Solid State Chemistry
Prof. Madhav Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture – 32
Lattice Imperfections in Crystals

Now, I will start the 2nd lecture of week 7 of this course. In this lecture I will start talking about Lattice Imperfections and we will talk about lattice imperfections in crystals and I will start the discussion on point defects in this lecture. So, week 7 lecture 2 will be Lattice Imperfections in Crystals ok.

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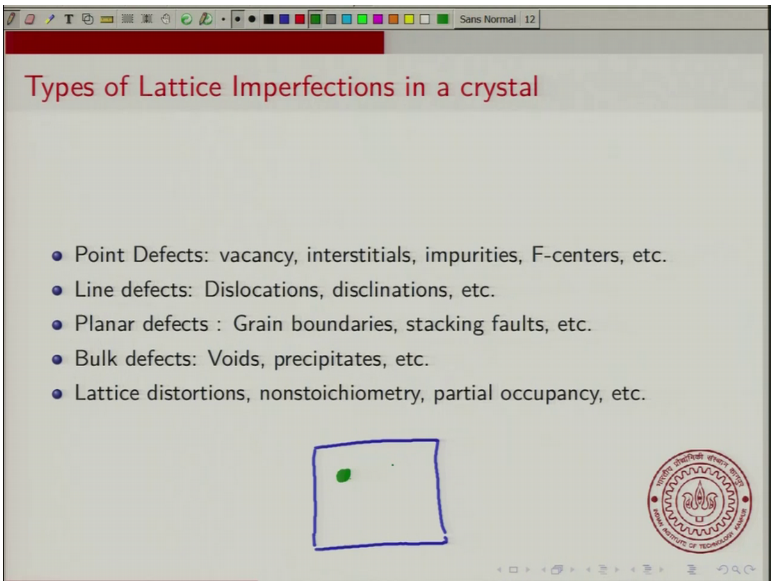

So, let us we will just you know we have been talking about crystals and crystal structure and we have sort of been focusing on the symmetries and the properties of a perfect crystals, but very often in fact, almost always you find imperfections and crystals and each of these imperfections leads to very it leads to it's own important phenomena ok. So, it's good to understand what are the kinds of imperfections that you can have and what kind of effects they can have? So, there are several different ways to classify these imperfections. So, I will look at through one way which is very convenient for us ok.

So, we can think of the defects as point effects or line defects or planar defects or bulk defects and then I will also mention that there are things like lattice distortion, nonstoichiometry and partial occupancy etcetera, which are also which can be put into one or more of these defect categories ok. So, point defects these an example is there could be a vacancy where one atom is just missing in a you know you have a perfect crystal, but one atom or is just missing ok.

Then that would be a vacancy and that would lead to something that would to a point effect. You could have an interstitial where an atom is found at a site that is not the standard site in a perfect crystal it is found; it is found in some other site which is not a perfect site in the crystal. There could be impurities, there could be foreign atoms that come and then we will talk briefly about F centers ok.

So, these are very specific this name is specific to ionic crystals and will and I will briefly introduce that. Line defects the examples of line defects are dislocations and disclinations again I will talk briefly about these. The line defects are actually very I mean they play a very important role in the main the mechanical properties of the material ok.

So, when you try to bend or try to strain material then these dislocations with turn out to be turn out to play a very important role. They can also be what are called what you can classify as planar defects, these are things like grain boundaries or stacking faults and then they can be bulk defects so what I mean by a wide here is that there are a whole bunch of atoms that are missing ok.

You can have voids, you can have cracks in the crystal, you could have; you could have a collection of atoms forming something like a little precipitate within the larger crystal. So, if you have; if you have a crystal of one material that I am showing in blue you could have; you could have some region where there is a precipitate or some sort of inclusion of some other material ok. So, this green region is different material I am really thinking of a very large crystal here ok.

You could have things like lattice distortions, you could have nonstoichiometry when the where the we will see examples of these as we go on in this course you could have partial occupancy like some sites in some sites are only partially occupied by atoms these would lead to other kinds of defects ok. Let us talk a little bit about the point effects and I will do a few examples of very well known point effects that you might also be familiar with, the first one is a Schottky defect.

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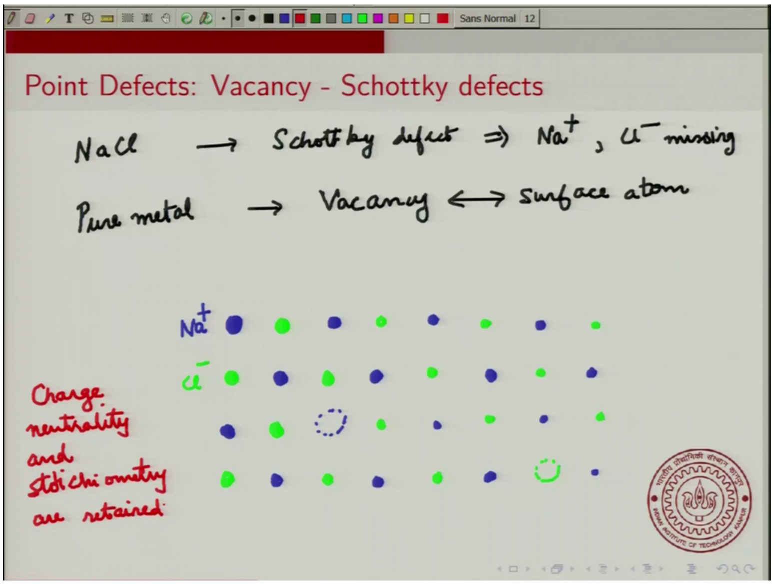

Schottky defect is actually you can I mean in if you had a; if you had an ionic crystal like let us say NaCl ok, then Schottky defect would be the effect would correspond to a Na plus and Cl minus missing. So, a pair of Na so 1sodium plus and 1 chloride ion missing. So, that combination would cover what would be a Schottky defect and the point is they need not be right next to each other.

If you had a pure metal a single element ok, then the Schottky defect would be a vacancy and surface atom; that means, an atom leaves it's site inside the crystal and goes to the surface so that would be an example of a Schottky defect ok. In sodium you can imagine that you know somewhere 1sodium is missing and 1 chloride is missing somewhere else and they together form a Schottky defect.

Just to remind you the head is so if I show the sodium atoms in blue and chloride atoms in green ok, then the sodium chloride is this rock salt structure which is essentially you can think of it as 2 interpenetrating FCC's. So, the sodium atoms will form an FCC I am just showing in one plane and the chloride atoms will also form an FCC ok.

And if you extend this you will get in all directions you will get the sodium chloride structure the rock salt structure ok. Now if you had; if you had some atom that is missing say for example, if this sodium is missing and some chlorine let me show it somewhere else that is missing a little far away, let us say the chloride and here is missing ok.

So, then this missing sodium and this missing fluoride so this pair would form a Schottky defect ok, so this would be a Schottky defect and the point is that the sodium at sodium ion is positively charged, the chloride ion is negatively charged ok. So, if you have 1 sodium and 1 chlorine missing then the crystal as a whole will be neutral, so the neutrality of the crystal is maintained ok. So, both you can see that both charge neutrality and stoichiometry are maintained; are retained ok.

And these Schottky defects actually play a big role in electrical conductivity and so Schottky defects are much studied in the area of you know when you are looking at conduction through materials then the Schottky defects actually play a role there ok.

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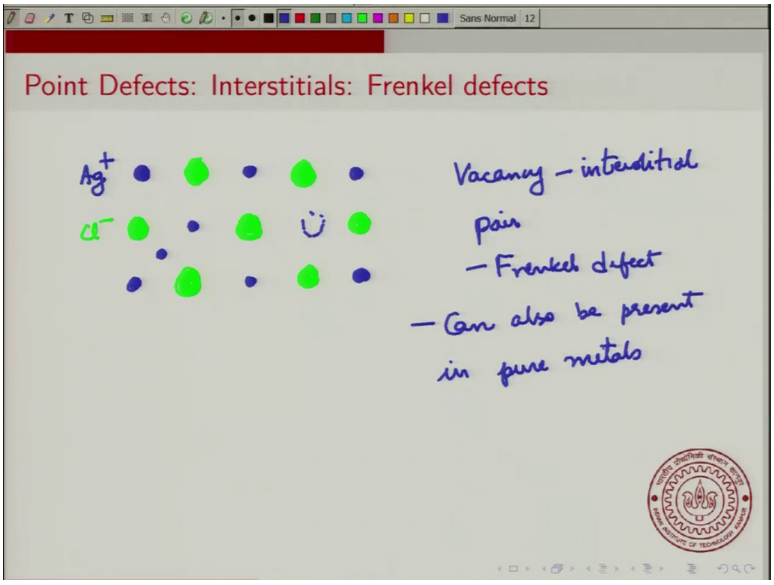

What about Frenkel defects? Frenkel defects are different kinds of defects these are like these are interstitials ok. So, for example, the canonical example of a Frenkel defect is a silver chloride so you have Ag plus and you have Cl minus silver chloride this is another ionic crystal which also crystallizes in the rock salt structure ok. So, it also forms a rock salt structure.

So, if you just show it in two dimensions. So, one of the defects that is observed is when one of these silver atoms they go to an interstitial site ok. So, you could have maybe this silver atom has left it's site and it has gone to some site let us Frenkel say somewhere here ok. So, this combination of I should show silver sorry I wanted to show the silver let me also emphasize that chloride being a negatively charged ion is actually much bigger than the silver ok.

And in this case a silver now the for the Frenkel defect corresponds to a silver atom leaving it's site so it could leave it's it leaves it's site and goes to some inter interstitial site ok. So, this would be an example of a Frenkel defect ok. So, this is a vacancy interstitial pair, so vacancy interstitial pair, this is a Frenkel defect in particular this is referred to as a cation Frenkel defect because silla plus is a cation and the cation is forming this Frenkel defect ok.

Now there is another defect again that is you could also from Frenkel defects in pure metals ok, it could also take it could also happen in pure metals where you just form a vacancy interstitial pair so can this can also be present in pure metals. Another kind of point effect which is traditionally these are referred to as color centers ok.

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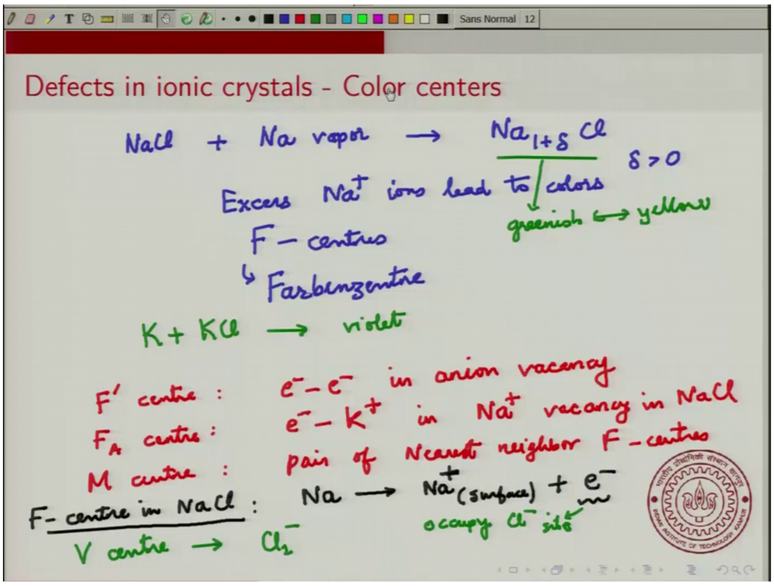

These are seen in ionic crystals and this is these are often nonstoichiometric ok, in the sense suppose you take; suppose you take sodium chloride and you put sodium vapor, you put it in some vapor of sodium ok. So, sodium you take sodium gas and you pass it over sodium chloride then you can get something like a crystal that has a slightly different stoichiometric so, the stoichiometry, so delta greater than 0 ok.

So, it is some small fraction it is a delta is some small number like 0.1 or 0.2 and this in this case these extra so these excess sodium atoms we will go to interstitials and the excess sodium will lead to colors and they are called as for example, they are called as F centers. F stands for F center or this in the F comes from the German word Farbenzenter ok. So, that is a that is an F center or a color center ok.

Similarly, this so essentially this excess sodium ions will they will actually lead to a change in the color of the sodium chloride ok. So, the sodium chloride crystal will actually show a different color in the presence of these excess sodium ions ok, there are other centers you can get I mean there are a number of these color centers.

So, for example, if you put this actually looks the color of this is actually greenish to yellow color; to yellow color depending on how much sodium is there ok. You can also get for example, in K plus KCl KCl. So, KCl with K vapor you get violet color and we and actually it is not very hard to show why these excess the presence of excess charge will lead to these colors.

So, there are other defect centers so this just as you have an F center you you can have things like I will just; I will just list the names of some of them you could have a something called an F prime center ok, in this case you have an electron pair a pair of electrons in anion vacancy. So, you can think of it this way that you have an anion missing and in from some site and in that site there is a pair of electrons ok.

So, that would lead to something like an F prime center, this is found in calcium fluoride in CaF2. You could have an F A center, this would be an electron and a K plus an example of this an electron and a K plus ion in Na plus vacancy in NaCl. So, this is a case where you have a way you have the sodium chloride structure and one in one of those sites the sodium atom is missing and it’s replaced by a K plus ion and an electron.

So, then there are things like M center, which is pair of F centers of nearest neighbors F centers and so on you could also get things like R centers and F centers in perpendicular plane in one one one planes and ionized centers and so on. Let me just once again show the nature of the F center ok.

So, if you take this; if you take this sodium 1 plus delta ok; so if you take the sodium 1 plus delta now there are some excess sodium atoms. Now those sodium atoms will get ionized. So, let us show the F center in NaCl so, I will just show you how this F center is formed ok. So, you have some excess sodium atoms that will get ionized to sodium plus which will stay on the surface and an electron and this electron will actually go inside the crystal and it will occupy an anion site and it will give the F center. So, this electron will occupy the anion site occupy Cl minus site and this is the color center that you get ok.

So, the way you get a F center in NaCl is it's actually this x even though it looks like excess sodium it's actually the excess electrons that are produced due to ionization of the sodium and then when those occupied the Cl minus site and you can you I should also mention that you can get things like V centers so V center ok. So, this is basically a Cl 2 minus.

So, instead of chlorine ion you have something like a Cl 2 minus in one of the site and that would be a V center and again so these color centers are actually very I mean there are there they are quite widely seen in ionic crystals and they are responsible for some colors in these ionic crystals ok. So, if you take a perfect sodium chloride you will just see it colorless you will see it white ok.

But in the presence of these if you have; if you have these defects which are called as color centers then the sodium chloride crystal will actually look colored ok, I do not want to spend too much time discussing the different kinds of color centers ok, but it's good that you are aware it's good to be aware that there are such things in these crystals ok. So, I will conclude this discussion on point effects in the next lecture I will change tracts and start discussing about line defects.

Thank you.