct.

So,. So, essentially if an A atom jumps to an A site alpha site where a vacancy is created then the order parameter does not change it is only the vacancy is moving around. So, no change in energy if A B atom jumps to that site order parameter is going to change; that means, a change of energy is there that is not the one which is preferred.

So, what essentially will happen is that, because of this reason now even though an adjacent atom is there which is of a different type it would not like to jump into that site correct. So, vacancy diffusion if you looked at it in an ordered alloy is going to be different from that which we see in a disordered alloy; that means, that an atom which is further away will be jumping into that site, because it is the same type of an atom.

So, each of the atoms can have a different type of mobility associated with it. So, there may be moving with different rates all these things could occur because of that what is essentially is going to happen is that diffusion rates could get reduced compared to that of disordered material what is the consequence of it in terms of choosing a material especially for creep behavior, if you try to look at it we would like to have a material when it is ordered you say that diffusivity comes down this is the reason why diffusivity comes down in an ordered material and the creep rate will be lower is it clear this is a type of a defect which is seen only in ordered materials in a disordered material we do not see this type of defect and we say its defect.

This is just an example where I have taken where we can have an A type of an defect as well as A B type of a defect both are possible in the lattice.

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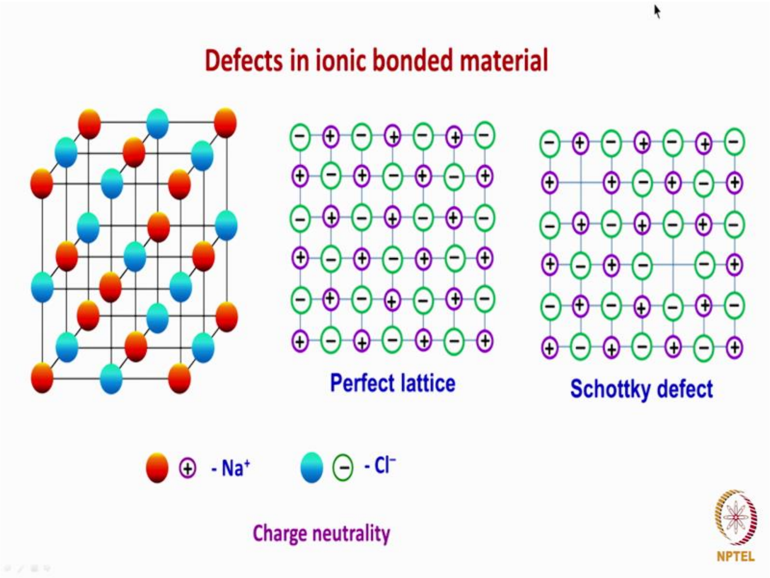

Defects in ionic bonded material

Perfect lattice

Schottky defect

● ⊕ - Na$^+$ ● ⊖ - Cl$^-$

Charge neutrality

Now, let us consider the case. So, far we have considered pure metallic are disordered systems alloy systems now we have considered a case where it is a perfectly ordered alloy now, let us consider the case where it is not a metallic type of a bonding. It is an ionic or covalent type of a bonding.

Let us take the example of an ionic bonding what I have considered here is I am just showing the defect which are the lattice of sodium chloride it is an ionic bonded crystal it is 2 FCC type of lattices occupied by is A 1 sodium and another by chlorine which are interpretating each other still it generates the FCC type of a ordered lattice as A 2 dimensional lattice I am just showing only one of the phases you consider that it is an 1 0 0 phase which I am showing it.

Here, the positive ions or the cations are shown with the red one not the pink color and the green color shows the chlorine ions and what is essentially important in A an ionic or covalent bonded materially is there the charge neutrality always has to be maintained whenever the defects are produced in the lattice whereas, in metallic systems you are not bother looking at the charge neutrality here that is very much important.

So, then what will happen when we look for the charge neutrality. So, if we produce a vacancy in this particular site where that nega cation is anion is missing then there should be some other in the lattice. We should create the vacancy of a cation also. So, that the charge neutrality is being maintained. So, to maintain charge neutrality in when point defects are produced both cations and the anions have to be produced in equal concentration in the material this type of defects are called as Schottky defects, yes.

Student: (Refer Time: 25:22).

Which I will come to that a little bit later how this the defects could be produced in the lattice the next one which I wanted is completed about the type of defects in material I will be talking about that aspect of it these are all the.

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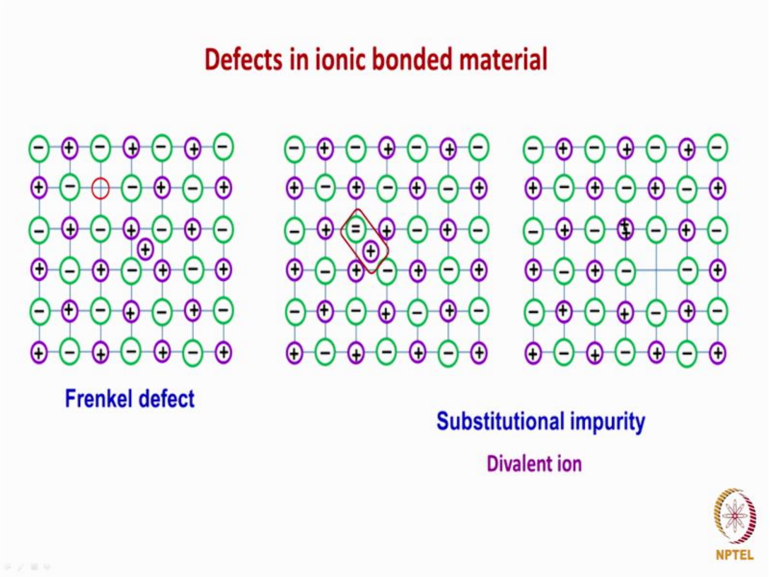

Defects in ionic bonded material

Now, let us look at now we have considered a Schottky defect is there any other way in which a defect could be produced the way in which it can produced in ionic bonded material the one way in which it could happen is that that a cation has been removed from this site and it is deposited in a region which is adjacent to it into an interstitial position then also charge neutrality is being maintained this type of defects we call it as the Frenkel defects this is the only type of a defect which we seen disordered materials when we do irradiation those conditions correct whether Schottky defects are seen only in directionally bonded materials.

Now, So, far we have considered the defects which are essentially by removing and add up from a particular lattice site whether it is a cation or anion as I mentioned earlier most of the materials are imperfect we can have impurity atoms into that material. So, it could be this impurity can have a charge state which is different from that of the charge state of the other ions which are present in the sample let us take the case where it is essentially the anion has got a charge which is not single singly ionized it is doubly ionized. If it occupies your position like this in these lattice to compensate for the one negative charge which has come into this site one excess positive charge has to be added if the lattices otherwise perfect lattice then only place which it can come to be some interstitial site is very closed by if it goes very far away then it will be locally creating a field.

So, generally they would try to prefer to form as close as possible to where the defect is present about these aspects we will talk about it much later some consequences of this. And another possibility this is what I am showing it is how these defects will be produced the other possibility is that we have this particular position where we have a cation divalent cation has been introduced. If a divalent cation has been introduced to compensate for the negative charge I can introduce one more negative charge like in this case where is ten interstitial position or what I can do it is because one positive charges in excess. So, I remove from one lattice site one of the ion then also the charge will be compensated.

So, this way I can create the charge neutrality could be maintained these two possibilities excess way in which charge neutrality can be maintained in that system, but if I have to introduce 1 cation no, not cation anion into an interstitial site the energy which is required is going to be high. So, generally in most of the systems it is essentially creation of an vacancy which is been seen.

So, these vacancies are not the once which are generated, because of the charge neutrality the charge neutrality is the reason, but this is because of the type of impurity which we have added if we add a divalent impurity the concentration of that impurity will decide how much is going to be the vacancy that is cation vacancy concentration which we are going to introduce into the lattice you understand that this is apart from thermodynamically dictated Schottky defects which will be produced in the lattice this is going to be the case in most of the materials because no material is perfectly pure correct some impurities are always there in the material.

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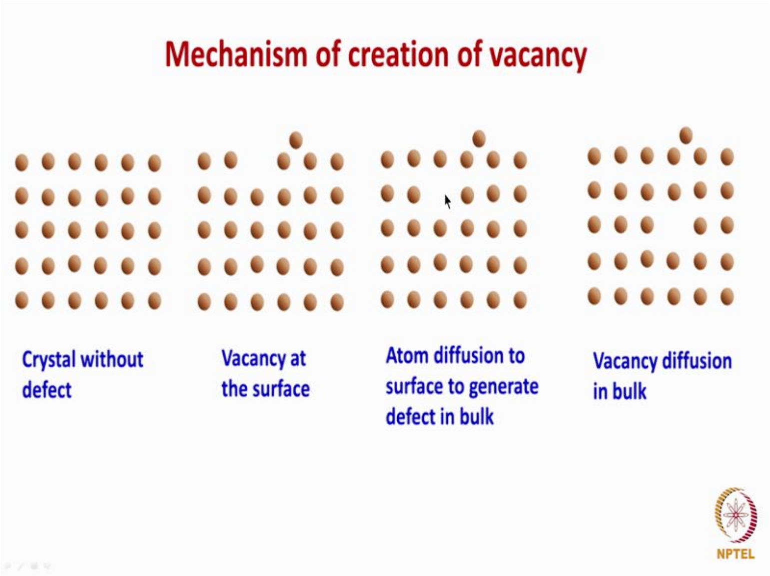

Mechanism of creation of vacancy

Now, let us look at the mechanism of a creation of a vacancy how can a vacancy be created in a lattice we consider the crystal without a defect it is a perfect ideal crystal how can we create a vacancy in this crystal what is the possibility an atom has to be removed what is the way in which it can happen is that at any particular temperature when we consider it atoms are vibrating around the lattice points you can. So, when the not only that the vibrational energy with each of the sites though we talk about average energy some sites could have got energy which is higher than that of the other it can. So, happen that one of the atom is knocked out from a site that is an atom from this site has just moved out of it and come to the surface.

So, here one sub vacancy has been created on the surface suppose, an atom from here now moves to the surface then what will happen this vacancy will become the one which is generated in the bulk that is the next case which we have considered it correct now again this process can take place, because now an atom from this site has moved to here like this with few moments you find that the vacancies now.

The vacancy is within the sample, but an atom has been removed and that is put onto the surface this is the mechanism by which now to answer your question this is how vacancies are created in the system this is coming essentially, because of the thermal vibrations which are associated with it and though we talk about all atom positions is any particular atom sitting on any particular lattice at high temperatures no they are all moving around continuously because of diffusion. On the average we will say that this is the way the atoms are distributed, but if we look at one particular atom to find out whether it is sitting at a specific particular position can be fix the coordinates no it is just moves around. Yes.

Student: (Refer Time: 32:47).

Yes.

Student: Sir, in case of ionic crystal the mechanism would be similar.

In the case of ionic crystals also the same thing has to happen, but there the defect concentration which we produce will be both cation and anion concentration has to be produced and we have to consider both the sub lattices separately; like the way we do for order alloys.

Student: Ok, first step of defect formation will be (Refer Time: 33:12).

First step of defect formation is from the surface is the one which is the which one can easily think of this is one way of explaining how the defects are formed which we can logically understand it can once the, because otherwise how will be the other way in which we can think of this mechanism itself is that suppose we assume that I remove an atom from the by applying some energy. Because if you look at in this case there are 4 bonds are there in a 2 dimensional bond are in this cubic lattice 6 bonds are going to be nearest neighbor bonds.

Some energy is required to break this bond each of this bond. So, how many it will be there essentially we are going to have some nearest neighbor bonds if you can 6 bonds have to be broken this atom is removed from there and assume that by some means we are bringing it and putting it on the surface. When you put on the surface it will be again forming some bonds. What is the difference between the number of bonds that is going to give you the energy which is required and there will be some relaxation which will take place the net effect of all these things is going to decide what is going to be the energy which is required for a vacancies to be created. But in that what I described just now we are not talking about how we are removing it atom, but logically if we think of it the best easiest way in which a vacancy could be produced is first creating a vacancy in the surface and that vacancy moving inward by diffusion.

Generally, that is if I like to break a bond what has been seen in most of the cases especially in the radiation damage it has been lot of calculations have been done people have seen them that it requires around on the average 25 electron volt 240 electron volts in most of the material it the value lies in this range to generate a vacancy interstitial (Refer Time: 35:27). These are other which is required, but generally when we talk up for formation energy of a vacancy what we talk about it is very small value of the order of maybe around point 5 E V to 4 E V that is, because in that case the whatever is the way can atom which has been removed since that comes onto the surface the net energy difference only what we have to consider as a formation energy, because there is some energy loss and there is a some energy gain is also going to be there the net difference is what the energy which is required .

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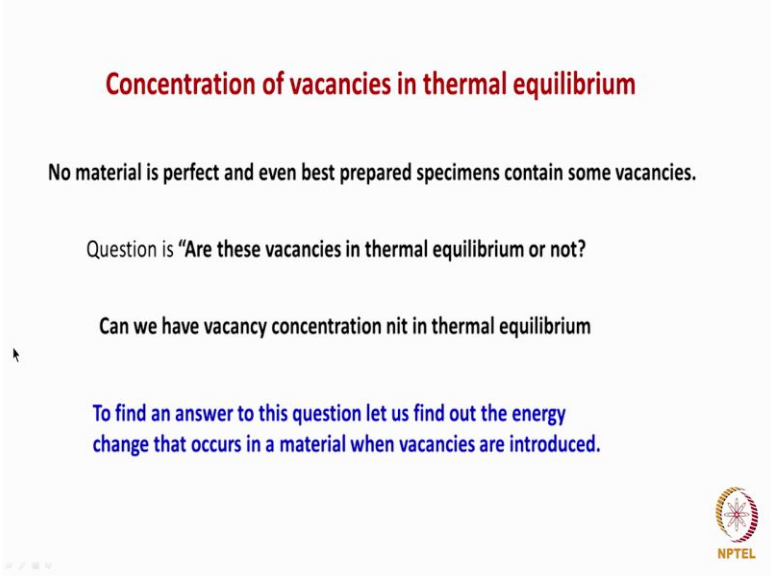

Concentration of vacancies in thermal equilibrium

No material is perfect and even best prepared specimens contain some vacancies.

Question is "Are these vacancies in thermal equilibrium or not?

Can we have vacancy concentration nit in thermal equilibrium

To find an answer to this question let us find out the energy change that occurs in a material when vacancies are introduced.

Now, the question which comes is that we have to look at these vacancies what is the concentration of these vacancies and whether first this vacancies, because as I mentioned earlier that the various sites of defects whether the defects could be in equilibrium or not how do we find out whether the defect will be in equilibrium or not. So, what are the energy changes which are takes place let us take the case of a point defect a vacancy we have removed an atom from a lattice site to remove that atom some free energy change is going to take place that much energy has to be spent to remove an atom from that site the net energy of formation of a vacancy then when this vacancy has been created.

Now, if you look at what are sites which this vacancy can occupy in the lattice in the lattice it can occupy. So, many positions which are available anyone of this position it could recite. So, we this is what we call it as this gives rise to what is called as a configurationally entropy term. So, one is a energy which has to be spent there is a gain in energy which comes from the configurationally entropy the total energy change is a sum of these 2 which decides whether there is going to be a change in energy or not this is what the philosophy which we use it to calculate suppose, N vacancies are produced then what will be there we can find out what is going to be the equilibrium concentration of the effects we can calculated by taking the what is going to be the free energy change when N vacancies are created.

Then try 2 minima differentiate it to find out the minimum free energy which will occur with respect to a number of defects, which are going to be there. That is how theoretically we try to find out the free energy change which will take place. Or the same thing can be used to find out the equilibrium concentration of the vacancies which are going to be there in the material.

This is one; and one question which I have added is that one is that question which is are the vacancies in thermal equilibrium or not. Another question is that can we have a vacancy concentration which is not in thermal equilibrium, is it possible to have it any situation which you can think of where it can happen.

Student: During radiation damage.

During radiation damage, any other case we can think of?

Student: Yes, by in (Refer Time: 38:52).

By applying stress you can do that the other is that when we deform a material when dislocation dislocations interact they produce lot of vacancies are you do mechanical alloying which you do lots of defects are introduced into the lattice that energy into, but these defects are all non-equilibrium defect concentration. So, there are many ways in which we can have defects, but then that question also comes is that when they will become come to equilibrium this we will talk about it later, but now just I just post this question that there are many situations we can have non-equilibrium concentration of defects as well.

So, to find out an answer to whether the defect concern what is going to be the defect concentration how much we can have it, what we are trying to find out is that what is going to be the free energy change.

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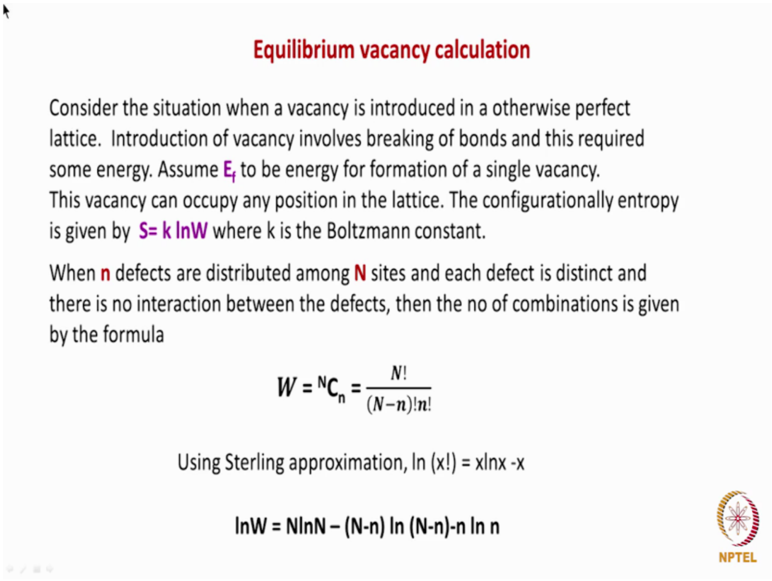

Equilibrium vacancy calculation

Consider the situation when a vacancy is introduced in a otherwise perfect lattice. Introduction of vacancy involves breaking of bonds and this required some energy. Assume E_f to be energy for formation of a single vacancy. This vacancy can occupy any position in the lattice. The configurationally entropy is given by **S= k lnW** where k is the Boltzmann constant.

When **n** defects are distributed among **N** sites and each defect is distinct and there is no interaction between the defects, then the no of combinations is given by the formula

$$W = {}^{N}C_{n} = \frac{N!}{(N-n)!n!}$$

Using Sterling approximation, ln (x!) = xlnx -x

$$\ln W = N\ln N - (N-n)\ln(N-n) - n\ln n$$

When we introduce defects in the lattice how do you find out the configurationally entropy the configurational entropy part of it this W K is the Boltzmann constant W is nothing, but the number of combinations or the number of ways in which these vacancies could be arranged in the lattice correct that is given by this formula N C N where capital N is the number of capital N is going to be the total number of atoms and N is a going to be the number of vacancies.

This using sterling approximation we can write it in this form these are all the things which are given in a standard text book I am not going into any of these derivations.

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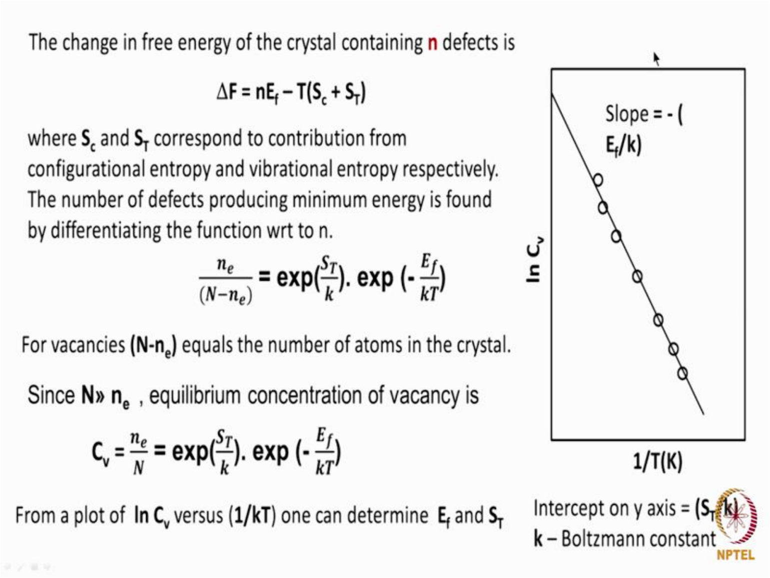

The change in free energy of the crystal containing **n** defects is

$$\Delta F = nE_f - T(S_c + S_T)$$

where S_c and S_T correspond to contribution from configurational entropy and vibrational entropy respectively. The number of defects producing minimum energy is found by differentiating the function wrt to n.

$$\frac{n_e}{(N-n_e)} = \exp(\frac{S_T}{k}).\ \exp\ (-\ \frac{E_f}{kT})$$

For vacancies **(N-n_e)** equals the number of atoms in the crystal.

Since **$N \gg n_e$** , equilibrium concentration of vacancy is

$$C_v = \frac{n_e}{N} = \exp(\frac{S_T}{k}).\ \exp\ (-\ \frac{E_f}{kT})$$

From a plot of **ln C_v** versus (**1/kT**) one can determine **E_f** and **S_T**

Intercept on y axis = **(S_T/k)**

k – Boltzmann constant

So, we can write that the change in free energy here I use the term delta F, because Helmholtz free energy here used, because E F is the formation energy and then T S is a configurationally entropy term there are 2 are there one is S C is a configurationally entropy and S T is that around each vacant site which were created the thermal vibration there will be a variation will come. So, what is the contribution from the thermal vibration also has to be taken into concentration, we can substitute to S E the using sterling approximation the value which we have got it for S and if you do differentiate it and then try to find out the ratio of vacancy concentration to the number of atoms in the lattice. Then we will find that it is related to the energy of formation in an exponential term and another is S T by K another exponential time comes into this picture.

In this we assume that by some means we are able to measure the vacancy concentration at different temperatures. Then we can get information about the E F and also about that S T by K. So how will the plot look like? So, if you plot log off the C V the vacancy concentration versus 1 by K T 1 by T, then this will this should be a straight line plot the slope will give us E F by K. We know the Boltzmann constant we can find out the point at which it cuts this Y axis this will give information about that S T by K. So, we can get both the information about the entropy term thermal entropy term as well as the formation energy which we can get it.

Or if we know these values then we can calculate theoretically what is go what will be the concentration of the defects which will be produced in the material what has been seen experimentally is that in most of the material close to melting point the point defect concentration is of the order of close to around 10 to the power of minus 3 to 10 to the power of minus 4 it is within that range which is what it has been observed.

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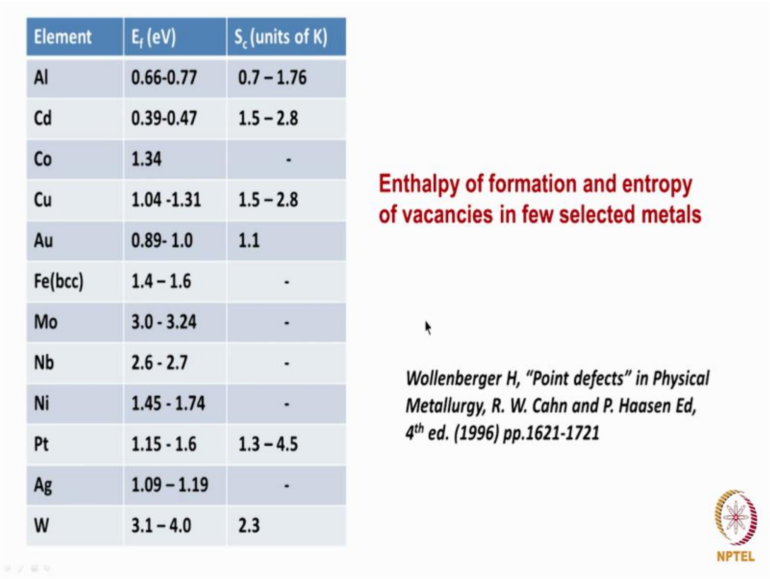

Element	E_f (eV)	S_c (units of K)
Al	0.66-0.77	0.7 – 1.76
Cd	0.39-0.47	1.5 – 2.8
Co	1.34	-
Cu	1.04 -1.31	1.5 – 2.8
Au	0.89- 1.0	1.1
Fe(bcc)	1.4 – 1.6	-
Mo	3.0 - 3.24	-
Nb	2.6 - 2.7	-
Ni	1.45 - 1.74	-
Pt	1.15 - 1.6	1.3 – 4.5
Ag	1.09 – 1.19	-
W	3.1 – 4.0	2.3

Enthalpy of formation and entropy of vacancies in few selected metals

Wollenberger H, "Point defects" in Physical Metallurgy, R. W. Cahn and P. Haasen Ed, 4th ed. (1996) pp.1621-1721

So, here what I have done is that a technique from the literature the value which has been determined experimentally for various pure elements and here you ca n see that aluminum melts at the low temperature tungsten melting point is high correct the lower the melting point then we can talk about, if the bond strength is going to be weak correct the higher the melting point the bond strength will be high this is reflected in the energy of formation also. So, if you look at the aluminum it is around the point 62 point 77. E V is the formation energy electron volt whereas, in the case of tungsten it is going to be like you can see that molybdenum niobium high melting elements they have a higher formation energy correct, but irrespective of this at the melting point the vacancy concentration is seen to be between 10 to the power of minus 3 to 10 to the power of minus 4 for most of these materials correct.

But what is essentially important is that this tells what is going to be the equilibrium concentration of the vacancies one more thing which we have to consider it is that what do we mean by an equilibrium concentration of the vacancies that is that that concentration of the vacancy which brings about maximum reduction in free energy in the material you understand that that is

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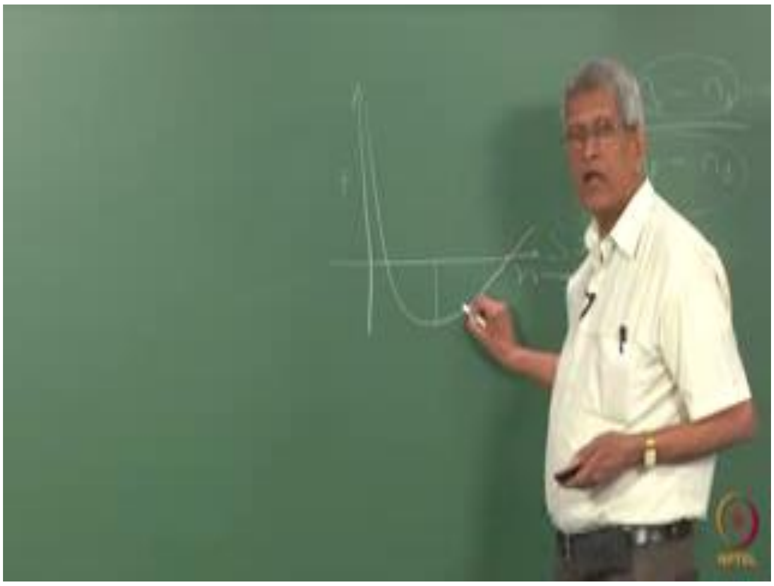

if I look at try to plot the free energy change that is it comes like this with a number of vacancy concentration.

So, at this particular point when the vacancy concentration is going to be there maximum reduction in free energy, but if the concentration of vacancy increases beyond that also or less than that also there is a reduction in free energy is going to take place. So, that system is stable because free energy changes, but that is not the maximum and up to this point this is the critical concentration at which by adding one more defect vacancy into that system it goes into a free energy becomes high now it will not be no more in thermal equilibrium correct in all other cases yes the defect concentration is there, but that defect concentration is bringing about a free energy reduction this one should keep it in mind.

Now, if you have produced defects in the material at some particular temperature whatever be the various means will the defect always this defect is going to move around. Finally, what is going to be the concentration of the defect in the sample depends upon how fast the defect move that is a migration energy part of it what we will do it is that in the next class we will talk about that.

We will stop it now.