Non-Metallic Materials
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Module - 02
Defects, and reaction kinetics of non - metallic materials
Lecture -06
Defects in crystalline materials: point, line, planar and three Dimensional defects

Welcome to the course Non-Metallic Materials and today it is the 6th lecture of module number 2, where I will be discussing the Defect and reaction kinetics of this non metallic materials.

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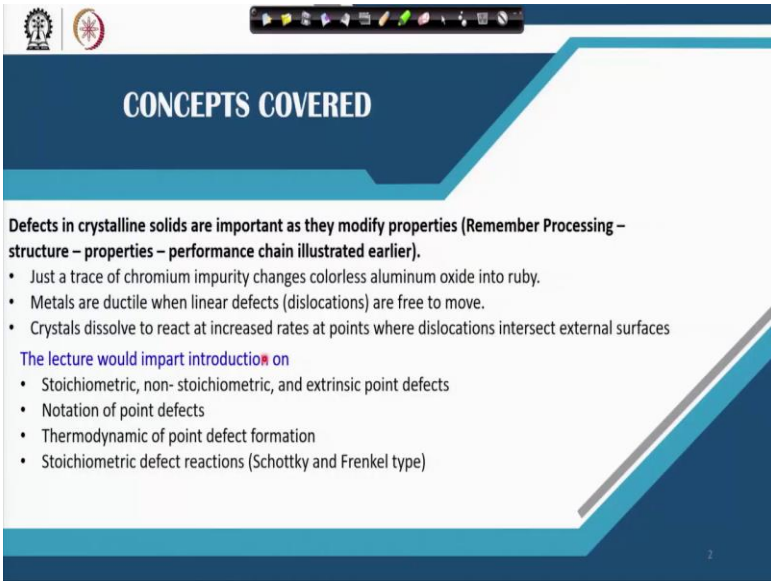

CONCEPTS COVERED

Defects in crystalline solids are important as they modify properties (Remember Processing – structure – properties – performance chain illustrated earlier).

- Just a trace of chromium impurity changes colorless aluminum oxide into ruby.
- Metals are ductile when linear defects (dislocations) are free to move.
- Crystals dissolve to react at increased rates at points where dislocations intersect external surfaces

The lecture would impart introduction on

- Stoichiometric, non- stoichiometric, and extrinsic point defects
- Notation of point defects
- Thermodynamic of point defect formation
- Stoichiometric defect reactions (Schottky and Frenkel type)

And first let us start with the concept of defects in crystalline solids. And in the last module lecture as you remember, I discussed about the polymeric material which are either amorphous or semi crystalline in nature. Now we are graduating ourselves to crystalline material and mostly I will be focusing on ceramic material.

And for ceramic material the defects are of immense importance. For metal also defect plays the major role as an example can be sighted that if you take aluminum oxide crystal and then you droop it with the small amount of chromium into it, then the resultant material can be used as ruby.

So, this is one of the examples of the point defect that is being created inside the material. For metal the ductility that is related to the dislocation presence of line defects and when dislocations are free to move across the slip plane then the material becomes ductile. Also at the crystal surface where the dislocations are terminated, it has been shown that they are more reactive. So, this crystal dissolves to react at increased rate at the surface.

So, defects are of immense importance in the non-metallic materials and this lecture will basically cover the different types of defects particularly to start with the point defects which include the stoichiometric and non-stoichiometric defects and also extrinsic point defects. Then we will learn how to write the notation of this defect, how you can make someone understand make someone understand about the notation of this defects.

Then the thermodynamical aspect of the defect formation will be covered. And finally, we will take up two stoichiometric defects. Stoichiometric defects are those where the crystal chemistry is not changed and this defect reaction for this stoichiometric defect we will also cover in this particular lecture.

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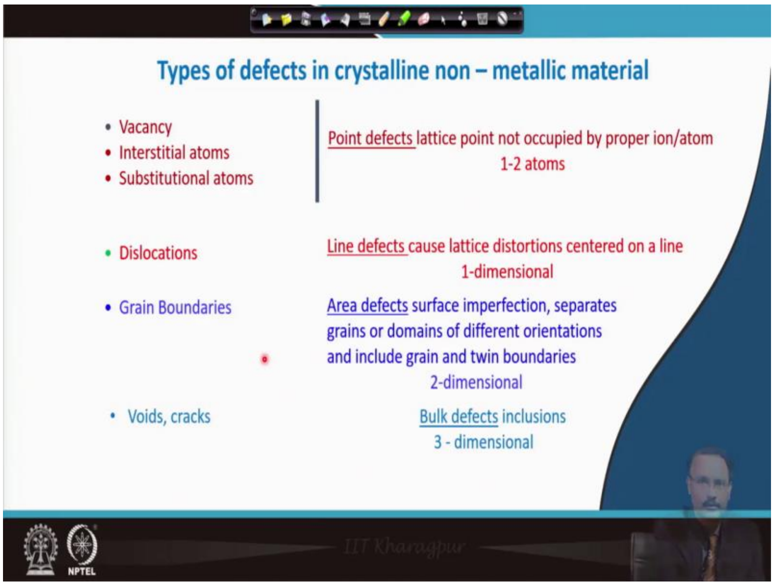

Types of defects in crystalline non – metallic material

- Vacancy
- Interstitial atoms
- Substitutional atoms

Point defects lattice point not occupied by proper ion/atom
1-2 atoms

- Dislocations

Line defects cause lattice distortions centered on a line
1-dimensional

- Grain Boundaries

Area defects surface imperfection, separates grains or domains of different orientations and include grain and twin boundaries
2-dimensional

- Voids, cracks

Bulk defects inclusions
3 - dimensional

So, if I categorize the defects in different types, as you can see you can have starting from a point defect where the dimensions are very small only 1 or 2 atoms and remember in the last module lecture we told that structure plays an important role and structure at different lens scale. So, here the point defects are 1 to 2 atom you are talking about.

And mostly we are concerned about vacancy where the atom or ion were supposed to be there, but they are not there and sometimes this atom or ions go to the interstitial position of the crystalline lattice. So, then it is crystalline interstitial defects or sometimes one type of atom is replaced by foreign atoms.

So, we call this is a substitutional kind of point defects. Then we will talk about dislocation prominently there are two types of line defect one dislocation is called edge dislocation we will briefly introduce it and another one is screw type of dislocation both are line defects.

And the ductility of the metal as I have told they are basically depend on the concentration of this defects line defects as well as its movement through their slip plane. So, then we will talk about the planar defects mainly grain boundaries one of them or twin boundaries will be talking about.

So, those kind of defects are two dimensional defect of planar origin. And finally, the defects like void or precipitation of a secondary material that also does that also actually influence the property particularly the mechanical property of the material. So, we will also touch up on that.

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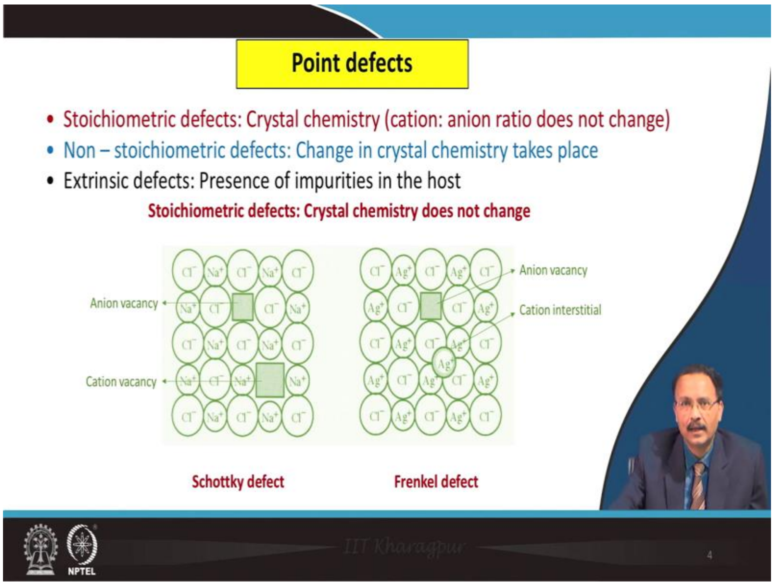

Point defects

- Stoichiometric defects: Crystal chemistry (cation: anion ratio does not change)
- Non – stoichiometric defects: Change in crystal chemistry takes place
- Extrinsic defects: Presence of impurities in the host

Stoichiometric defects: Crystal chemistry does not change

So, to start with this point defects broadly when categorized into three type the first one is stoichiometric type where the crystal chemistry does not change. So, defects are there either Schottky or Frenkel, but the basic composition on the material they will remain same. The second one is in staff contrast and you will find that the stoichiometric of the oxide itself is changed. So, crystal chemistry composition change is there and this type of defect in fact, I will be focusing more on it because particularly for the ceramic system it is of at most importance to understand this non stoichiometric defects.

And third one is extrinsic type that you are adding something from outside intentionally or in your raw material itself there are impurity atoms. So, that will also introduce defect point defects in the material. So, mostly we will be talking about these three different types of defects. So, to start with the stoichiometric defect where the crystal chemistry is not changed is a simultaneous creation of both anion and cation vacancies. As you can see that both sodium ion vacancy is there.

So, one sodium ion is missing from its original position and also chloride ion is also missing from its original position they goes to the surface. So, the stoichiometry remains same, but point defects are introduced. We call this type of defects as Schottky defect. Frenkel defect is something where mostly cation which is having smaller size they go to the interstitial size.

So, you have creation of one interstitial cation and where from it is coming their cation vacancies there. So, one interstitial ion and another vacant lattice side they constitute the defect and charge is balance and Frenkel defect also does not change the stoichiometry of the material.

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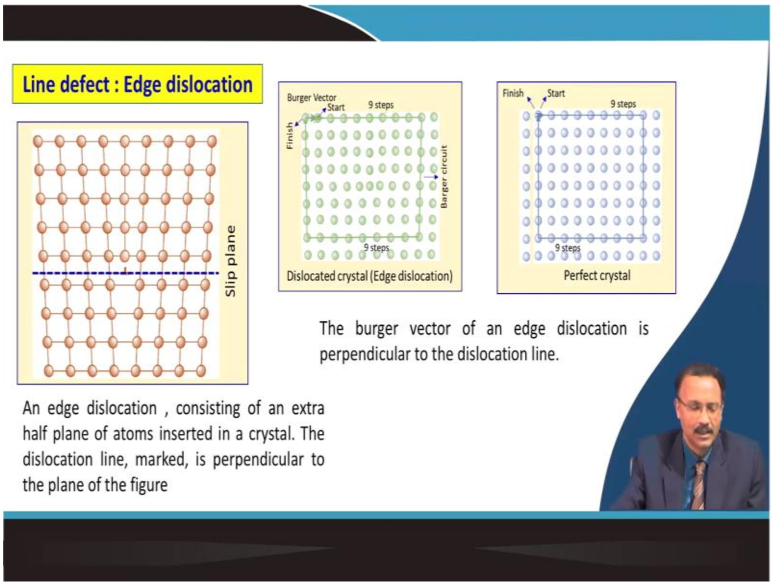

Line defect : Edge dislocation

The burger vector of an edge dislocation is perpendicular to the dislocation line.

An edge dislocation , consisting of an extra half plane of atoms inserted in a crystal. The dislocation line, marked, is perpendicular to the plane of the figure

As far as the line defect is concerned, the prominent one is we call edge dislocation where you can see in the crystal lattice you have an extra half plane this atoms are not there.

So, it is an extra half plane and you can compare it in three dimension. So, this is basically form a line and that line is perpendicular to the plane of the paper. So, this is called as dislocation and it contains a extra half plane and this dislocation can move through this slip plane and that yields to ductility and several other properties in metal system.

In ceramic it is not that that dislocations are not there, but the slip system they are not that much. So, slip system is scanty. So, ductility of the ceramic material is usually not as much I mean it behaves like a brittle fracture its not ductile at all under normal condition.

So, a burger circuit that you can develop at along with this line of this dislocation plane and you can see that if I start from here move 1, 2, 3, 4, 5, 6, 7, 8 and then move 7 atoms here, then move 7 atoms here and then or 8 items here and then again move 7 atoms here we will end up somewhere else.

So, we have started from here, but since the edge dislocation is there we are ending up somewhere else and this vector this small vector which is in order of atomic dimension this is known as burger vector and actually this burger vector is perpendicular to the dislocation line. If the crystal is perfect if there is no edge dislocation present, then such kind of behavior will not be observed.

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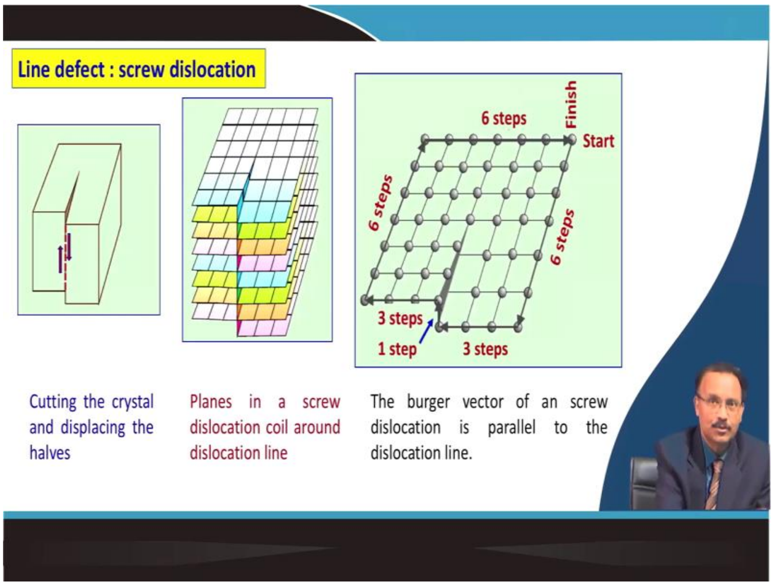

Line defect : screw dislocation

Cutting the crystal and displacing the halves

Planes in a screw dislocation coil around dislocation line

The burger vector of an screw dislocation is parallel to the dislocation line.

In case of screw dislocation it is something like that that crystal is here and it has been cut and displaced half of it along this plane. So, if you consider along this line this straight line, all the planes they are having some kind of coil kind of movement of the planes takes place and here also if you take the burger vector you can see that in order to complete the circuit you will have to move from this plane up to here.

So, the movement is required, but this time the burger vector is parallel to your dislocation line. So, in case of screw dislocation burger vector is parallel to the dislocation line.

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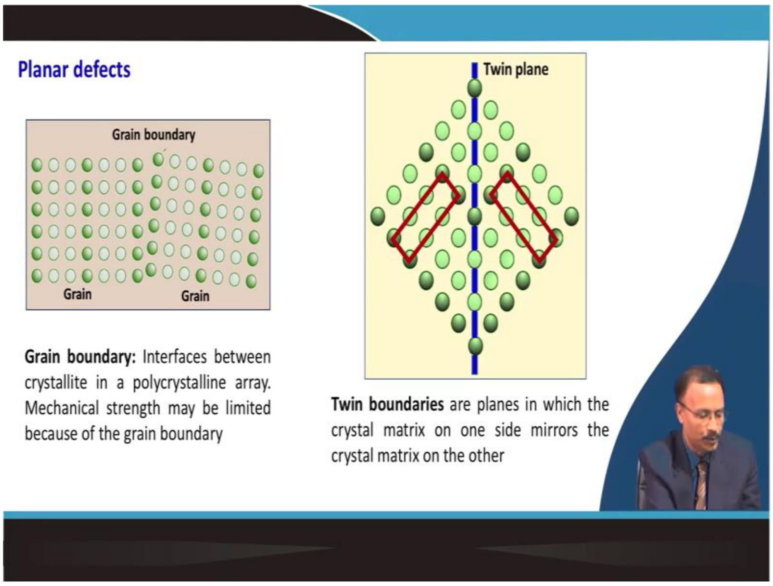

Planar defects

Grain boundary: Interfaces between crystallite in a polycrystalline array. Mechanical strength may be limited because of the grain boundary

Twin boundaries are planes in which the crystal matrix on one side mirrors the crystal matrix on the other

If you see the planar defect the most prominent one is the grain boundary. So, this is one particular grain which is single crystalline in nature have regular arrangement of cation and anion you can you can see and this grain also is having regular arrangement, but at the boundary region this regular arrangement is lost.

So, this polycrystalline array actually it is formed where otherwise single crystalline between there are discrepancy as far as the atom orientations are concerned. So, this is also one kind of planar defect the grain boundaries.

Twin boundaries is basically a mirror plane where the left hand portion is actually the mirror reflection of the right hand portion. So, if you just fold it, fold this crystal along with the twin boundaries all these atoms will fall top on top of each other. So, this is another type of planar defect and this is termed as twin boundary. Not only atom wise if you see that this configuration here also across this line you can fold it and one will fall on top of another.

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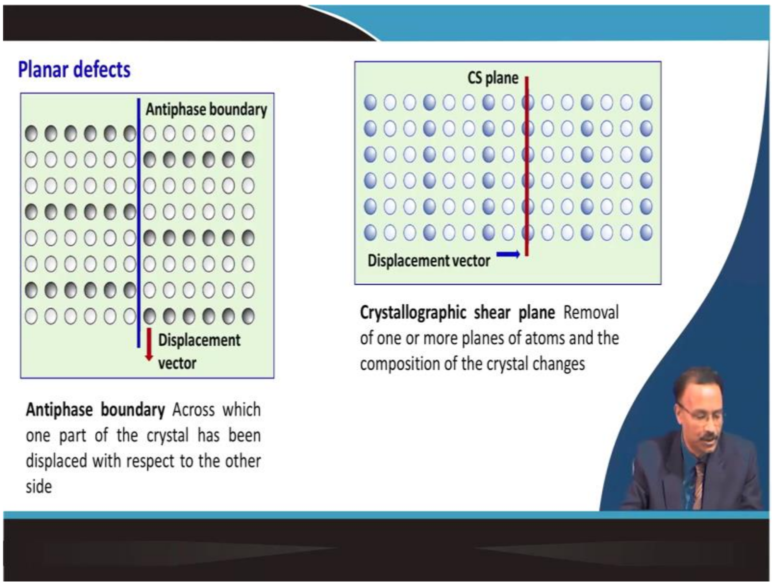

Planar defects

Antiphase boundary Across which one part of the crystal has been displaced with respect to the other side

Crystallographic shear plane Removal of one or more planes of atoms and the composition of the crystal changes

Another type of planar defect is termed as antiphase boundary and in antiphase boundary there is a small shift of all these atoms. So, you can see that this part of the crystal has been displaced. So, this part is displaced as compared to this one only one atomic dimension it is displace along with that you can see that with respect to this part. this part is displaced in one atomic distance .

So, this is called antiphase boundary and crystallographic shear plane another type of planar defect here one set of atom is missing. You can see that this is removed you start with dark and then sky blue sky blue, then dark sky blue sky blue, then dark again then sky blue then it used to be a sky blue, but it is missed and you have another type of atom which is dark one has come into its place then again it is regular.

So, this plane is called crystallographic shear plane

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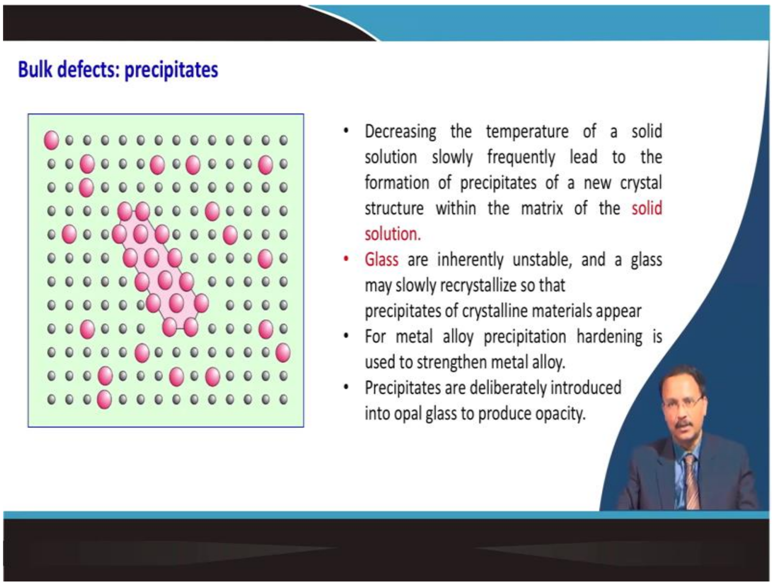

Bulk defects: precipitates

- Decreasing the temperature of a solid solution slowly frequently lead to the formation of precipitates of a new crystal structure within the matrix of the solid solution.
- Glass are inherently unstable, and a glass may slowly recrystallize so that precipitates of crystalline materials appear
- For metal alloy precipitation hardening is used to strengthen metal alloy.
- Precipitates are deliberately introduced into opal glass to produce opacity.

The three dimensional defect actually it may have different sources and when I will teach the phase diagram you will see that the solid phase can be precipitated in a matrix of a different phase which is very common in case of solid solution. In case of glass also they are inherently unstable.

So, if you wait for long time then devitrification takes place and small crystalline are dispersed in the glassy matrix. So, that is also a three dimensional precipitation kind of defect. For metal as you know that this alloying is quite important and that is one way to strengthen the metal and we call it say precipitation hardening due to the precipitation of secondary phase.

And also in sudden glass like opal it is intentionally added to make the glass instead of transparent to make it opaque. So, the trade men is opal glass and there also these three dimensional defect are of utmost importance.

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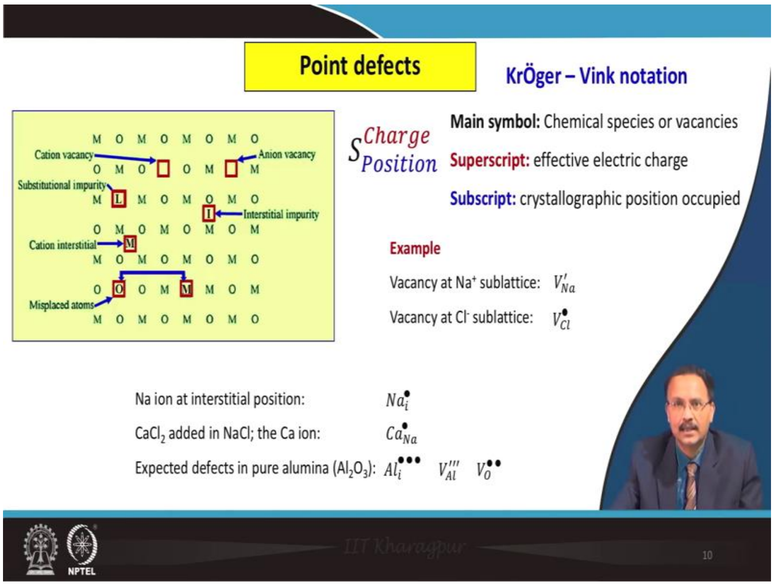

Point defects

KrÖger – Vink notation

$S^{Charge}_{Position}$

Main symbol: Chemical species or vacancies

Superscript: effective electric charge

Subscript: crystallographic position occupied

Example

Vacancy at Na^+ sublattice: V'_{Na}

Vacancy at Cl^- sublattice: $V^{\bullet}_{Cl}$

Na ion at interstitial position: $Na^{\bullet}_{i}$

$CaCl_2$ added in NaCl; the Ca ion: $Ca^{\bullet}_{Na}$

Expected defects in pure alumina (Al_2O_3): $Al^{\bullet\bullet\bullet}_{i}$ V'''_{Al} $V^{\bullet\bullet}_{O}$

So, now, if I just summarize this you can have from this view graph, you can see that there are cation vacancy one of the point defects substitutional impurity, then interstitial cation then misplaced atom we call its antisite defect or cation interstitial, anion interstitial these are the prominent type of point defects.

Now, one should have a prominent type of notation and this notation actually we have gotten in terms of Kroger and Vink notation right. And please be attentive to understand this you have three position like this one main symbol S, then you have a superscript and then you have a subscript.

So, the main symbol that denotes the chemical species, it could be vacancy, it could be sodium ion or it could be chloride ion. So, this is the main species main chemical species and the charge associated with that species you will have to write in the superscript.

And the position of that particular point defect you will have to write in the subscript position. So, the site one example say you want to write vacancy in sodium sub lattice. So, it is vacancy. So, the chemical notation is V, then the position is in sodium. So, you will have to write sodium here and sodium ion they are positively charge. So, when the vacant site is there; that means, the positive site has done positive charge has come out.

So, this is negative charge it is coming. So, negative charge is given by this small hyphen and in case of chloride ion again if vacancy occurs. So, chloride ion was there, but now it is not there. So, it is still a vacancy in chloride ion site and the charge will be positive.

If it is an interstitial like sodium interstitial, it will bring positive charge. So, I will put a dot if calcium replace sodium. So, calcium is having plus 2 valence state, it is replacing sodium plus 1 valence state, it is bringing one extra positive charge. So, I will write calcium sodium dot will be there.

Similarly, you can write for aluminum interstitial or vacancy in aluminum, alumina is having plus 3 valence state. So, 3 negative sign will be there and this kind of notation is known as Kroger and Vink notation which is used to define the chemistry of this kind of defect.

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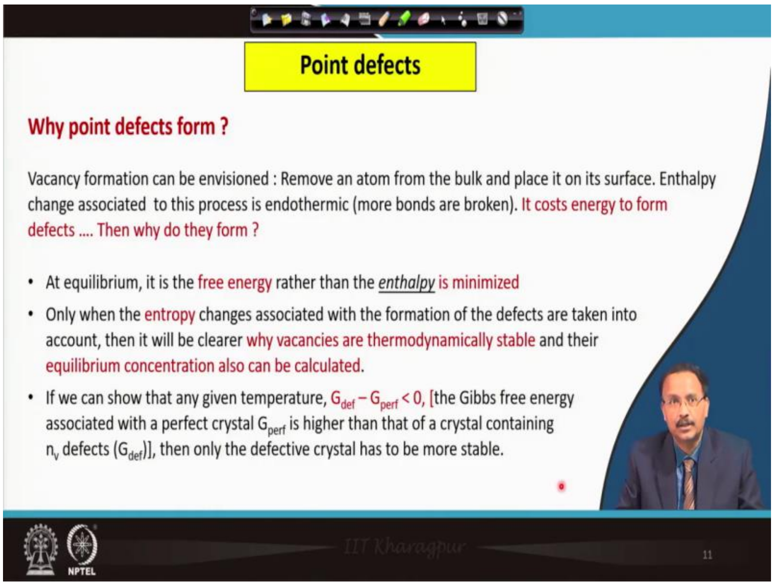

Point defects

Why point defects form ?

Vacancy formation can be envisioned : Remove an atom from the bulk and place it on its surface. Enthalpy change associated to this process is endothermic (more bonds are broken). It costs energy to form defects .... Then why do they form ?

- At equilibrium, it is the free energy rather than the *enthalpy* is minimized
- Only when the entropy changes associated with the formation of the defects are taken into account, then it will be clearer why vacancies are thermodynamically stable and their equilibrium concentration also can be calculated.
- If we can show that any given temperature, $G_{def} - G_{perf} < 0$, [the Gibbs free energy associated with a perfect crystal G_{perf} is higher than that of a crystal containing n_v defects (G_{def})], then only the defective crystal has to be more stable.

Now, the question arises why exactly the defect will form because you see that a bulk atom which is coordinated with say covalent bond. So, it will have to the bond will have to be broken and then this atom you will have to take it out right. So, its you will have to spend energy, it is endothermic in nature you will have to spend energy for the defect creation. So, the question is that if I have to spend energy then how come this defect formation is energetically favorable?

But the point is that you know that we are not In fact, for the equilibrium when the equilibrium defect concentration once get then it is not free energy that is being minimized it is actually sorry it is not the formation this each enthalpy is not minimized, but the free energy is getting minimized. So, that is number 1. Second is the entropy change also takes place and this entropy change entropy having different types of entropy I will introduce. So, this entropy change is some way related to this vacancy formation.

And finally, we will show that the energy free energy after the defect is form and free energy of otherwise perfect crystal, this if you subtract this the formal from the latter it is negative. So, it is energetically favorable. So, once it is energetically favorable then the defect formation will be there. In fact, if you cross the temperature the sub zero the temperature then all material will have defect.

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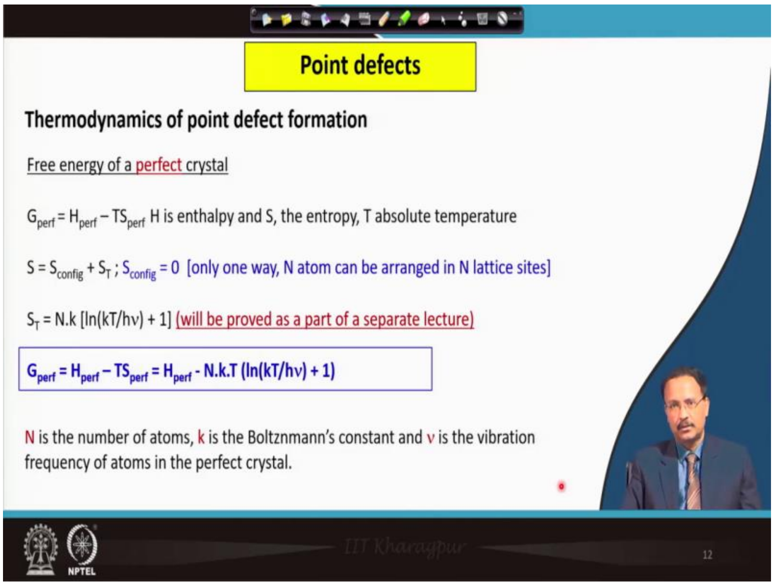

Point defects

Thermodynamics of point defect formation

Free energy of a perfect crystal

$G_{perf} = H_{perf} - TS_{perf}$ H is enthalpy and S, the entropy, T absolute temperature

$S = S_{config} + S_T$; $S_{config} = 0$ [only one way, N atom can be arranged in N lattice sites]

$S_T = N.k\,[\ln(kT/h\nu) + 1]$ (will be proved as a part of a separate lecture)

$$\boxed{G_{perf} = H_{perf} - TS_{perf} = H_{perf} - N.k.T\,(\ln(kT/h\nu) + 1)}$$

N is the number of atoms, k is the Boltznmann's constant and ν is the vibration frequency of atoms in the perfect crystal.

So, in order to understand it better let us take help of thermodynamics. In fact, many of these thing again I will discuss in another lecture, but to start with if you start to write the free energy of a perfect crystal, then you can write that energy for a perfect crystal is related to enthalpy, temperature and is entropy right.

So, this entropy they have two parts: one is configurational entropy that you have to say in lattice site in the crystal. So, how many way you can arrange it in a lattice side? Because crystal site the lattice site you cannot change. So, we will have to arrange it. So, only one way you can arrange it. So, if you can arrange only one way for a perfect crystal then configurational entropy is 0.

Now, the thermal entropy because the continuously your atoms are vibrating at a particular temperature. So, thermal entropy can be given by this formula N is the number of atom, k is Boltzmann constant and υ is the frequency of vibration of this atom right. So, this thing I will proof part of my other lecture. So, at present you just take it that the thermal entropy can be related by this particular equation.

Now you put it back you get it the free energy for a perfect crystal. So, I have just put perfect enthalpy minus this S T I have just put it. So, this is my equation for the free energy. So, as I said N here is a number of atom, k is the Boltzmann's constant and υ is the frequency of atoms for the perfect crystal.

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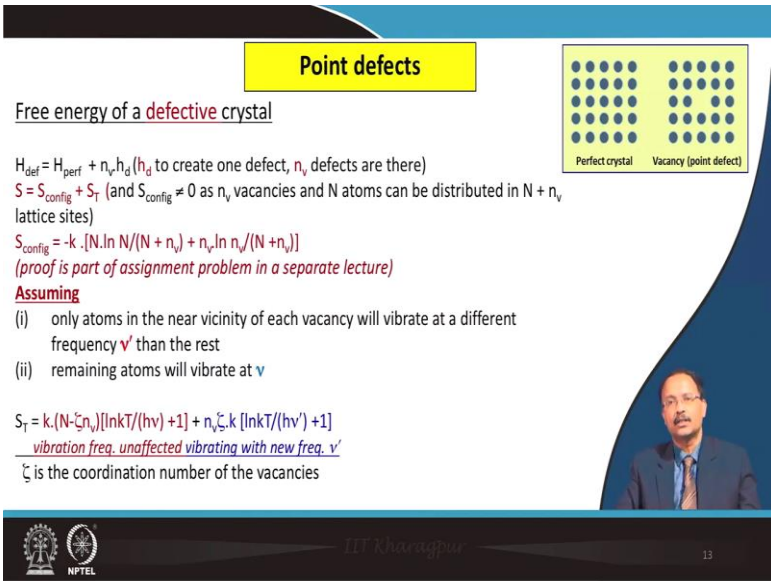

Point defects

Free energy of a defective crystal

$H_{def} = H_{perf} + n_v.h_d$ (h_d to create one defect, n_v defects are there)

$S = S_{config} + S_T$ (and $S_{config} \neq 0$ as n_v vacancies and N atoms can be distributed in $N + n_v$ lattice sites)

$S_{config} = -k.[N.\ln N/(N + n_v) + n_v.\ln n_v/(N + n_v)]$

(proof is part of assignment problem in a separate lecture)

Assuming

(i) only atoms in the near vicinity of each vacancy will vibrate at a different frequency **v′** than the rest

(ii) remaining atoms will vibrate at **v**

$$S_T = \underbrace{k.(N-\zeta n_v)[\ln kT/(hv) + 1]}_{\text{vibration freq. unaffected}} + \underbrace{n_v\zeta.k\,[\ln kT/(hv') + 1]}_{\text{vibrating with new freq. } v'}$$

ζ is the coordination number of the vacancies

Now, let us look at the situation where defect is been created. So, this is the perfect crystal and now here a point defect has been created. So, these bonds are broken and this material this particular atom has done somewhere else towards the surface right. So, the vacancy has been created. So, again I will write the equation for the enthalpy it will be for perfect crystal, the internal enthalpy will be there and say number of vacancy that is created per unit volume is n v and the enthalpy associated with each volume.

So, that will be there. So, my enthalpy will be this and h_d is to create one defect this enthalpy and n_v is the defect that has been created. Now here configurational entropy you cannot omit because now there are n_v number of vacancy and this can be distributed regular lattice site plus vacant lattice site.

So, there is a possibility for distribution. So, you cannot neglect it. So, configurational entropy again it can be defined by this relation, at present you just go with me and one can prove it. In fact, I will show you how to prove that in my next lecture next to next lecture actually.

So, configurational entropy you can derive from this equation. Now you see the thermal entropy is always there thermal entropy will be there, but now there is a difference when the vacancy is there, the frequency is different from the regular lattice site right. So, we have two different types of frequency one is υ' dash which is nearby to this vacancy and another one a regular vacancy which is υ.

So, now, your thermal entropy has two part one part is for the otherwise regular lattice and other part is related to the defect right. So, here the total number of site was N. So, I am assuming n_v vacancy has created with the coordination number of ξ. So, therefore, this total numbers minus this site I will just put and remaining relation will be same like the last slide also I have defined. So, one component is vibrational frequency unaffected and another is vibrating with a new frequency.

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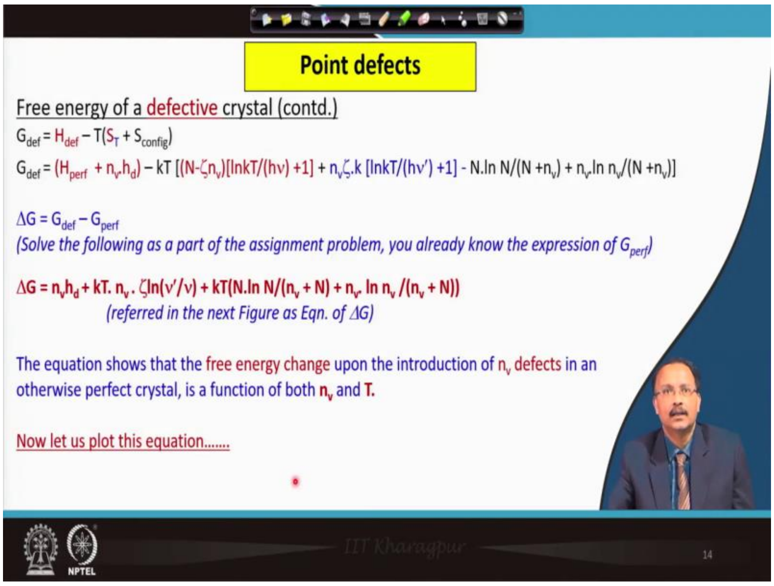

Point defects

Free energy of a defective crystal (contd.)

$G_{def} = H_{def} - T(S_T + S_{config})$

$G_{def} = (H_{perf} + n_v.h_d) - kT\,[(N-\zeta n_v)[\ln kT/(h\nu) + 1] + n_v\zeta.k\,[\ln kT/(h\nu') + 1] - N.\ln N/(N + n_v) + n_v.\ln n_v/(N + n_v)]$

$\Delta G = G_{def} - G_{perf}$

(Solve the following as a part of the assignment problem, you already know the expression of G_{perf})

$\Delta G = n_v h_d + kT.\, n_v\,.\,\zeta \ln(\nu'/\nu) + kT(N.\ln N/(n_v + N) + n_v.\ln n_v/(n_v + N))$

(referred in the next Figure as Eqn. of ΔG)

The equation shows that the free energy change upon the introduction of n_v defects in an otherwise perfect crystal, is a function of both n_v and T.

Now let us plot this equation.......

Now if you write the free energy of a defective crystal then this relation is valid. So, I will just put this value. So, H defect I will put, then T will be there k will be there and I will put the configurational entropy and thermal entropy. So, the difference between these two is this one and this algebra you have to do you have already derive the G of perfect and you have derived what is G for the defect. So, now, you subtract it you will come up with this relation this relation.

So, here in this relation you can see that the free energy change. This free energy change this upon introduction of the defect in an otherwise perfect crystal is a function of the defect density n_v and temperature.

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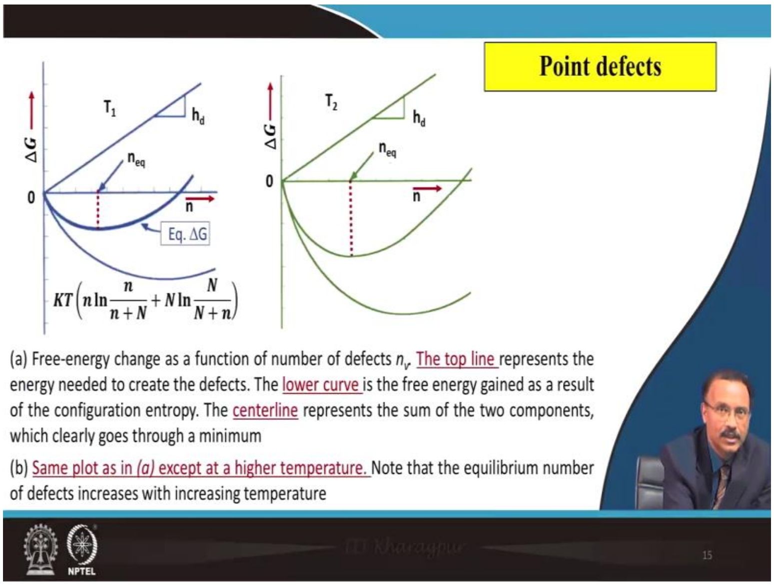

Point defects

(a) Free-energy change as a function of number of defects n_v. The top line represents the energy needed to create the defects. The lower curve is the free energy gained as a result of the configuration entropy. The centerline represents the sum of the two components, which clearly goes through a minimum

(b) Same plot as in *(a)* except at a higher temperature. Note that the equilibrium number of defects increases with increasing temperature

We will plot this relation and this relation will be something like this. So, you have two component, one component is related to the formation of the defect is a straight line related to h_d, another one is the entropy term part and then this is the actual subtraction or addition whatever you do out of these two curves, you will get a curve with a minimum. So, this curve is having a minimum; that means, if you just differentiate that the free energy position you will be able to calculate the equilibrium defect concentration we will be doing that.

But as I said the first the free energy change as a function of number of defects the top line this is the energy needed to create a particular defect, the lower curve is energy gained as a result of the configurational entropy and the center line is basically the sum of these two components.

So, then you see the same plot here, but at higher temperature. So, in higher temperature what is the difference? That this depth will be more it is more stable the defect is more stable and not only that this equilibrium concentration this is also shifted to relatively higher temperature. So, that is the difference.

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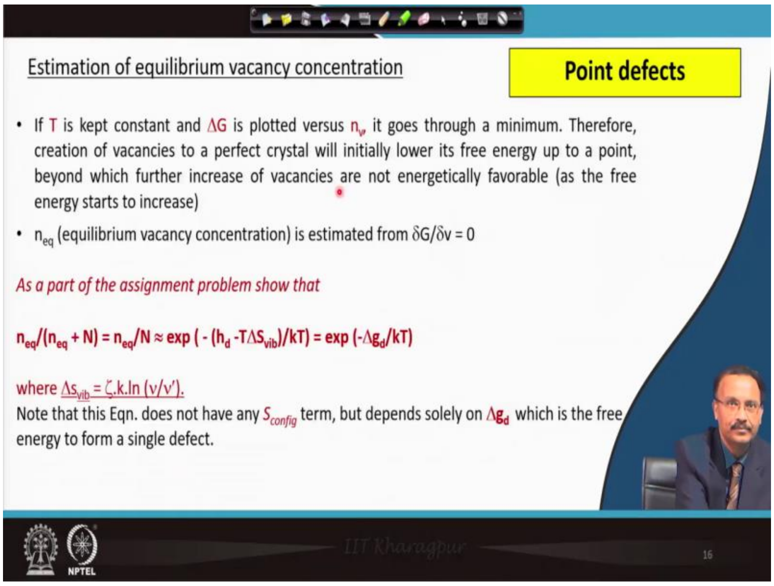

Estimation of equilibrium vacancy concentration

Point defects

- If T is kept constant and ΔG is plotted versus n_v, it goes through a minimum. Therefore, creation of vacancies to a perfect crystal will initially lower its free energy up to a point, beyond which further increase of vacancies are not energetically favorable (as the free energy starts to increase)
- n_{eq} (equilibrium vacancy concentration) is estimated from $\delta G/\delta v = 0$

As a part of the assignment problem show that

$$n_{eq}/(n_{eq} + N) = n_{eq}/N \approx \exp\left(-(h_d - T\Delta S_{vib})/kT\right) = \exp(-\Delta g_d/kT)$$

where $\Delta s_{vib} = \zeta.k.\ln(\nu/\nu')$.

Note that this Eqn. does not have any S_{config} term, but depends solely on Δg_d which is the free energy to form a single defect.

Now, you can estimate the equilibrium vacancy concentration by just differentiating this free energy curve and we will come up with this relation. This is the equilibrium defect concentration and this is related to a particular defect formation. This defect formation a particular term and this part is your vibrational entropy remember there is no configurational entropy is there.

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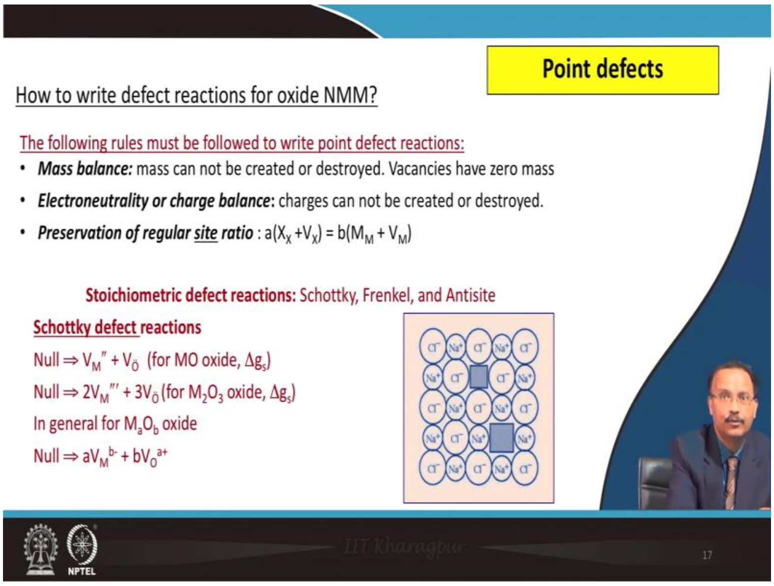

Point defects

How to write defect reactions for oxide NMM?

The following rules must be followed to write point defect reactions:

- ***Mass balance:*** mass can not be created or destroyed. Vacancies have zero mass
- ***Electroneutrality or charge balance*:** charges can not be created or destroyed.
- ***Preservation of regular site ratio*** : $a(X_X + V_X) = b(M_M + V_M)$

Stoichiometric defect reactions: Schottky, Frenkel, and Antisite

Schottky defect reactions

Null $\Rightarrow V_M'' + V_{\ddot{O}}$ (for MO oxide, Δg_s)

Null $\Rightarrow 2V_M''' + 3V_{\ddot{O}}$ (for M_2O_3 oxide, Δg_s)

In general for M_aO_b oxide

Null $\Rightarrow aV_M^{b-} + bV_O^{a+}$

So, this formulation now I will write I will used to write a Frenkel relation and as you can see three things you will have to consider one the mass balance there should not be any change in the mass during this process electroneutrality will have to be maintained and the total site ratio should be constant. So, this is a typical relation written for the Schottky defect that creation of anion vacancy and cation vacancy depending on what type of composition it is there and this is the general form.

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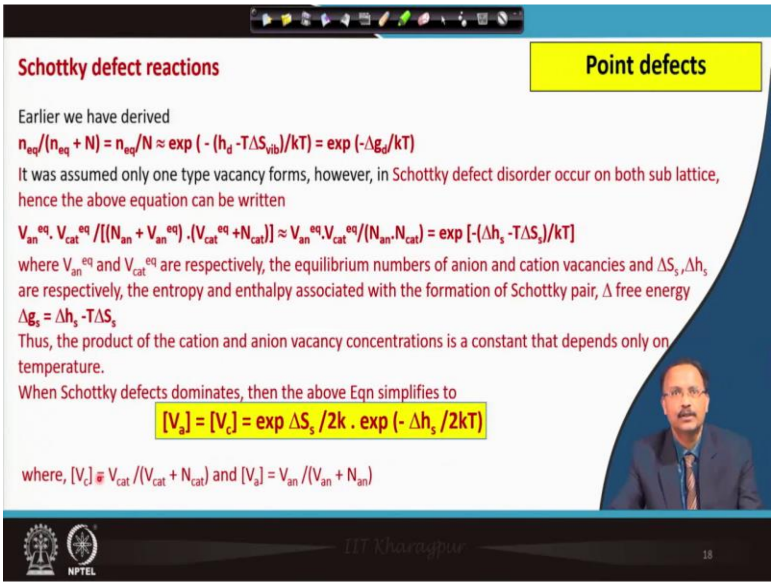

Schottky defect reactions

Point defects

Earlier we have derived

$n_{eq}/(n_{eq} + N) = n_{eq}/N \approx \exp(-(h_d - T\Delta S_{vib})/kT) = \exp(-\Delta g_d/kT)$

It was assumed only one type vacancy forms, however, in Schottky defect disorder occur on both sub lattice, hence the above equation can be written

$V_{an}^{eq} \cdot V_{cat}^{eq} / [(N_{an} + V_{an}^{eq}) \cdot (V_{cat}^{eq} + N_{cat})] \approx V_{an}^{eq} \cdot V_{cat}^{eq} / (N_{an} \cdot N_{cat}) = \exp[-(\Delta h_s - T\Delta S_s)/kT]$

where V_{an}^{eq} and V_{cat}^{eq} are respectively, the equilibrium numbers of anion and cation vacancies and ΔS_s, Δh_s are respectively, the entropy and enthalpy associated with the formation of Schottky pair, Δ free energy

$\Delta g_s = \Delta h_s - T\Delta S_s$

Thus, the product of the cation and anion vacancy concentrations is a constant that depends only on temperature.

When Schottky defects dominates, then the above Eqn simplifies to

$$[V_a] = [V_c] = \exp \Delta S_s / 2k \cdot \exp(-\Delta h_s / 2kT)$$

where, $[V_c] = V_{cat}/(V_{cat} + N_{cat})$ and $[V_a] = V_{an}/(V_{an} + N_{an})$

So, a defect equation whatever we already created now I will put instead of one defect to different defects. One is anion vacancy and cation vacancy and then finally, we do the algebraic way to get the relation something like this the anion vacancy concentration is equal to cation vacancy concentration because it is a Schottky defect and that is related to the entropy and the enthalpy of Schottky defect formation.

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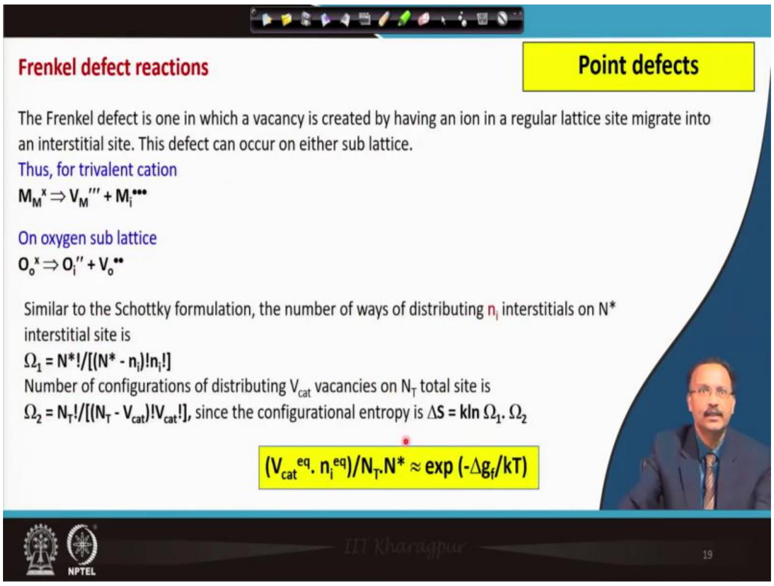

Frenkel defect reactions

Point defects

The Frenkel defect is one in which a vacancy is created by having an ion in a regular lattice site migrate into an interstitial site. This defect can occur on either sub lattice.

Thus, for trivalent cation

$M_M^x \Rightarrow V_M''' + M_i^{\bullet\bullet\bullet}$

On oxygen sub lattice

$O_o^x \Rightarrow O_i'' + V_o^{\bullet\bullet}$

Similar to the Schottky formulation, the number of ways of distributing n_i interstitials on N* interstitial site is

$\Omega_1 = N^*!/[(N^* - n_i)!n_i!]$

Number of configurations of distributing V_{cat} vacancies on N_T total site is

$\Omega_2 = N_T!/[(N_T - V_{cat})!V_{cat}!]$, since the configurational entropy is $\Delta S = k\ln \Omega_1 . \Omega_2$

$(V_{cat}^{eq}. n_i^{eq})/N_T.N^* \approx \exp(-\Delta g_f/kT)$

Similarly, we can write for the Frenkel defect exactly the same formulation you will have two way and in one of the assignment problem I have asked you to solve this relation in fact. So, it is a same principle that is followed and this is the final relation of the vacancy of cation and interstitial and how it is related to the Frenkel energy.

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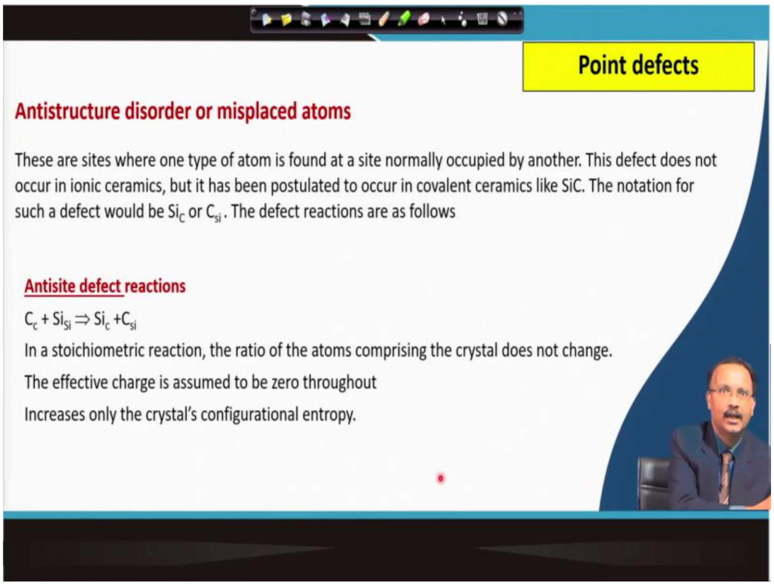

Point defects

Antistructure disorder or misplaced atoms

These are sites where one type of atom is found at a site normally occupied by another. This defect does not occur in ionic ceramics, but it has been postulated to occur in covalent ceramics like SiC. The notation for such a defect would be Si_C or C_{Si} . The defect reactions are as follows

Antisite defect reactions

$C_c + Si_{Si} \Rightarrow Si_c + C_{Si}$

In a stoichiometric reaction, the ratio of the atoms comprising the crystal does not change.

The effective charge is assumed to be zero throughout

Increases only the crystal's configurational entropy.

So, finally, there is an antisite defect where instead of one particular atom this is replaced by another particular atom. No stoichiometry is changed and it is a straight forward defect only the configurational entropy changes for antisite defects.

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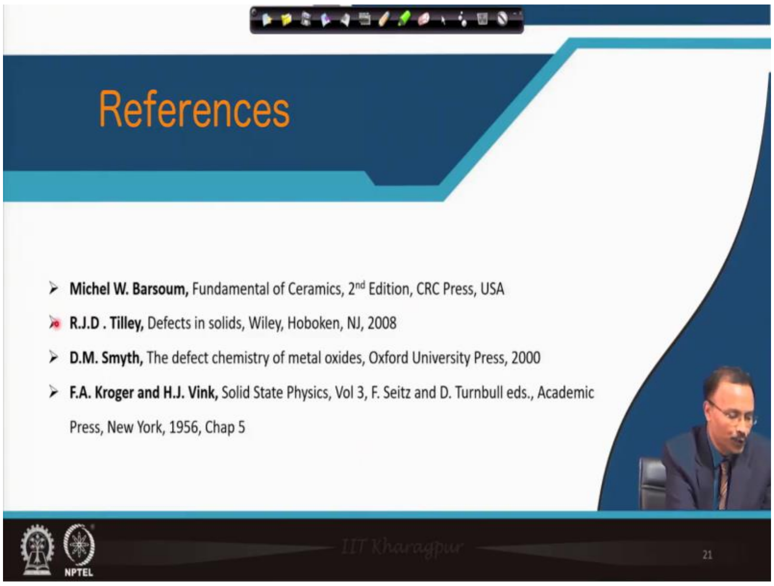

References

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- **D.M. Smyth,** The defect chemistry of metal oxides, Oxford University Press, 2000
- **F.A. Kroger and H.J. Vink,** Solid State Physics, Vol 3, F. Seitz and D. Turnbull eds., Academic Press, New York, 1956, Chap 5

So, that ends the part of the stoichiometric defect how you can write stoichiometric defect equations and these are four very major book and you can consult as a reference book.

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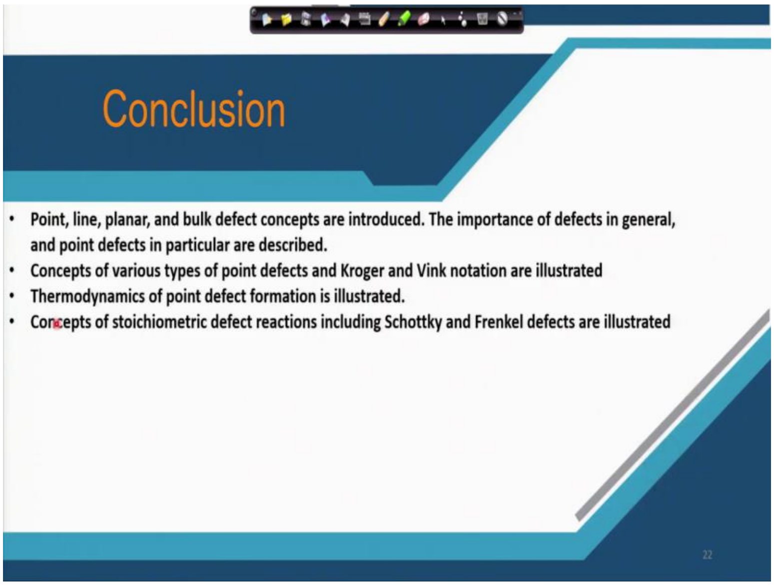

Conclusion

- Point, line, planar, and bulk defect concepts are introduced. The importance of defects in general, and point defects in particular are described.
- Concepts of various types of point defects and Kroger and Vink notation are illustrated
- Thermodynamics of point defect formation is illustrated.
- Concepts of stoichiometric defect reactions including Schottky and Frenkel defects are illustrated

And in this particular lecture I have introduced point defect, line defect, planar defect and three dimensional defect.

Concept of various types of point defect and how it is written in terms of Kroger and Vink notation that we have done, the thermodynamic basis for the point defect creation is illustrated and concept of the stoichiometric defect reaction particularly for Schottky and Frenkel we have walked it out and then we have described it. So, in the next class we will be talking about non stoichiometric defect.

Thank you so, much for your attention.