**Structure of Materials**
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# Lecture - 23
# Defects in Crystals

I got with me here some models, what you might call toy models.

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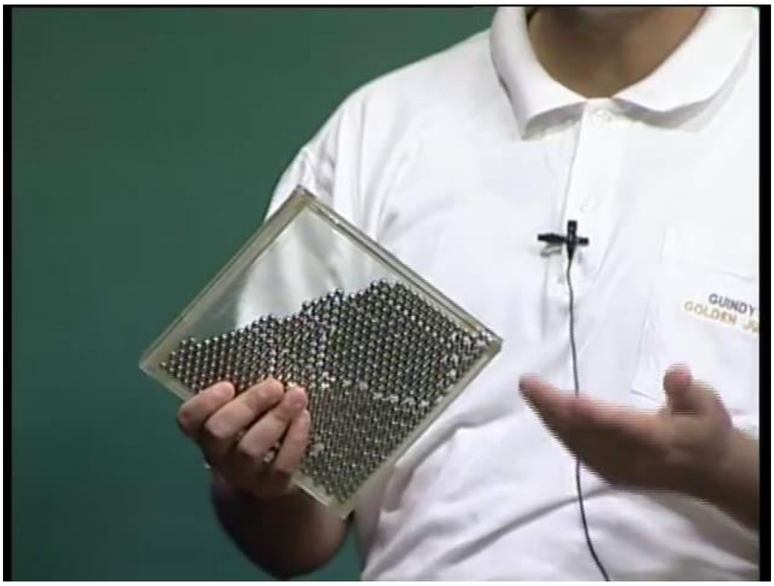

They consist of basically spherical metal balls. To illustrate some of the concepts here, we are trying to understand here, which include defects in crystals, specific defects. We will focus on or will be defects like grain boundaries, vacancies etcetera. So, I have you can see this model little more. I will show this from an alternate camera angle for you for better visibility. So, what I can do to this model, which is nothing but two transparent sheets, where in I have filled some metal balls. Again, shake this thing around. Rotate it around. Of course, try to simulate some of the conditions, which will be found in a metal. For instance, about I am shaking. This is something like thermal vibrations.

So, using this toy model, let us see how we can form some of the defects, which we have been considering so far. So, let me shake this a little bit and I have got now for instance, structure which I can show you in the other vision, which is the top camera view. So, you can see here this ball the in this region are arranged in a perfect crystalline array. This is my high pad density, which is the highest packing in two dimension, which is the hexagonal packing.

Similarly, this region again is arranged in a perfect crystalline array. This is the third region, which is arranged in a perfect crystalline array between these 3 regions. For instance, of course, you can consider some disorder division here. Within these 3 main crystalline regions, you can see there is a boundary. So, this is what like. We will, shall define can be called as a grain boundaries. See above grain boundary, which goes like this is one kind of a defect, which in we can nicely simulate using this toy model. So, let me take this model and do a little more of shakings so that I can show you some more defects and especially, the formation of vacancy.

So, I have done some shaking here and so, try to create different kind of crystalline orders in this. So, let me perfect view for you, where an I can get a vacancy. Now, for instance, I got a picture here. Now, I will little zoom in a little bit for you to show them a better picture of this. So, this is now my crystalline array balls. Within this crystalline region, as you can see, this crystalline region you can see two vacancies. So, two vacancies are here. An important thing of course, which an experiment we can do keeping this vacancies.

For view that, I take this model again and try to give some thermal vibrations to this. So then, I put my model back and you see low and be hold in spite, of all the vibration I gave. You see these two vacancies are still there. So, this is something like we can visualize as equilibrium thermo dynamics presents of vacancy. Of course, this is just a toy model. But, still you can see that these vacancies are difficult to shake away and the persist. This is taking knowledge from understanding vacancies.

These are like our equilibrium concentration or vacancies. So, we can see that some small toy model like this just consists of some spherical metal balls between two perspect sheets can actually give you a nice picture. What is a crystalline array, the concept of grain boundaries etcetera. Apart, from this model here, in which I showed you vacancies.

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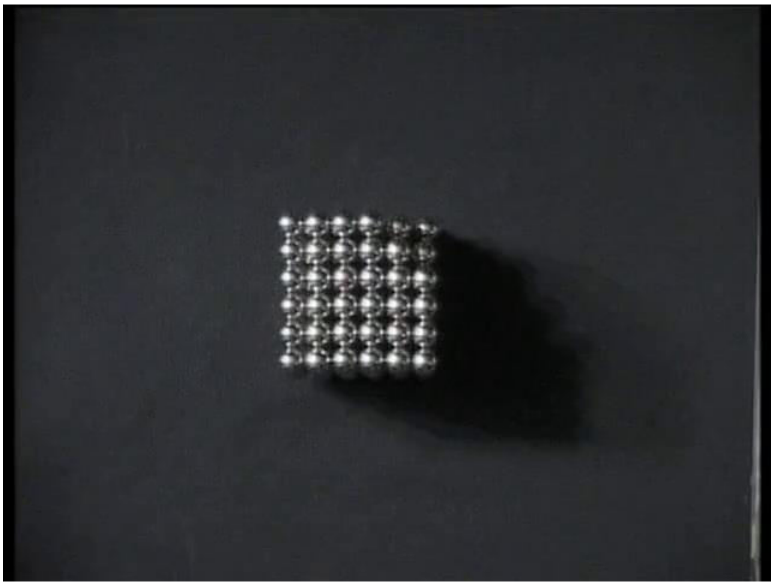

I got couple of other models. One is this model of a cube here. This model of a cube shows for instance, the presents of surfaces. So, any as I told any crystal in innovatively real practical crystal has to have surfaces. So, for instance, this is my one 0, 0 surface of the simple cubic crystals. So, this is a simple cubic arrangement. As you can see, this is my one 0, 0 surface. Similarly, you could have other surfaces in the crystal. Later on, we will make a relative calculation of the surface energy. For instance, in a copper crystal, this is not simple cubic.

It is phase 100 cubic. So, for instance, this will be a 1, 1, 1 crystal. If I look a little more carefully at this 1, 1 surface; I zoom in a little bit here. So, you can see that this 1, 1, 1 surface actually has these atoms here. So, these are known one surface atoms. You can see that this 1, 1, 1 surface actually is more loosely packed in the simple cubic crystal as compared to the 1, 0, 0 surface. In the case of later on, we already made the calculation that in the case of phase 100 cubic crystals actually the 1, 1, 1 surface is the close pack surface.

There is a higher density as compared to the 1, 0, 0 surface. Similarly, I am going to show you another surface of the crystal, which can see in focus here. This is now I cut my crystal like this is vertical plane. That means this is my 1, 1, 0 kind of a surface. Again, you can see this 1, 1, 0 kind of surface has a lower density as compare to the 1, 0, 0 surface. It is not a close pack plane. But still it has high density than this 1, 1, 0 surface in a simple cubic crystal.

So, already I made these calculations before to see actually see more this things. But, this actually shows some sort of what I might call a toy model of surfaces in a crystal. Now, for instance this one; 0, 1, 1 surface has been disturbed. So, you can see that this atom as move to around place. Therefore, this can be thought of as a defect. In a defect, that means surface itself is a defect. This surface has been detected by the wrong position of this atom, which of course, I can try to move back to its original place.

So, these are nothing but magnetic metal balls from which I made these models. So, let me show you one more defect and this pertains the question asked me Sowmya in a previous class, previous lecture. Here, the defect I see in the center for instance, previous model to the center. So, the defect I see in the center is actually associated with the rotational symmetry of this crystal. It is actually what might call disclinations. So, let me for assume, out a little bit from this position. We can see clearly that there is a pentagon in the center. So, the normal coordination as you can see from this model on the left hand side the normal coordination is actually in a preferred orientation.

I will bring other model back to focus. So, normal coordination is 6. That means around this any centrals, we have there are 6 spheres. This is what we preferred. This I would call normal crystalline array in two dimensions. But in this case, the normal coordination has been bren. You can see there is a pentagon in the middle. This is a defect associate with rotational symmetry of this crystal. This, I can call as a disclinations. This is a nice model of a disclination; as you can see pentagons, when you talk about filling space with two dimensional figures.

Hexagons can fill flat space. That means euclidean flat space pentagons can fill spherical two dimensional space. Heptagons 7 fold, 7 sided figures can fill actually hyperbolic two dimensions surfaces. So, if I want to introduce curvature in to a flat surface. Then, hexagons alone will not do. I need to introduce pentagons in the surface. Therefore, the introduction of this pentagon introduces curvature to the surface. It makes its sphere spherical. That means I got a curvature here. So, this is a nice model of a disclination in a crystal. The third model I am going to show you perhaps little head. We will come back to this later in during the course of this lecture.

This is again a ball model, in which I am showing this location. This is of course very crude model. It is not a realistic model of this location. But nevertheless, you can see that the crystal, if you look at this corner, perfect crystal here, perhaps downwards. But here, there is an extra half plane of atoms. You can otherwise think of it as a missing half plane of atoms in the bottom somewhere. Here, I can visualize this middle line, where the pen is. I can visualize this location lines.

This is my of course, in two dimensions. This is just a two dimensions crystal. Therefore, this is a dislocation point. But in 3 dimensions, suppose we had crystal like this pervading many layers below that is a dislocation line. So, with this small toy models, I can try to understand some of these simple crystals. Many of you can actually make this kind of toy models at home with these cycle ball bearing balls. Then, actually try to understand some of these structures, which form when you actually try to make a crystalline array.

Before we take up defects in ionic crystals, let me revise some of the concepts we are been talking so far with regard to defects. We been trying to classify defects based on dimensionality, their association with symmetry, based on their origin, based on their position.

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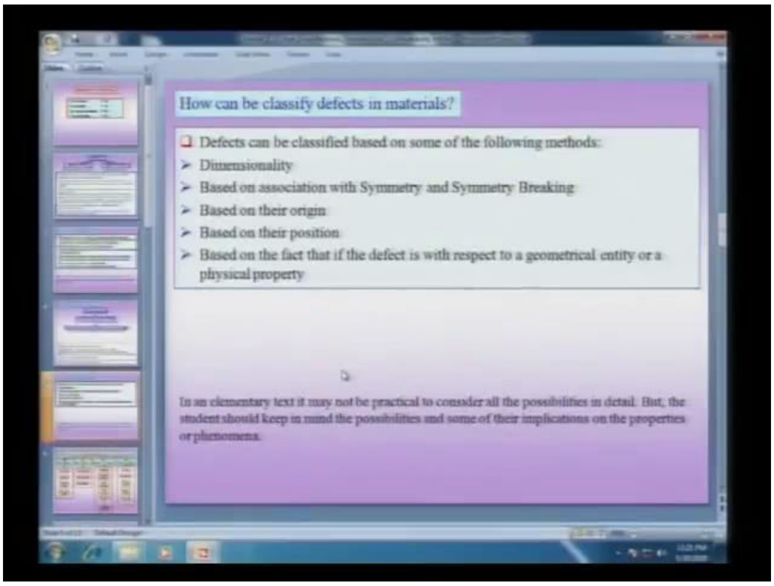

How can be classify defects in materials?

❑ Defects can be classified based on some of the following methods:
- Dimensionality
- Based on association with Symmetry and Symmetry Breaking
- Based on their origin
- Based on their position
- Based on the fact that if the defect is with respect to a geometrical entity or a physical property

In an elementary text it may not be practical to consider all the possibilities in detail. But, the student should keep in mind the possibilities and some of their implications on the properties or phenomena.

The important question of course, that how crystallize been define enhance, how the defect itself has been define, has it been with respect to geometrical entity or a physical property. The path to understand defects, we said was that we take up an isolated defect.

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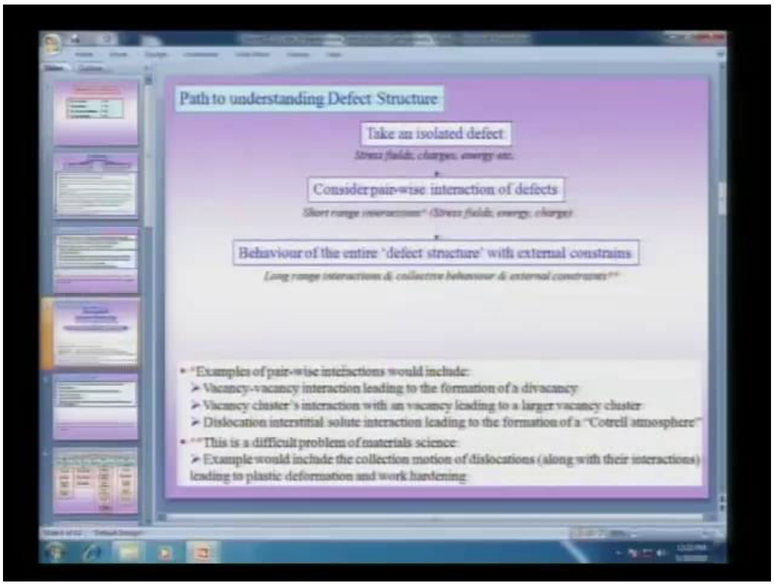

Path to understanding Defect Structure

Take an isolated defect

*Stress fields, charges, energy etc.*

Consider pair-wise interaction of defects

*Short range interactions* (Stress fields, energy, charge)*

Behaviour of the entire 'defect structure' with external constrains

*Long range interactions & collective behaviour & external constraints***

- *Examples of pair-wise interactions would include:
  - Vacancy-vacancy interaction leading to the formation of a divacancy
  - Vacancy cluster's interaction with an vacancy leading to a larger vacancy cluster
  - Dislocation interstitial solute interaction leading to the formation of a "Cotrell atmosphere"
- **This is a difficult problem of materials science:
  - Example would include the collection motion of dislocations (along with their interactions) leading to plastic deformation and work hardening

Then, try to understand all aspects of this isolated defect. Then of course, we try to ask that can the defect associate with other kind of defects of the same kind and different kind. We study their interactions, binding energies etcetera. Then of course, we proceed to the more difficult challenging problem, which is not only problem in terms of the difficulty in understanding. But, also the difficulty in terms of the multiple length scales of the problem involved. That means typically if I am talking about dislocations, I need to worry about isolated dislocations. I need to worry about dislocations cell walls, dislocation grain boundary interactions etcetera.

It would take us across various length scales starting from nanometers to almost microns. So, this is a kind of multi scale integration. I would like to do. In that case, I am considering the behavior of defects under imposed constraints, which could be stresses or forces on the material and also the collective behavior of many kind of defects interacting with each other. So, this is we said was the path to understanding defects. We had especially; in this context define the term called the defect structure.

Now, let us proceed 2 ionic crystals. They have charge specious that means they have an anion and a cation. Therefore, there are special requirements, when we are talking, considering defects in ionic materials. We will note that suppose, I leave some un balance charge in the material. Then, this is going to cause lot of energy for me. Therefore, in ionic materials, charge neutrality becomes out of sort of unwritten rule for maintain low energy state.

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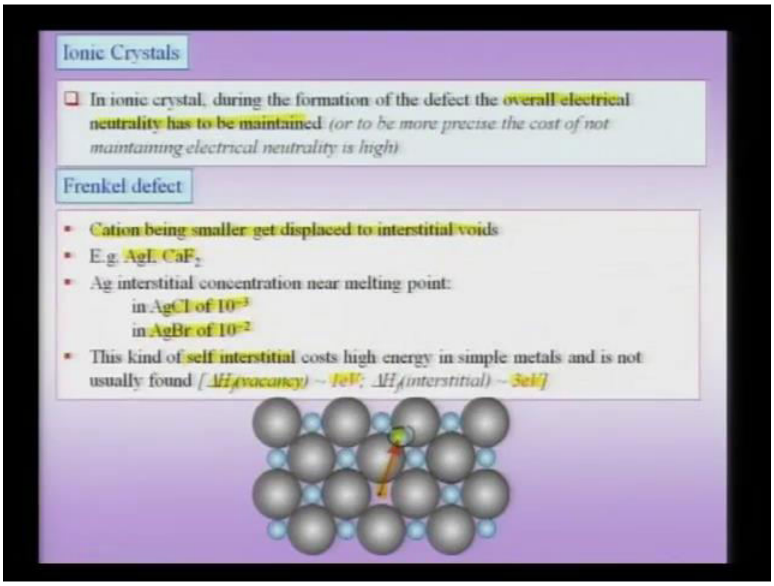

Ionic Crystals

- ☐ In ionic crystal, during the formation of the defect the overall electrical neutrality has to be maintained *(or to be more precise the cost of not maintaining electrical neutrality is high)*

Frenkel defect

- Cation being smaller get displaced to interstitial voids
- E.g. AgI, $CaF_2$
- Ag interstitial concentration near melting point:
  in AgCl of $10^{-3}$
  in AgBr of $10^{-2}$
- This kind of self interstitial costs high energy in simple metals and is not usually found *[$\Delta H_f$(vacancy) ~ 1eV; $\Delta H_f$(interstitial) ~ 3eV]*

That means of course, I do not mean the global energy minima. But, what I mean here is sort of their preferred local energy minimum. So, in the context of ionic crystals, the overall charge in a electrical neutrality is some criteria, which I would follow. The first defect I consider, I think we did was there was no analog with that. We do not consider that in the context of metals. It is the Frenkel defect. In Frenkel defect typically, the cation gets displaced and gets in to interstitial positions. Now, what we went call this is in terms of normal terminology. It is called self interstitial.

The reason that self interstitial are not found in metallic materials for instance, if I take silver or copper, one of these FCC materials, we have noticed that the enthalpy of formation of vacancy was the order of 1 electron volt. But suppose, I am talking about a self interstitial. The energy is about 3 electron volts. So, we see that it cause lot of energy to put a self interstitial in a normal material like copper. Therefore, self interstitial are not found in metallic materials and a normal circumstance.

You could always do an heavy ion bombardment or some kind of an non equilibrium processing. It would take you to such a state, where in such kind of energies can be tolerated so that what I might call them a high energy state as compared to the preferred state. This is of course, the formation of vacancies. Now, examples of Frenkel defect formation can be found in silver iodide and calcium fluoride; if you notice the concentration. Later on, we will make a calculation for instance, the point defect concentration in a material like copper even close a melting point. We would note that this concentration of Frenkel defects is much larger and that found in typical vacancy concentration in metallic materials.

So, you can see in silver chloride, it is about 10 power minus 3 at melting point. In AgBr, it is 10 power minus 2. That means this is the fraction of Frenkel defects as compare to the atomic sights or the number of cations in the material. So, this is one kind of a defect, where in you could clearly see from the picture below. A cation which is supposed to sit in a sub lattice of the cation has been displaced to an interstitial position. Of course, this is a schematic. Like many other pictures, we will be presenting in this lecture.

They all be schematics. So, we should not what we call mistake them to be a true picture of the physical situation. They will be other kind of displacements are on the atom. Of course, these are two dimensional version. The real 3 dimensional structure could be slightly different. So, using of course, this schematic we are understanding that how an interstitial, how an cation, which is originally present in the its sub lattice has been displaced and has moved to the interstitial position. So, this is from the original position. In this case of course, I do not have to worry about charge neutrality because the specious has not been removed from the system. Therefore, in Frenkel defects, the issue of charge neutrality does not arise because it is automatically charge neutral.

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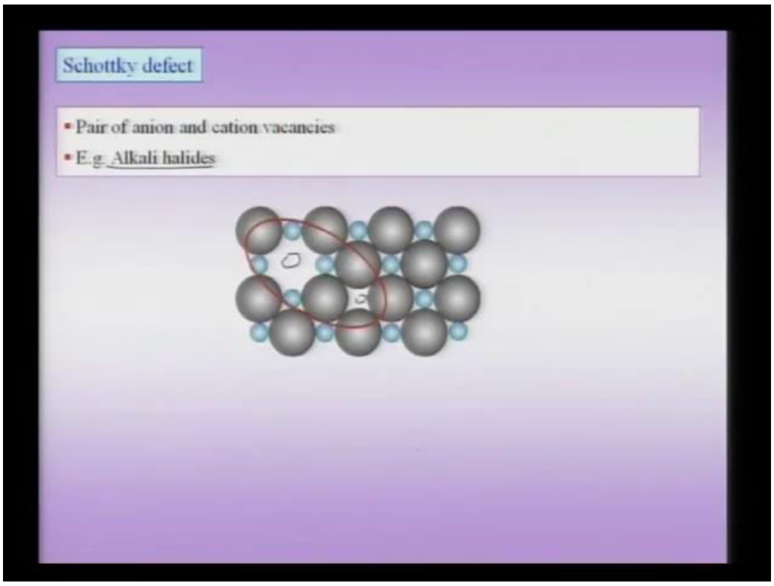

Schottky defect

- Pair of anion and cation vacancies
- E.g. Alkali halides

The second kind of defect which I think is a good example illustrating the bases of charge neutrality is a pair of anion and cation vacancies. So, if a single anion goes missing or a single cation goes missing then, you will have either a positive or a negative charge in the material. So, cation will give you; if cation goes missing then, you have charge im balancing. Similarly, anion goes missing. Schottky defects are typically found in alkali halides. But, suppose I have cation and anion missing together. Then, the charge system charge is maintained neutral.

So, this is called Schottky defect and obviously, there is no analog of this in the normal metallic materials. We have considered before. So, the Frenkel and Schottky defects are two common defects, which I discussed in the context of ionic crystal. But then, we have many more possibilities. So, let me just revise these two important defects in the Frenkel defect. You have an interstitial typically, of this smaller ion, which is the cation. Of course, in theory of course, you could also consider an anion interstitial. But as you can see, the anion is much bigger in size.

Hence, it is usually the cation which gets this place to the interstitial position. The second important one being the Schottky defect, where you have a pair of anion and cation vacancies typically associated with each other. Now, if they are well separated then, they would tend to get associated because of the charge associated with these kinds of defects.

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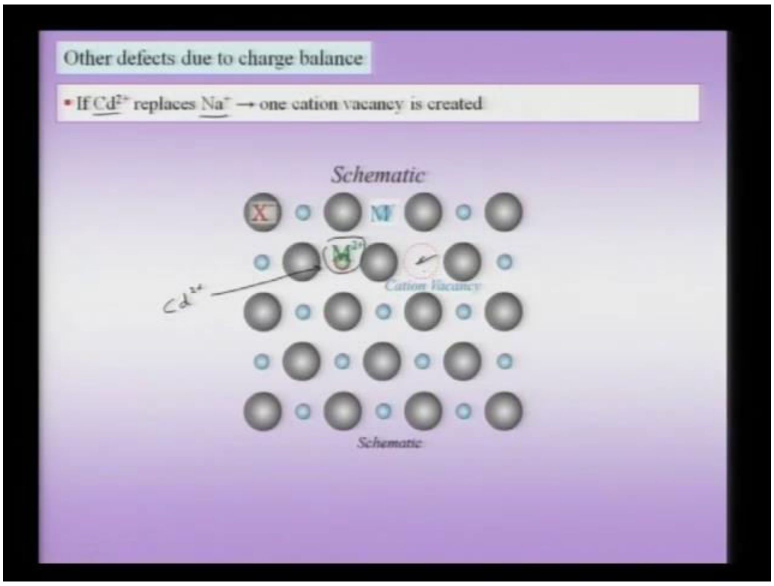

Other defects due to charge balance

- If $Cd^{2+}$ replaces $Na^{+}$ → one cation vacancy is created

There are other possible defects in ionic materials. This illustrates actually very very long. But, we will take up a few illustrative examples to understand some other defects in charge materials, in ionic materials and especially, the concept of charge balance in these materials. Now, for instance, suppose I have a sodium chloride crystal. Instead of a positive mono valent ion in one of those sub lattices, I have a divalent ion. Example, I could consider is if a sodium ion is replaced by a cadmium ion. So, the cadmium is 2 plus.

Suppose, this is my sight where the cadmium ion sits. This is my site Cd2 plus. So that means there is an extra positive charge which is been added to the system to compensate the charge. Typically, a cation will be created. That means if there was 1 M plus. So that I put 2M plus the 2M plus compensate for charge of 2 metal ions; say sodium plus. Therefore, one of these sides is left vacant so that I can have charge neutrality. So, this is another possibility, when it comes to ionic crystals.

That means you have a ion of higher valency replacing one of a lower valency correspondingly to maintain charge neutrality. The number of ions of that type go missing in. So, this is another simple possibility defect in ionic materials. Of course, it depends on the particular system like for instance; I am talking about sodium chloride. I am talking about potassium bromide. Which kind of a defect is lower in energy? Under what circumstances those defects has been produced? So, many of these could be non equilibrium defects. They could be a yield away. I mean you wait for at a certain temperature for long time.

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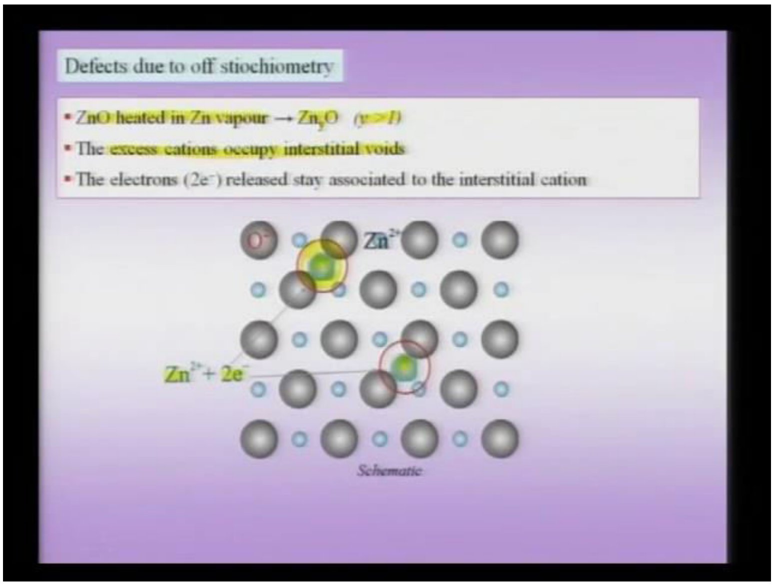

Defects due to off stiochiometry

- ZnO heated in Zn vapour → $Zn_yO$ ($y > 1$)
- The excess cations occupy interstitial voids
- The electrons ($2e^-$) released stay associated to the interstitial cation

There could be defects, which are arising out of non off stoichiometry. Later on, we will discuss this again once more in this kind of defects in the context of structural point defects. So, that aspect we already discuss that how some of the defects could play a structural role. We call them structural defects. We will come back to this topic of off stoichiometry in that context. But here, we will consider the experiment where in zinc oxide vapor has been heated in zinc. Oxide has been intended, zinc vapor that means the zinc, which is now in the way perform can be incorporated into the zinc oxide crystal.

The stoichiometry is of the compound as will be affected. In that, more and more zinc is be in corporate within the material. Now, this y is greater than 1. That means there is a zinc excess in the crystal. These excess cations occupy interstitial void positions as shown in the figure below. For instance, now, this zinc would go in to interstitial positions. Remember, this is a cation and smaller in size. Therefore, based on the principle we saw before that it is actually the cation, which can sit in interstitial position.

Similarly, the zinc can also set in a interstitial position to maintain charge neutrality, the electrons associated with zinc. For instance now, zinc can give 2 electrons. They stay close to the zinc. So, it is not just a zinc 2 plus ion which is sitting there. It is a zinc 2 plus ion with electrons associated with that zinc 2 plus which I created for zinc 2 plus which sit around this interstitial position. Therefore, we maintain charge neutrality in this system. So, as you can see not only can be self interstitials, but they can be interstitials of this type.

In some sense this self interstitial, but which is coming from off stoichiometry. That means I incorporated more zinc. Then, the sub lattice can allow. Therefore, this extra zinc cannot sit in the sub lattice position and hunt has to go in to interstitial positions. To maintain charge neutrality, this interstitial defect is also associated with electrons. So, this is an possibility in ionic materials.

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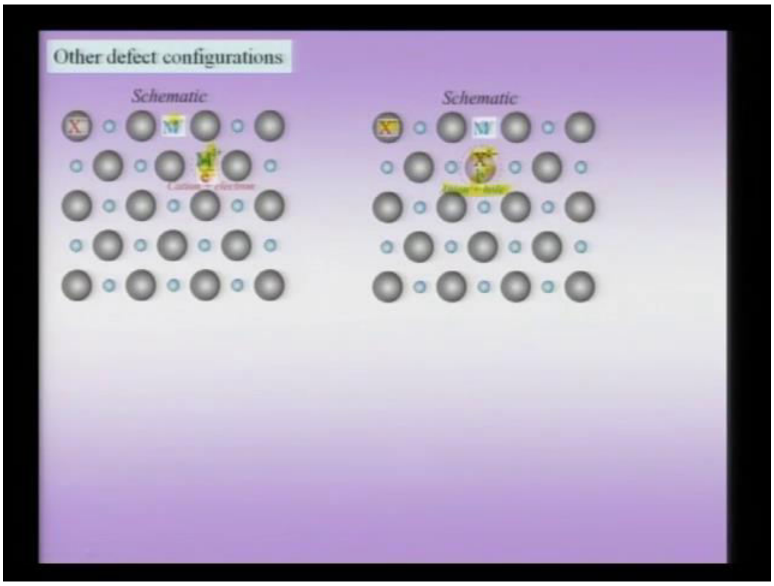

Other defect configurations

They are other defect concentrations for configuration. For instance, there are 2 which I shown in this slide. As I again point out, that is many of these are schematic diagrams. They should be interpreted appropriately. So, for instance here, I have 2 configurations; one in which there is cation and electron and other case there is an anion in a hole. So, this cation when is this kind of a configuration possible, where in instead of an M plus ion, I have an M2 plus cation, which is present in these sub lattice.

That means down this is the defect in the cation sub lattice. Now, because it is a 2 plus for maintaining charge neutrality, there has to be electron present. This electron is typically localized around this M2 plus ion giving overall charge neutrality. So, this a defect configuration, in which there is an electron present near and cation defect. So, this is a cation. For instance, this could be divalent cation with an associated electron, either possibility. Of course, I could have an instead of having a mono valent from since an example or monovalent anion, I could divalent anion.

In this case to maintain charge neutrality, I would need a hole. So, this would be an anion in a hole combination, which is giving me my charge neutrality in the system. So, these are two nice examples. It is in cations sub lattice defect with an electron or an anion sub lattice defect with the hole. So, these are two possibilities. Obviously, this will show up, these electrons. Additional electrons and holes will show up us additional states in the band diagram. It would correspond to additional resonance and absorptions. So, this you can actually experimentally investigate these structures.

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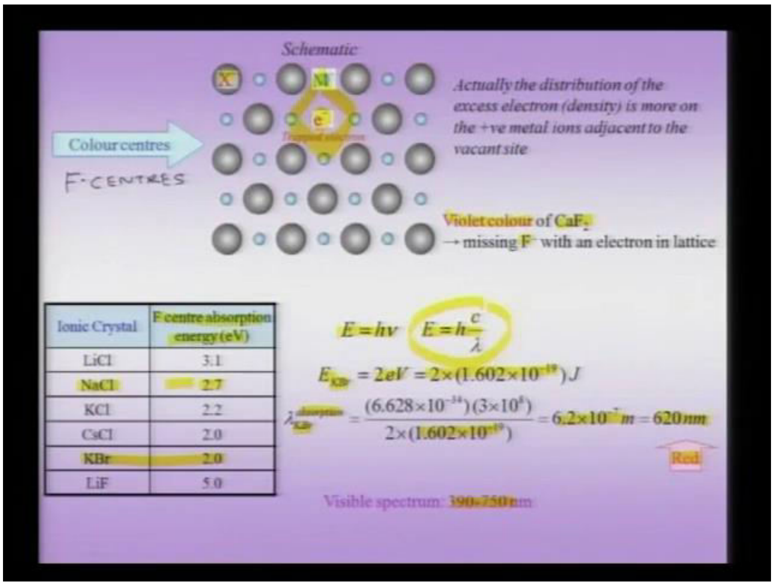

Colour centres

F-CENTRES

*Actually the distribution of the excess electron (density) is more on the +ve metal ions adjacent to the vacant site*

Violet colour of $CaF_2$

→ missing $F^-$ with an electron in lattice

| Ionic Crystal | F centre absorption energy (eV) |
|---|---|
| LiCl | 3.1 |
| NaCl | 2.7 |
| KCl | 2.2 |
| CsCl | 2.0 |
| KBr | 2.0 |
| LiF | 5.0 |

$E = h\nu \quad E = h\frac{c}{\lambda}$

$E_{KBr} = 2eV = 2\times(1.602\times10^{-19})J$

$\lambda^{absorption}_{KBr} = \frac{(6.628\times10^{-34})(3\times10^{8})}{2\times(1.602\times10^{-19})} = 6.2\times10^{-7}m = 620nm$

Red

Visible spectrum: 390-750nm

There is an important kind of defect in the context of ionic materials. This is important because often these defects impart color to the material. Therefore, they are called color centers. The typical name used for them some for instance; they are often called the f centers. So, let me write that down for instance, these current centers are also called the f centers. So, these color centers would impart color to other wise a normally a transparent kind of a material. It does not absorb in the visible region.

So, let me take an example here. For instance, now, this is for instance MX, kind of n ionic crystal. What happens is that you have an anion vacancy now to maintain charge neutrality. The anion vacancy traps an electron. So, you have a taped electron in the position of an anion vacancy here. This trapped electron of course, gives you charge neutrality. But additionally, what they might call gives a separate level in the absorption spectrum. It would correspond 2 of you electron volts. So, the typical absorption center for f centers is listed in this crystal. For instance, lithium sodium chloride has 2.7eV absorption band on absorption level.

Now of course, I will make a calculation here to show actually this kind of few electron volt level actually corresponds to the visual spectrum that we will do below. But, an important point to be noted is that in this schematic diagram, for instance this is MX crystal, M plus X minus crystal. I have shown in cat anion vacancy. The anion vacancy has been shown to have an electron present, which is been trap there. But typically, the electron distribution is not like the way it has been shown here.

The electron density is more around the not exactly at the position of the vacancy, but around the atoms, the ions which are surrounding that. So, it is something like this. So, there is a sort of a charge distribution around center level. Maybe, I will use a board to actually now, you a slightly better picture than one I have drawn.

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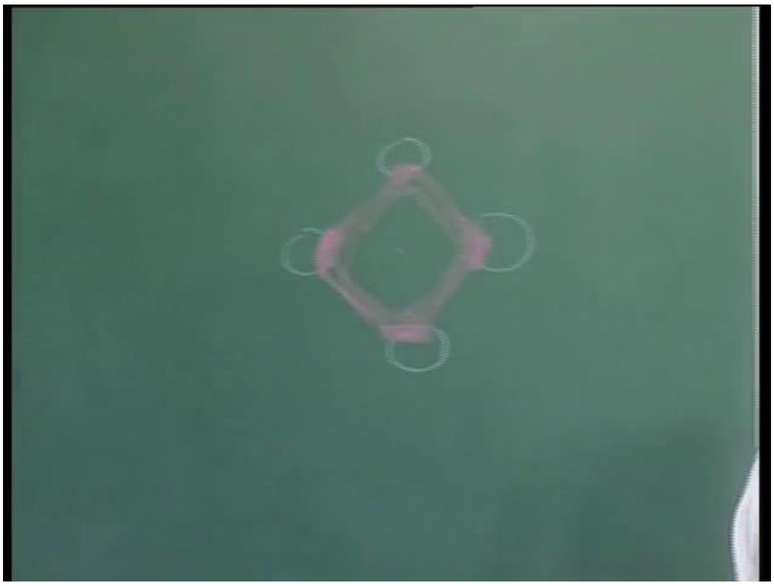

So, suppose I consider my 4 cations here. Now, I need to worry about the electron distribution. Suppose this is I use a red color chalk for the electron density, maximize does not lie in the center. It actually lies a little both to other sides. That means at more it provides more towards these kinds of crystals. Here, these positions have some sort of distribution around and localize more towards the cations. So, I would have a larger density distribution. This is to be expected because now, this electron is present actually to neutralize the charge present on the cations. So, this is why it is present.

Therefore, you would expect the delocalization of this electron charge density distribution. So, a good example of such would be the f center. In crystal, it imparts violet color to the material. So, in this case of course, you have a cation which is associated to the electron in the sub lattice. Of course, as I pointed out it is not localize to the sub lattice. But, its center of some sort of center of gravity of the electron distribution, which is the position of the lattice point or the missing lattice point, where there this no atom.

So, I was telling you that these f centers are important because they impart color to the crystal otherwise some of them are very transparent crystals. You know sodium chloride is a transparent material. Now, let me make a calculation and find out for instance for that example of potassium bromide. It has about absorption level of about 2eV. So, I can see that e h mu that means e equal to h c by lambda e. The absorption is 2Ev, which I have to convert into joules by multiplication by the charge of an electron.

The lambda of absorption of KBr, I can write down from this equation above as this. h and c, this is 2 into the conversion factor for electron volt to joules. It comes out to be about 6.2 into 10 power minus 7 meters. This is about 620 nanometers, which is in the red region of the visible spectrum. So, you can see that suppose, I have f center in potassium bromide. Then, I would see that the, a sort of reddish color has been important to the potassium bromide crystal. This is because of the presence of this anion vacancy which is now associated with an electron density.

The visible spectrum of course, as we know is from about 390 nanometers to about 750 nanometers. This is close of course, red region of the spectrum which is the larger wave lengths. So, f center is one possible defect, which is could be present in anionic crystals.

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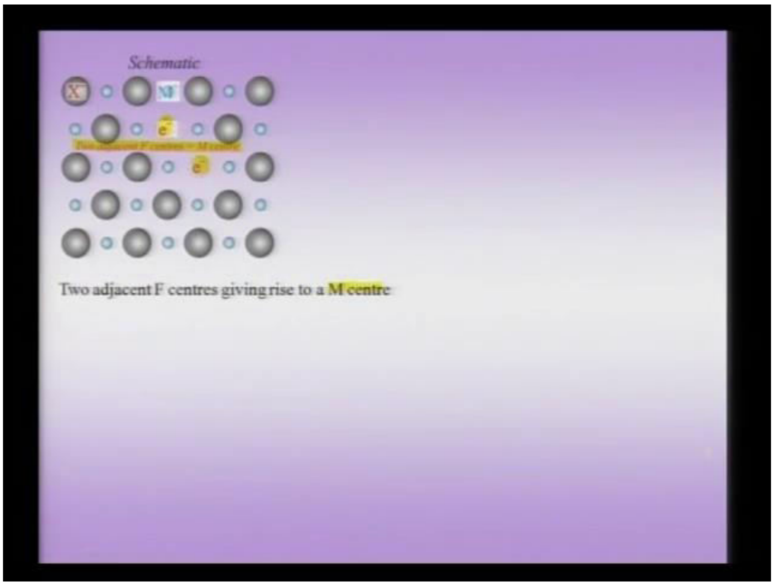

Schematic

Two adjacent F centres giving rise to a M centre

Then, we have to note that there could be a series of these kinds of defects, where in these f centers get associated with each other. There are complications where one kind of defects gets outside other kind of the defect in an anionic crystal. One example we will consider later, which is this some example of such an association. But, an immediate example I can side, which is called the m center. It is nothing but an association of 2 f centers.

So, if you have 2 f centers, which is called an m center. You have an f center localized on this position of the center of mass. It lies in this position and is an f center again. It is located in a neighboring position. This kind of an association is called an m center. Thus, I pointed out there could be association of 3 more. Association of these f centers with other kind of defects in ionic crystals would actually could lead to more complicated situation, as for as defects and ionic crystal scope. So, before maybe we should take up the structural point defects.

Let me summarize some of examples we have considered so far with regard to ionic crystals. We consider Frenkel defect, which was not associated with any kind of issue in with respect to charge neutrality. It was nothing but a cation. Interstitial Schottky defect again had an anion and a cation. We can see which we are coupled together. We also talked about for instance, divalent cation replacing a monovalent cation. It is now associated correspondingly with a way missing cation in a neighboring position. We also talked about off stoichiometry, which could again give rise to interstitials.

Now, they are of course, neutral interstitials. But they are again associated with charge around them. Then, for instance, zinc to plus associate with electrons around them. We also consider defect configurations, where there are anion and holes present or cations and electrons, which I present. They have localized to lattice positions or sub lattice positions. The more colorful of these was the f center. We saw that how for instance, in KBr, the f center gave rise to an absorption in the red region of the visible spectrum. We also saw that these kinds of defects could actually get associated and give rise to more complex configurations. So, defects in ionic materials.

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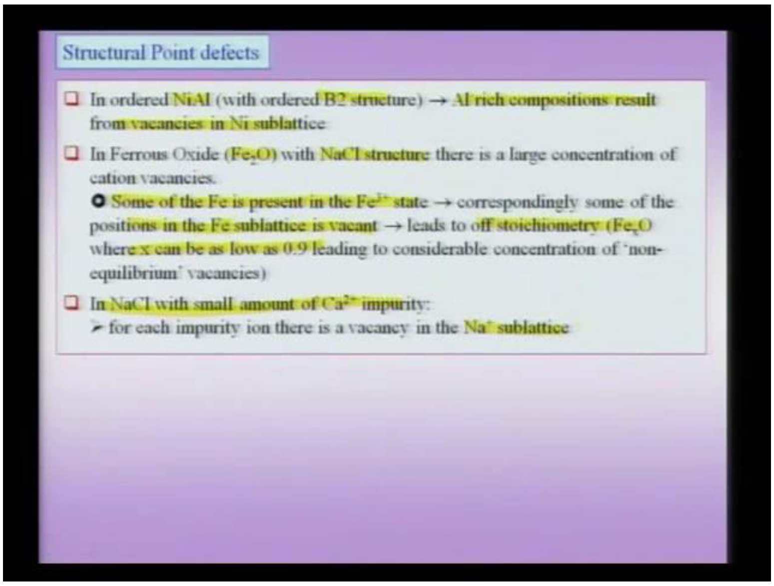

Structural Point defects

- ☐ In ordered NiAl (with ordered B2 structure) → Al rich compositions result from vacancies in Ni sublattice
- ☐ In Ferrous Oxide ($Fe_xO$) with NaCl structure there is a large concentration of cation vacancies.
  - ○ Some of the Fe is present in the $Fe^{3+}$ state → correspondingly some of the positions in the Fe sublattice is vacant → leads to off stoichiometry ($Fe_xO$ where x can be as low as 0.9 leading to considerable concentration of 'non-equilibrium' vacancies)
- ☐ In NaCl with small amount of $Ca^{2+}$ impurity:
  - ➢ for each impurity ion there is a vacancy in the $Na^+$ sublattice

So, let us take up this concept of structural point defects. In principle of course, any kind of defect could play a structural role. But in this specific case, functions we are considering structural point defects. We already sighted this example of nickel aluminum NiAl, nickel aluminite. They had an ordered B2 structure, where in aluminum bridge compositions result from vacancies in the nickel sub lattice. So, this example we have already seen. This was an example of a structural point defect in a metallic kind of a material, in an ionic analog of this.

For instance, let me take the example of ferrous oxide Fe2O. This is got NaCl kind of structure. We just as we know to interpenetrating FCC sub crystals or FCC sub lattices integrated one with sodium ion; so, in with chlorine ions. In this case, Fe ions and oxygen ions; often it happens, some more the Fe present as the Fe3 plus state. So correspondingly, some of the positions of the ion sub lattice are vacant. So, if you have some of the ions, which is in Fe3 plus state. Correspondingly some of the positions ions and sub lattice are vacant. This is of course because of the charge neutrality. This leads to off stoichiometry in other words.

Now, we could not have an ideal composition. We have Fe2O. We could actually have a FeO. I think they may be small mistake here. This concentration x can be as low as 0.9 lead. Now, the vacancy, which is coming in this crystal, would come in the ion sub lattice or not because of thermo dynamic equilibrium criteria. This is coming because of off stoichiometry. This would constitute 4 structural vacancies. Another example would be in sodium chloride crystals.

Suppose, I replace the calcium 2 plus impurity. There is a vacancy in sodium plus sub lattice. This vacancy again is a structural vacancy. Therefore, the more I add the calcium impurity, the more of the sodium would go in. You see that this is not coming from thermo dynamic considerations of equilibrium but because of the off stoichiometry I am considering. In this case of course, the stoichiometry is going from a pure sodium chloride to sodium. It is sort of a calcium chlorite of a structure. Another example of voice stoichiometry is perhaps the same.

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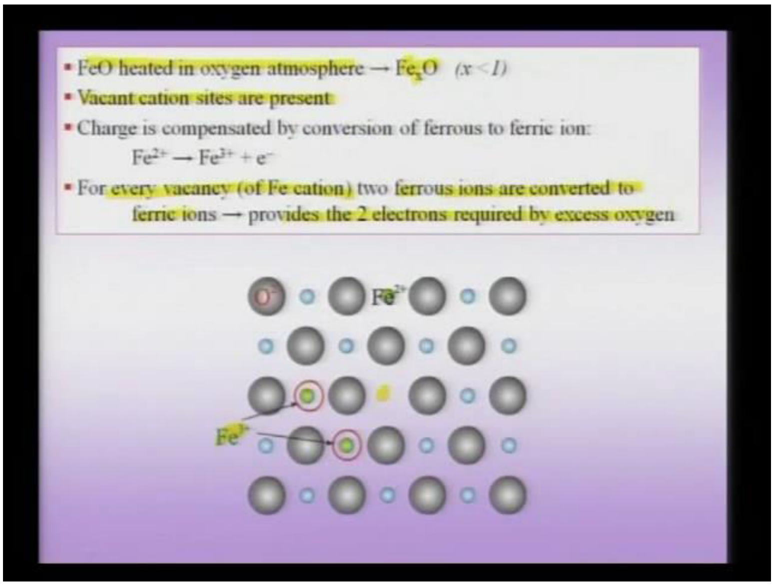

- FeO heated in oxygen atmosphere → $Fe_xO$ $(x < 1)$
- Vacant cation sites are present
- Charge is compensated by conversion of ferrous to ferric ion:

  $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- For every vacancy (of Fe cation) two ferrous ions are converted to ferric ions → provides the 2 electrons required by excess oxygen

It is a different version of the example I consider above, which is the ferrous oxide. In this case, what happens if FeO is heated in oxygen atmosphere. Then, you find that the stoichiometry disturb from Fe1O1 and x. In this formula of FeO can be less than 1. So, there are vacant cation sites are present, which you can see in this illustrative example one. Suppose, I have an Fe3 plus ions sitting instead of an Fe2 plus ion. It is now shaded in green. Correspondingly, you have some of the equations.

The normal lattice equation is occupied by Fe2 plus ion is which is been shown in blue. So, you would find some of the cation sub lattice positions are vacant, which is actually coming from the off stoichiometry. Therefore, for every vacancy of ion cation, 2 ferrous ions are converted to ferric ions, provides 2 electrons required by the excess oxygen. So, this is again coming from charge neutrality. But origin of all these defects happens to be structural, which is off stoichiometry. Now, the next topic we consider and perhaps the best example of defect ordering is point defect ordering. Here it is easy to visualize some of these concepts.

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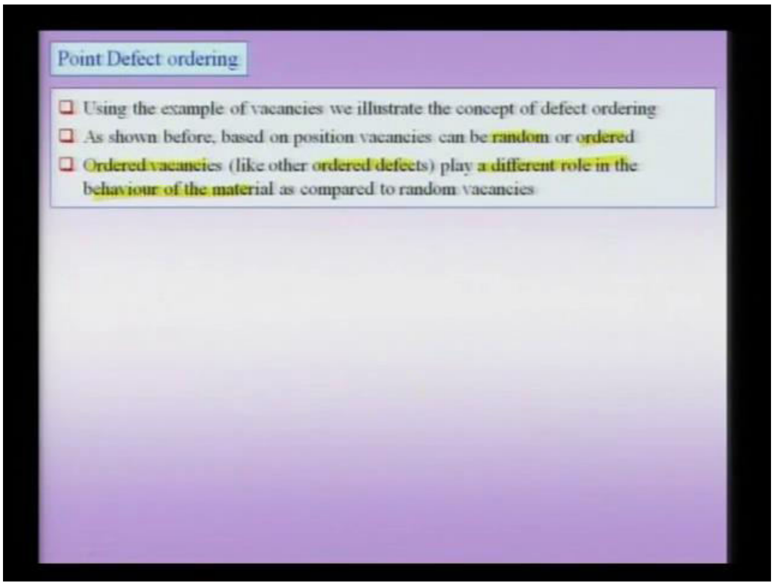

### Point Defect ordering

- Using the example of vacancies we illustrate the concept of defect ordering
- As shown before, based on position vacancies can be random or ordered
- Ordered vacancies (like other ordered defects) play a different role in the behaviour of the material as compared to random vacancies

I will take a perhaps schematic example to show you what I mean by this point defect ordering. How this can actually change the symmetry of the structure in this? Perhaps, for instance, it can serve as a template. For understanding other kind of defect ordering like for instance, stacking fault ordering and even in under circumstances this location ordering. This is coming from the classification, which we talked about as defect as a random or in ordered kind of a defect.

The important point to note why this ordering phenomenon is very important is that order vacancies like other ordered defects play a very different role in behavior of material as compared to a randomly present defect. This is something which we need to note and this will become obvious when we talk about the ordered defect configuration.

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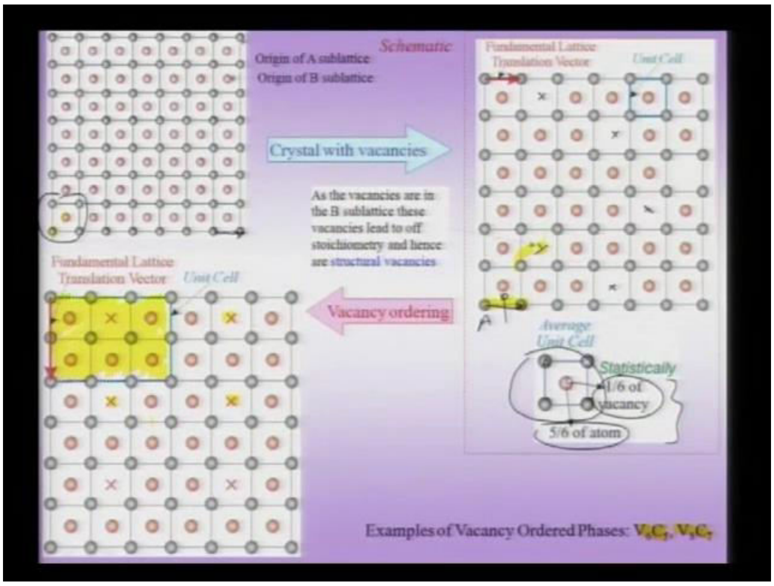

Schematic

Origin of A sublattice

Origin of B sublattice

Crystal with vacancies

As the vacancies are in the B sublattice these vacancies lead to off stoichiometry and hence are structural vacancies

Vacancy ordering

Fundamental Lattice Translation Vector

Unit Cell

Average Unit Cell

Statistically

1/6 of vacancy

5/6 of atom

Examples of Vacancy Ordered Phases: [illegible]

So, let me take up a perfect crystal, which is there on the left hand side of this figure. So, for this again, a schematic where in you see 2 sub lattices, one red sub lattice and one gray shaded sub lattice. There are two sub crystals, which is they are; origin of one is at 0 0 0 that is half or 0 0 0. The other one is half 0 half half. Now, I introduce some vacancies into this crystal. As you know, these vacancies could be introduced purely because of thermo dynamics regions.

Now, we have these vacancies introduced in various positions in these crystals. So, let me mark these vacancies. For instance, there is a vacancy here. There is a vacancy here and there is a vacancy here. There is a vacancy here and so forth. These vacancies are obviously, now structural vacancies because once these vacancies are introduced into the sub lattice, the crystal goes off stoichiometry. This very reason this vacancies could be present in this material. For instance, suppose I am talking about a disordered crystal.

Then, these vacancies could be thermal vacancies. But suppose, I am talking about ordered crystal. This could be coming from off stoichiometry if they are thermal vacancies. Then of course, these vacancies could also be present in the other sub lattice as well. Of course, the energy of these 2 sub lattice may not be equivalent. But anyhow, because of the thermo dynamic vacancies could also be present in the other sub lattice. But if they are coming from off stoichiometry, they are localize to the for instance, in this example. It is shown it is localize to the B sub lattice.

Now, if I want to describe this in my language of probabilistic ordering or a statistical ordering of this crystal. So once, sub lattice is purely occupied by completely for instance, this is my A atoms are ions and others. Sub lattice is not occupied by an atom, a pure atom on a ion. But actually for instance, suppose I am talking about a concentration resource is 1 by 6 then, I can talk about for instance, 5 by 6 design atom and 1 by 6 is a vacancy to this is a statistical picture of the occupation of the B sub lattice. Now, this is 1.

So, this is an important concentration and to be kept in mind. It is at one sub lattice is purely occupied by the other sub lattice. Now, it is disordered with respect to the vacancies. That means the vacancy could present in any one of the position of the sub lattice. Actually, they could move from one position to the other as well. This can be described by a statistical picture. I have shown here for example, of about a concentration of one sixth of a sub lattice position of vacancy concentration. Now, there is a possibility that these vacancies get ordered. Now, obviously they would get ordered in these sub lattices. Now, when they get ordered in the B sub lattice for instance and this is now my disordered vacancies.

What would be my disordered structures unit cell? The disorder structures average unit cell would be a structure, which as I shown here on the right hand side. This is my average unit cell, where in a atom located at d corners and have what them. I called A B; vacancy combinations statistically 5 by 6 then, 1 by 6 occupying the central position. could this just a specific example? This would depend on the concentration of vacancies. Of course, they are pure crystal, would have a pure units cell.

As we normally know, this my pure crystals unit, where in a s r are located in the corner and b s r located in the center of the unit cell. Now, there is a possibility that this vacancies get ordered on this B sub lattice. On the left hand side, I have seen here, left hand below picture, the vacancy ordered phase. In the vacancy ordered phase, you can see that I am just considering example. This is schematic example for instance, now you vacancies get ordered in every 1, 2, 3, fourth position on this direction.

We will just a second position on this direction typically of course, they could on both the equal I just considering a example just to illustrate the symmetry lower ring. It is caused by this kind of vacancy ordering. But typically, the vacancy ordering would lead to an in such a structure would a within unit cell, which is a square unit cell. But you can see I am just considering a rectangular unit cell. Now, if I am talking about a fundamental lattice translation vector.

Then, in the case of disordered crystal, my lattice translation vector would about from the corner to the center. So, let me draw this using a ball pen. So, this would be my fundamental lattice translation vector. In this picture here, this would be my at a translation vector. But in the case of this ordered phase, you can see my new unit cell would be the one, which is now which I am shading here. So, this is my shortest lattice translation vector. You can see that the vacancies have got ordered in to sub lattice of them.

So, I can now talk about the structure in downs of 3 sub lattices, one with A atoms, one with B atoms and one with vacancies. So, this is now one vacancy ordered structure. Now, if I had such a structure then, I would have for instance not a small unit cell. But a larger unit cell we just shown in the blue out line. So, this my new unit cell, which is of course, got a periodicity of 2 A in the original in divide direction and 3 A m d x direction. So, this is perhaps and schematic example of a vacancy ordered phase.

This illustrates the important concept that when defects get ordered, they get in corporate into the crystal structure; symmetry of the structure changes. The properties obviously would change along with the structure itself. In this case like in case of normal ordering suppose, in the normal ordering. We would consider is vacancies at the atomic species. So because this is ordering of vacancies, you can see that the symmetry has been lowered.

My unit cell to describe the structure of also change along with this ordering process. Example of vacancy ordered phases can be found for instance, in vanadium carbide. The two examples is study here V6C5 and V8C7. We can also be found in aluminum, copper, nickel kind of systems. In some of the examples for instance, vacancy ordered phase is you can correlate the vacancy ordered phase as what might call as quasi periodic super lattice approximates to a something known as a one dimensional quasi crystal.

So, they need structures are very interesting structures, where in not only vacancies play a role. As if they were elements or they were species in themselves, they also have interesting connections with other structures like quasi crystals. In this example, we have considered we should of course, note that again to emphasize an important point for instance, A sub lattice could also have vacancies. Some of these vacancies could be thermal vacancies. Some other could be structural vacancy.

They are now localized on the B sub lattice. Of course, this sub lattice also could have thermal vacancies, which would remain for instance suppose, even we working a stoichiometry composite. Now, the sub vacancy is in the B sub lattice. If it wants to jump to for instance a position in the A sub lattice, it would mean that an anti site defect would be created the two positions for a vacancy or non equivalent. That is something which we have to note. This would cost energy.

Suppose, I am talking about diffusion of a substitution along element then you would notice that this vacancy has a different role to play. Then, a thermal vacancy, which could reside either in the A sub lattice or in the B sub lattice. Of course, in any case, if A we can see jumps from A sub lattice or B sub lattice, it would mean a exchange of an atom with that sub lattice. Anti side defects would be created and that would be energetic unfavorable. But important point to be noted here is the fact that this vacancy prefers to set energetically on the one of the sub lattices. So, that is an important point to be noted. This is different from a normal thermal vacancy, which could set perhaps on both sub lattices.

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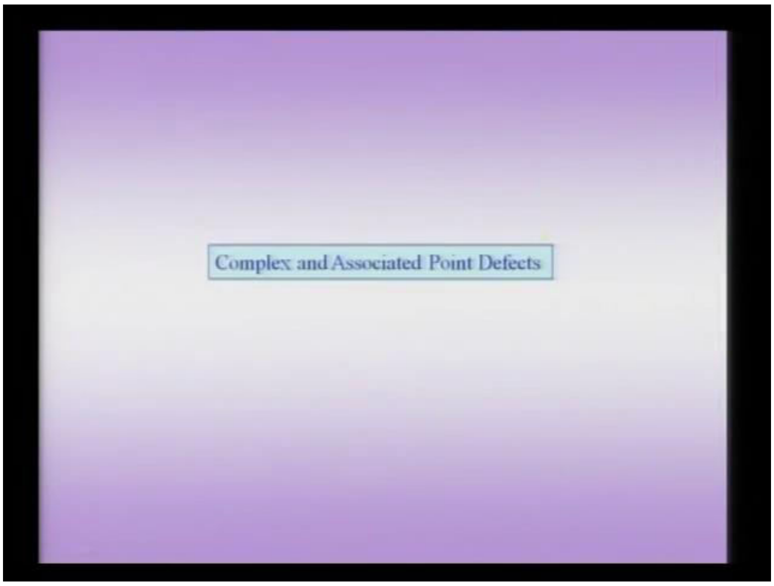

Complex and Associated Point Defects

After having considered some of these isolated point defects and also of course, thought a little bit about some the possible associations, some of these defects, let us take up some examples of association of point defects. We have to note that point defects and the again, the behavior of isolated point defects could be very different from an associated point defect. So, that point has to be noted.

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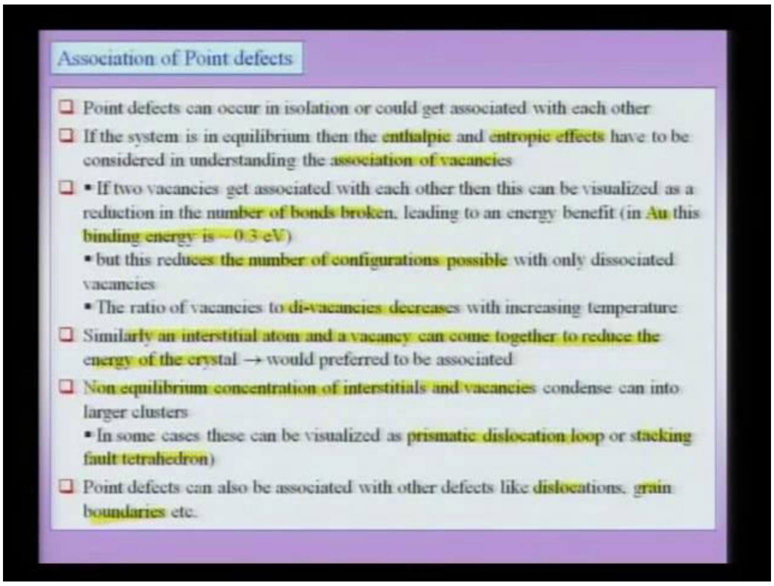

Association of Point defects

- ❑ Point defects can occur in isolation or could get associated with each other
- ❑ If the system is in equilibrium then the enthalpic and entropic effects have to be considered in understanding the association of vacancies
- ❑ ▪ If two vacancies get associated with each other then this can be visualized as a reduction in the number of bonds broken, leading to an energy benefit (in Au this binding energy is ~0.3 eV)
  - ▪ but this reduces the number of configurations possible with only dissociated vacancies
  - ▪ The ratio of vacancies to di-vacancies decreases with increasing temperature
- ❑ Similarly an interstitial atom and a vacancy can come together to reduce the energy of the crystal → would preferred to be associated
- ❑ Non equilibrium concentration of interstitials and vacancies condense can into larger clusters
  - ▪ In some cases these can be visualized as prismatic dislocation loop or stacking fault tetrahedron)
- ❑ Point defects can also be associated with other defects like dislocations, grain boundaries etc.

For instance suppose 2 vacancies get associated to form a di-vacancy. Then, this would typically involve something known as a binding energy. For instance, this could be of the order of 0.3 electron volt in gold. Now, if you want to dissociate this di-vacancy that would cause me energy. So, this di-vacancy once form could be stabilize because of this pointing energy.

Of course, the question I would have to ask myself is that at any given temperature, how many of these vacancies are present, isolated vacancies. How many of them are di-vacancies because once I have a di-vacancy then, it lowers my configurational entropy of the system. So, at higher temperature, I would assume that are where is some assumption to make that there are more vacancies are isolated. At lower temperature, there is a better possibility for association.

So, when I am talking about understanding this kind of defect association, I have to worry about enthalpic and entropic effects. When I need to worry about, when I need to consider association of vacancies then, the reason of course, the vacancies get associated is that they give you a certain energetic benefit. The way to nicely visualize that; for instance, suppose, I am talking about an isolated vacant, 2 isolated vacancies. There are number bonds which are bren. If these 2 vacancies can get associated with each other then, the number of bond bren would be reduced. So, this is an easy nice way of visualizing why they di-vacancy should form. This energy benefit as I told you is called the binding energy.

As I also pointed out, but once I have this di-vacancy formation; then, it reduces the configurational entrepreneur the system. So, as a function of temperature, there would be a certain not in equilibrium concentration vacancies. But also an equilibrium concentration of di-vacancies, I would expect that with increasing temperature, the di-vacancy concentration would increase. As I talked about di-vacancy, you could have formation tri vacancy and higher order associations.

In the case of non equilibrium systems, there would be the formation of a entire region in a for instance, crystallographic plane. For instance, in copper where in you have a full what they might call a plate of vacancies or a disc of vacancies. This, we of course, will take up later, when we talk about the concept to dislocation and the concept of frank partial dislocations. Similarly, an interstitial atom and a vacancy can come together to reduce energy of crystal.

This is again obvious for instance, had a vacancy and interstitial atom. One is associated with one kind of a strain other, opposite kind of strain. There association would over all reduce my energy of the system. They would like to come together. So, this is an obvious case of defect of opposite type pointing to come together to each other as a dimension. If I have a non equilibrium concentration of for interstitial vacancies of course, interstitial in one system vacancy in other system then, they can also come together and form clusters.

For instance, one important thing as I pointed out is at some these associations can be spent about in a totally different language like a prismatic dislocation loop. In the case of vacancies, it is nothing but disc of condensed vacancies. It is now a non equilibrium concentrational vacancies or in some cases, as a stacking fault tetrahedron. So, these are some cases, where in there are association of vacancies. Important point to notice a not only point defects can get associated with themselves, but they can also get associated with other kind of defects like dislocations and grain boundaries.

This again would lead to the lowering of the energy of the system in many cases. So, we start with isolated point defects like vacancies are interstitials. Then, we worry about their associations like how vacancies can get associated with other vacancies. How vacancies can get associated with interstitials? How this now affect my energy of the system? I talk in a language of binding energy of these two defects and also worry about how this is going to affect by entropy.

When I am talking about a point defect, point defect association obviously, the effect on entropy is going to be performed. Later on, we will see the importance of association some of these defect. For instance, how an interstitial atom like carbon can get associated dislocation. How it affects my stress end diagram? How there association grain boundaries can be; for instance, in many cases very deleterious. We will take a bond example of a complex point defect formation. As I pointed out, there are very many such possibilities. We just are taking up one example to illustrate the, what I might call the path a head, in which we can go in to more and more difficult and more complicated examples.

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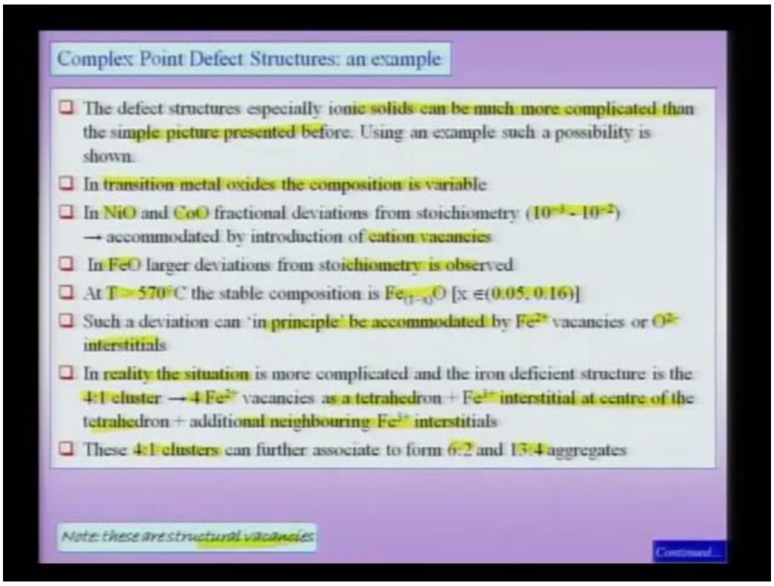

Complex Point Defect Structures: an example

- The defect structures especially ionic solids can be much more complicated than the simple picture presented before. Using an example such a possibility is shown.
- In transition metal oxides the composition is variable
- In NiO and CoO fractional deviations from stoichiometry ($10^{-3}$ - $10^{-2}$) → accommodated by introduction of cation vacancies
- In FeO larger deviations from stoichiometry is observed
- At T > 570°C the stable composition is $Fe_{(1-x)}O$ [$x \in (0.05, 0.16)$]
- Such a deviation can 'in principle' be accommodated by $Fe^{2+}$ vacancies or $O^{2-}$ interstitials
- In reality the situation is more complicated and the iron deficient structure is the 4:1 cluster → 4 $Fe^{2+}$ vacancies as a tetrahedron + $Fe^{3+}$ interstitial at centre of the tetrahedron + additional neighbouring $Fe^{3+}$ interstitials
- These 4:1 clusters can further associate to form 6:2 and 13:4 aggregates

Note: these are structural vacancies

Continued...

Now, these we are the example, I am writing are the case of the structural vacancies. So, the defect structures and ionic solids can be much more complicated than the simple picture. We have seen some other examples before. One example of course, one possibility we consider here. It is the case of this transition metal oxide were in the composition is variable. For instance, in nickel oxide and cobalt oxide. The deviation from stoichiometry could be pretty large, which is about 1 in 100 or 1 in 1000.

This typically is accommodated by the introduction of cation vacancies in iron oxide. For instance, again, we have previously noted that there could be large deviations from stoichiometry in iron oxide. Temperature is greater than about 570 degrees. The stable composition is about Fe 1 minus X O. We arrange x could be 0.05 to about 0.16. This is the pretty large number for a number of cation vacancies. We are talking about so such a deviation. In principle of course, to be a accommodated by if you 2 place vacancies are over to minus interstitials.

We already noted that the anion is much larger. It would not prefer to set in their interstitial position. This part we have noted. The real picture goes much more complicated in the simple picture of just cation vacancy or anion interstitial. The name given to it is typically it is called a 4 is to 1 cluster. So, the real situation is more complicated and some the defect, which actually form in something. That I showed in a picture in the next slide is a 4 is to 1 cluster. 4 Fe 2 plus vacancies as a tetrahedron, Fe 3 plus interstitial at the center of the tetrahedron are accommodated and additional Fe 3 plus interstitials around this tetrahedral configuration. The story does not end here if you have a 4 is to 1 cluster. Actually, they can form larger clusters or larger association of defects to form something known as a 6 is to 2 per 13 for aggregates.

So, you could have an isolated cation vacancy. You could have a association of these kind vacancies. You could have an function of known association in this example. It is a formation of this tetrahedron and associated Fe 3 plus interstitials. This whole complex itself can get associated and form larger clusters. They would then of course, be even more difficult to understand. So, an ideal geometrical representation of the defect we are talking about, which is now the 4 is to 1 cluster and talking about the 4 is to 1 cluster.

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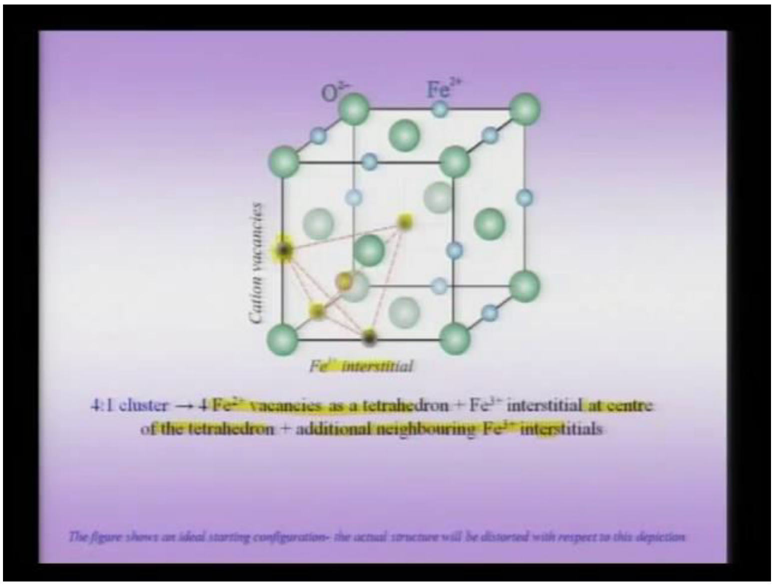

4:1 cluster → 4 $Fe^{2+}$ vacancies as a tetrahedron + $Fe^{3+}$ interstitial at centre of the tetrahedron + additional neighbouring $Fe^{3+}$ interstitials

The figure shows an ideal starting configuration- the actual structure will be distorted with respect to this depiction

This is an ideal geometrical representation. This consists of an some Fe 3 plus interstitial at the center of this tetrahedral. If Fe 2 plus vacancies are present, so this is my Fe 2 plus vacancies, which are present at the vertices of the tetrahedral. Of course, these are missing sub lattice positions. So, these are Fe 2 plus vacancies around this central Fe 3 plus interstitial. This Fe 3 plus interstitial is at the center of the tetrahedral. To maintain charge neutrality, additional neighboring Fe 3 plus interstitials are also cleared. So, this whole cluster would now constitute my 4 is to 1 cluster, which includes these additional neighboring Fe 3 plus interstitial.

I have not been shown in the figure. So, as we can see that defect picture and ammonic crystals can get actually very complicated. But in reality, we have to understand this defect picture. If I have to now understand for instance, the absorption spectrum from such a crystal or the color important to such a crystal and many of the other properties. I want to know about these crystals. Before I come to a close of consideration of these point defect chapter one, important question we can ask is that how can I produce is these point effects?

One example, one case we already seen is a natural production of these point effects because of thermo dynamics regions, it is the entropically stabilized vacancies. But typically, you will note that point defects can be present because of the way the synthesis has been made of the crystal. Impurities could get accommodated even though you did not want these impurities be present in the crystal.

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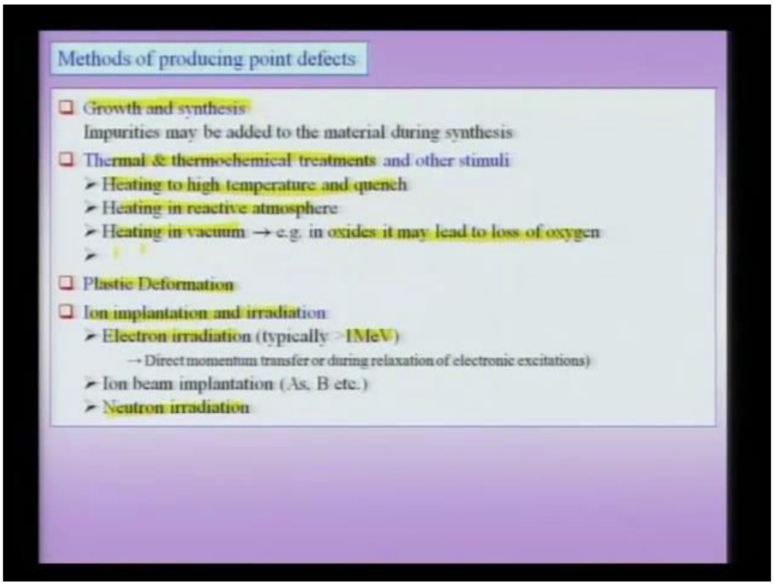

Methods of producing point defects

- ☐ Growth and synthesis
  Impurities may be added to the material during synthesis
- ☐ Thermal & thermochemical treatments and other stimuli
  - ➢ Heating to high temperature and quench
  - ➢ Heating in reactive atmosphere
  - ➢ Heating in vacuum → e.g. in oxides it may lead to loss of oxygen
- ☐ Plastic Deformation
- ☐ Ion implantation and irradiation
  - ➢ Electron irradiation (typically > 1MeV)
    → Direct momentum transfer or during relaxation of electronic excitations)
  - ➢ Ion beam implantation (As, B etc.)
  - ➢ Neutron irradiation

Of course, in many cases, we have seen intentionally add this as an alloying element or a dopant to have some properties imparted to the crystal. For instance, we want a p type or n type semi conductor. We had these point effects, but these could be incorporated during the growth of the synthesis of the crystal. We could have a thermal and thermo chemical treatments. They give rise to these kinds of point defects. One sense, we could have a larger than equilibrium concentration of vacancies by taking it to high temperature than quenching the material.

As I pointed out the very how do I know that there are more vacancies present than the equilibrium concentration? Now, we will have that the quenched sample would have a much high diffusivity as compare to of course, now I am talking about substitutional diffusivity or a diffusion taking place by the substitutional mechanism. This value is much larger for the quench sample rather than the equilibrated sample. For instance, at any temperature, we already have seen in that we could actually heat in a atmosphere of a different material.

We already seen one example or we could when heat in the reactive atmosphere or some kind of atmosphere. It would incorporate, react with my material. The other extreme possibility with the other end of the spectrum is actually heating in vacuum. In such cases, some oxide defect or the crystal structure, formation of a defect plastic defect. They are many other methods. Of course, we can consider under this thermal and thermo chemical treatment, plastic deformation is at totally distinct category.

Here, I am deforming the material. This can lead to the formation of point defects. This clearly shows up that how do I know that point defects are found. For instance, if I am deforming copper, you will notice that the resistivity of copper increases. The conductivity would stop. How do I restore my resistivity? I need the sample. You would notice that the conductivity thus deformed copper would increase again and come back to its normal values.

When I what we call an eulier deformed sample, ion implantation and irradiation is an perhaps very good example of reducing non equilibrium concentration of vacancies. Irradiation can be used for instance or electronic radiation and neutron irradiation. Electron irradiation typically, ampere values, which would keep rise to a good what we call good dosage. It would give rise to a concentration or production of a for instance, vacancies. They would be functions or an interstitial would be about 1 MeV. So, this is typically can be found in some of the 1 MeV source.

It could be here. Electron microscope typically operates at very high voltages. So, there been electron microscope for instance, which I have capacity at 1.25 MeV. Such kind of electron microscope, we have to worry about the electron irradiation damage on the specimen. So, in other words, if I am analyzing the things specimen under one of these very high voltage microscopes. Then, some of the defects I may be seen actually or not the original defects present in the material, but are actually been produced by the electron irradiation dimension.

So, if I have seen some such defects, I have to conform them putting such a sample in a rather low voltage microscope to conform that actually this is not damage. It has been produced by high voltages and even here, there are possibilities like functions. The direct momentum transfer from electrons can lead to the formation of the defect. It could be during the relaxation of the electronic excitations. That means if you have produced high energy level and the systems lacking to relaxing to grounds state, some of the emissions coming out could actual lead to the formation of the damage in the crystal.

That formation of point defects in this case, iron beam implantation is of course, the technology of focused ion beam etcetera. It can also give rise to some of these point defects. You can produce a large concentration of point defects in a material by relating with an ion b, which would be a heavier version of some of these electron and neutron radiations. So, I have various methods of producing point defects. Having produced them, I can use experiment like a measurement to conductivity to actually conform that you have produce a higher concentration of point defects.

Typically, a single point defect is difficult to see in an even in higher solution microscope or what you might call in atomic resolution microscope. But if you have a aggregation of these defects, they can be identified in an higher atomic resolution microscope. We will solve couple of examples to close this topic on point defects.

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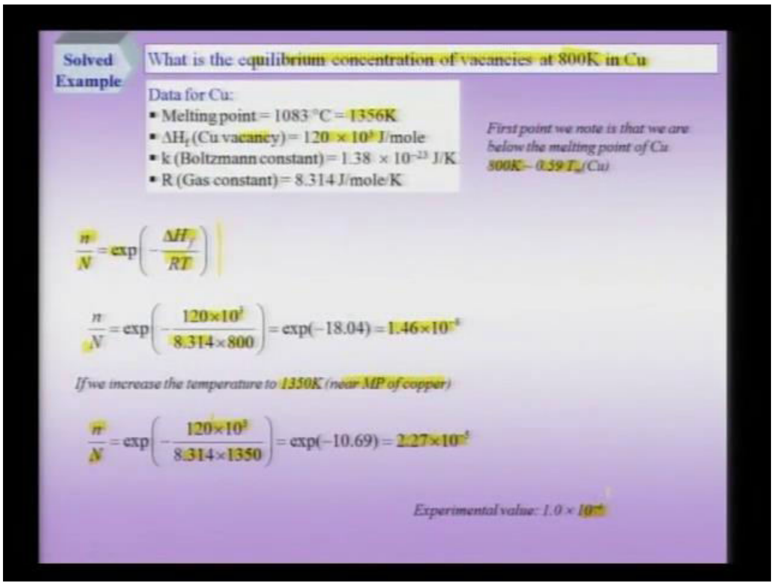

**Solved Example**

What is the equilibrium concentration of vacancies at 800K in Cu

Data for Cu:
- Melting point = 1083 °C = 1356K
- $\Delta H_f$ (Cu vacancy) = $120 \times 10^3$ J/mole
- k (Boltzmann constant) = $1.38 \times 10^{-23}$ J/K
- R (Gas constant) = 8.314 J/mole/K

*First point we note is that we are below the melting point of Cu*
*800K ~ 0.59 $T_m$(Cu)*

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{RT}\right)$$

$$\frac{n}{N} = \exp\left(-\frac{120\times10^3}{8.314\times800}\right) = \exp(-18.04) = 1.46\times10^{-8}$$

*If we increase the temperature to 1350K (near MP of copper)*

$$\frac{n}{N} = \exp\left(-\frac{120\times10^3}{8.314\times1350}\right) = \exp(-10.69) = 2.27\times10^{-5}$$

*Experimental value: $1.0 \times 10^{-4}$*

So, let us calculate in this example the equilibrium concentration of vacancies. For instance, copper. We will consider two temperatures. One temperature about eight 800 Kelvin is about slightly more than half the melting point of copper. One temperature is close to the melting point of copper, it is about 1350. So, what I am trying to calculate here is the equilibrium concentration of vacancies. That means that, which is been stabilize by entropic reasons. The first thing of course, I need to notice that I if whatever temperature, I am given has to be below the melting point of copper because otherwise you do not have the crystalline structure of copper.

So, in this case, with the two temperatures are for 1300 Kelvin. It is been given is below the melting point of copper. So, it is about 1356 Kelvin. The enthalpy of formation of copper vacancies is about 120 joules per mole. We know the diffraction of vacancies at any temperature is given by the function n by N. It is the fraction of vacancies where n is the number of vacant sites, N is the total number of lattice positions is exponential minus delta H of RT.

That means more the enthalpy of formation of vacancies, lesser the number of vacancies. Higher the temperature, more the vacancies. So, what you would expect is that at higher temperature, the number of vacancies would increase. That means as you heat the metal, we already seen a given might call an change in length. We shall calculate in the next example. So, we can write n by N as 120 into 10 power 3, which is the joule power mole delta H f, the gas constant.

We are dealing per mole quantities and not per vacancy. It is my temperature in Kelvin. This comes out to be about 1.46 into 10 power minus 8, which is very small fraction in terms of number of lattice positions. So, at 800 Kelvin, the concentration of vacancies is pretty small. Now, suppose, I heat my sample further to close the melting point of copper. We would notice that now my temperature is 1350. Other quantity remains as before. I get my n by N value to be above and 10 power minus 5.

So, there is a 3 orders of magnitude change in the concentration of vacancies and the typical value. It is been observed by measurements of for many materials, ionic and metallic materials. It is of the order of 0.4 into 10 power minus 4. So, you can see that even close the melting point, the concentration though it is not negligible, it is pretty small as compare to the number of lattice site possible. It is of the order of 10 power minus 4 or 10 power minus 5. It is the fraction of vacancies in a crystal, even close the melting point. This experiment value typically can be obtained from either lattice parameter measurements or changes in length of the material, which should be like which one call a dilatometric measurement.

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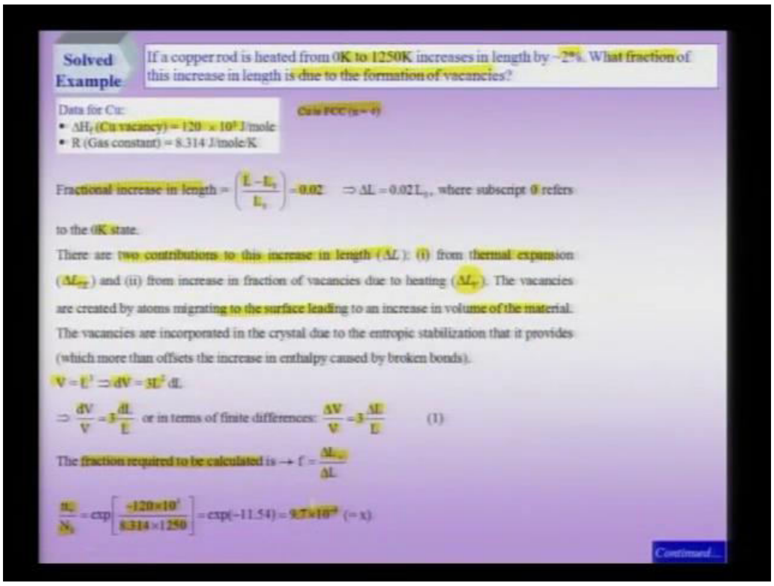

**Solved Example**

If a copper rod is heated from 0K to 1250K increases in length by ~2%. What fraction of this increase in length is due to the formation of vacancies?

Data for Cu:
- $\Delta H_f$ (Cu vacancy) = $120 \times 10^3$ J/mole
- R (Gas constant) = 8.314 J/mole/K

Cu is FCC [illegible]

Fractional increase in length = $\left(\frac{L - L_0}{L_0}\right) = 0.02 \quad \Rightarrow \Delta L = 0.02 L_0$, where subscript 0 refers to the 0K state.

There are two contributions to this increase in length ($\Delta L$): (i) from thermal expansion ($\Delta L_{TE}$) and (ii) from increase in fraction of vacancies due to heating ($\Delta L_V$). The vacancies are created by atoms migrating to the surface leading to an increase in volume of the material. The vacancies are incorporated in the crystal due to the entropic stabilization that it provides (which more than offsets the increase in enthalpy caused by broken bonds).

$V = L^3 \Rightarrow dV = 3L^2\,dL$

$$\Rightarrow \frac{dV}{V} = 3\frac{dL}{L} \text{ or in terms of finite differences: } \frac{\Delta V}{V} = 3\frac{\Delta L}{L} \qquad (1)$$

The fraction required to be calculated is → $f = \frac{\Delta L_V}{\Delta L}$

$$\frac{n_V}{N_0} = \exp\left[\frac{-120\times10^3}{8.314\times1250}\right] = \exp(-11.54) = 9.7\times10^{-6} \ (= x)$$

Continued...

We solve another example, where in I had mentioned that if I had a material on a heated it there are two reasons quite expands. One of the reasons, being the normal thermal vibration. The other one being because of the creation of vacancies, wherein atoms go and sit on the surface. Therefore, the material is increased in volume and also in its length. Therefore, so I am asking that if I am heating a rod of copper from 0 Kelvin to about 1250 Kelvin and the length increases about 2 percent. We want, I want to know the fraction of this length increase, which is coming from vacancies.

So, the delta H of formation of vacancy for copper is as before 120 kilo joule per mole. We know that copper is an FCC crystal structure with 4 atoms in the unit cell. The fractional increase in length, which is a 2 percent I am talking about can be written as 0.02, which is coming from the original length L 0 to the final length when I heat it to 1250 Kelvin by L 0. That means delta L by L, 0 is 0.02 or delta L is 0.02 L, 0, where 0 or a subscript as usual refers to the original state of results, 0 Kelvin state. The two contributions to the increase in length delta L coming as I told you coming from thermal expansion.

The normal which I read as with subscript V and from the increase of vacancies, I read which is up to delta L V. So, the total delta L is delta L V plus delta L d e. The vacancies created by atoms migrating to the surface will lead to a volume increase in the material. Therefore, V is equal to L cube. This length increases. This is what I am describing here by this is 2 percent. So, d V is 3 L square d L. In other words, d V by V, which of course, I can write is 3 into d L by L. In other words, what I am saying is that the volumetric strain delta V by V is related to my length strain by a factor of 3. So, suppose I am talking about length strain, which is measured from this experiment.

I need to convert the 2 percent. I need to convert it into volumetric strain, which is what I am dealing with, when I am heating the material using a factor of 3. This point, I have to note. So, the fraction which is required to be calculated in the problem, which is the question I am asking is what fraction of the increase in length is due to the formation of vacancies? The fraction I am trying to calculate is delta L V, which is the V subscript. Again, it refers to the vacancies as I mentioned before by delta L, this is the total increase in length.

It has these two contributions as before n vacancies by n, 0. I am assuming a mole of atoms here is given by the exponential delta H f by RT. It is 1250, which is increasing from 0 to the delta T being 1250. I get a fraction of vacancies, which is about 10 power minus 6 R 10 power minus 5. In this case, close to 10 power minus 5, which I call x.

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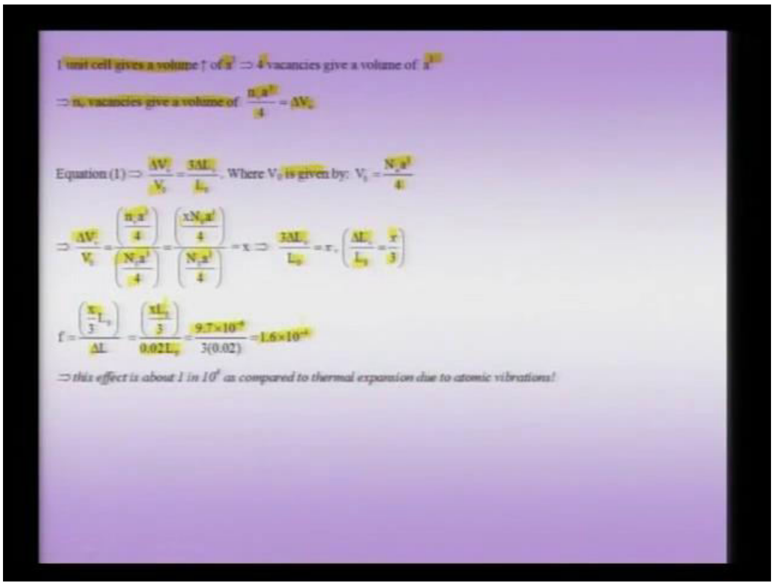

1 unit cell gives a volume ↑ of $a^3$ ⇒ 4 vacancies give a volume of $a^3$

⇒ $n_v$ vacancies give a volume of $\frac{n_v a^3}{4} = \Delta V_v$

Equation (1) ⇒ $\frac{\Delta V_v}{V_0} = \frac{3\Delta L_v}{L_0}$, Where $V_0$ is given by: $V_0 = \frac{N_0 a^3}{4}$

$$\Rightarrow \frac{\Delta V_v}{V_0} = \frac{\left(\frac{n_v a^3}{4}\right)}{\left(\frac{N_0 a^3}{4}\right)} = \frac{\left(\frac{x N_0 a^3}{4}\right)}{\left(\frac{N_0 a^3}{4}\right)} = x \Rightarrow \frac{3\Delta L_v}{L_0} = x, \left(\frac{\Delta L_v}{L_0} = \frac{x}{3}\right)$$

$$f = \frac{\left(\frac{x}{3} L_0\right)}{\Delta L} = \frac{\left(\frac{x L_0}{3}\right)}{0.02 L_0} = \frac{9.7\times10^{[illegible]}}{3(0.02)} = 1.6\times10^{[illegible]}$$

⇒ *this effect is about 1 in* $10^{[illegible]}$ *as compared to thermal expansion due to atomic vibrations!*

Now, if 1 unit cell increase gives the volume increase of a cube. That means if 4 atoms go missing from lattice sides go to the surface. That means that I would have volume increase of a cube. So, 4 atoms of copper or ions of copper would correspond to volume increase of a cube. So, n V vacancies would give a volume increase of a n V a cube by 4. It is my delta V vacancies that mean the increase in volume delta V is coming from the n V a cube by 4. The 4 factor as you know is coming from this 4 factor which is the number of atoms in unit cell in FCC copper.

We already seen from the previous equation, equation 1 here that delta V by V 0 is 3 delta L V by L 0, where V 0 is given by n 0 a cube by 4. a cube is the volume in unit cell. n 0 is the volume of a cube by 4 being the volume of the single unit cell. 0 is from mole of atoms. So, delta V by V 0 is n V a cube by 4 by n 0 a cube by 4. So, that means that now, I am trying to calculate my fraction here delta V delta L V by delta L. This is delta V by V 0 here. That means I am talking about x times n 0 a cube by 4 divided by n 0 a cube by 4. So, this is my change in volume and this is my original volume. This x is coming because n V a cube is x n 0 a cube.

So, this implies that 3 delta L V by L 0 is equal to x. so, delta L V by L 0 is we know x by 3. Therefore, 3 delta L V by L 0 is x. So, the fraction I am trying to calculate is x by 3

L 0 by delta L, which is x L 0 by 3 into delta L. We know it is about 2 percent, which is about 0.02 L 0. So, this value we already calculated. The L 0 cancels off in the numerator and denominator. So, the number becomes x divided by 3 into 0.02 L 0 x into 3 into 0.02. x, we already know. We have calculated before, which is the fraction of vacancies.

They are being created, which is about 9.7 into 10 power minus 6. Substituting these values, I fine the fraction of vacancies or the fractional increase in length. It is coming from purely creation of vacancies; is about 10 power minus 4. So, this effect of increase in length coming from thermal expansion is about 1 into ten power 4 as compared to the one coming from thermal vibrations. So, in normal circumstances perhaps, this can be ignored. But if you want a detail calculation of how the length increase is coming, we have to note that this is about 1 in a 10000 effect.

It is coming from increase in number of vacancies in the material. So, with this two examples, we have considered that how vacancies for instance increase in number as a fractional lattice sites. So, to heat the material and also how they can give rise to an increase in length in the material, which is now related to the volumetric increase coming from the increase of vacancies in the material.