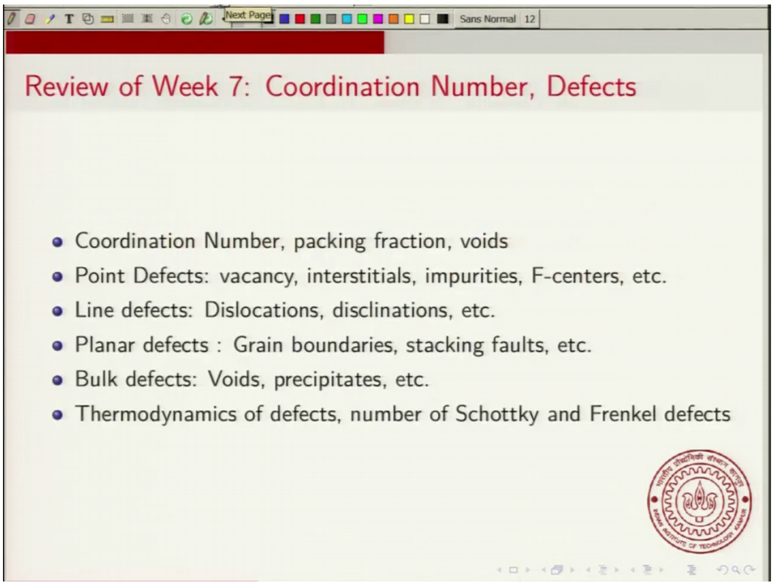
Solid State Chemistry
Prof. Madhav Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture – 35
Review of Week 7, Practice Problems

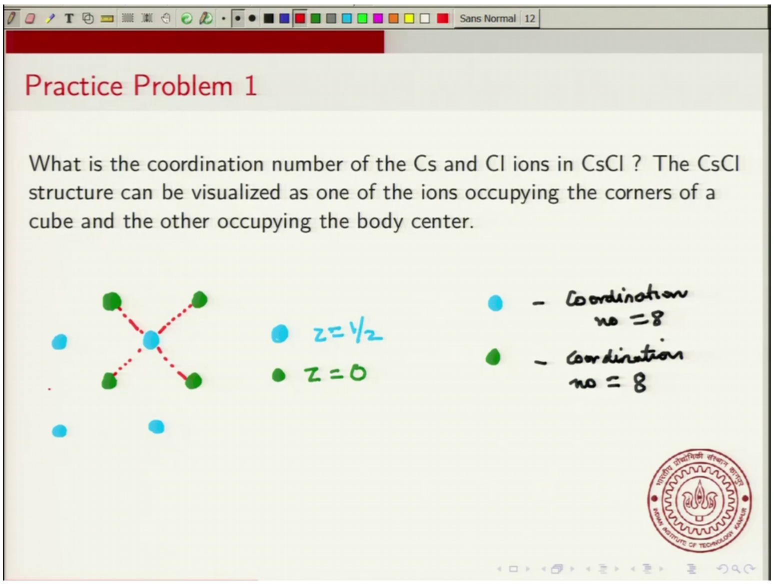
Now, I will go to the last lecture of week 7. So, I will recap what we did during this week ok and the n to practice some problems. So, this will complete this discussion on voids, defects, coordination number and dislocation and so on ok. So, week 7 lecture 5 review of week 7 and practice problems.

(Refer Slide Time: 00:41)



So, let us we review what we learnt. We basically overall we learnt about coordination number and defects. So, in the initially we learnt about coordination number, packing fraction and voids in crystals. Then we learnt about defects in crystals such as vacancy, interstitials, impurities, F-centers these are the points defects. Then line defects such as dislocations, declinations planar defects grain boundaries, stacking faults, a little bit about bulk defects like voids and precipitates. And then we studied the thermodynamics of defects and number of Schotty and Frenkel defects

(Refer Slide Time: 01:23)



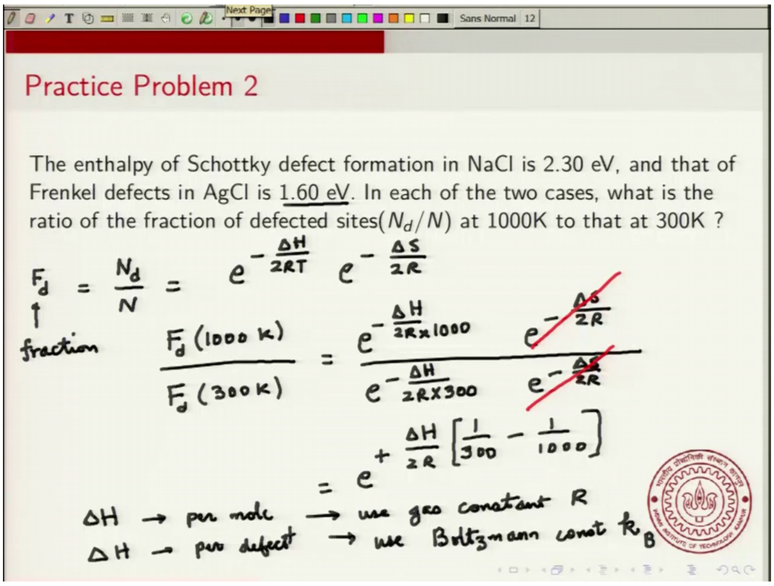
So, I will do a few problems fairly straight forward problems. So, the first problem is asked you what is the coordination number of cesium and chloride ions in CsCl? And it is said that the CsCl structure can be visualized as one of the ions occupying the corners of a cube and the other occupying the body center.

So, the cesium product structure I will just write. So, if you make if you put one set of the ions at the corners of a cube, which I will show in blue and the other is occupying the body center which is at the height of z equal to half and this is z equal to 0 ok. So, this is a cesium chloride structure and now you can see that that along with the z equal to 0, there will also be there will also be similar 4 plane of similar these 4 green atoms at z equal to 1 ok. And if you look at this blue point at z equal to half the blue atom or the blue ion ok.

Now, that is equidistant from these 4 green ions and it is also equidistant from the 4 green ions at z equal to 1 ok. So, clearly the coordination number is equal to 8. Oh shit, I meant not I meant was this color, yeah the coordination number of these ions is equal to 8 ok and now you just by extending the structure. So, suppose I just extend it here, now if I shift my plane to z equal to half, if I shift this screen to z equal to half, then you can see that what you have here is exactly equivalent to what you had here shifted by half and the shifting of the 2 ions ok. So, what I want to say is that this green ion is equidistant from these 4 blue ions and it will be equidistant from 4 more blue ions located at z equal to minus half ok.

So, the coordination number of the green ions is equal to 8. Now this completes this problem. I just want to make a little observation, we have defined the coordination number as the as the number of nearest neighbors and notice that for the blue ions which could be cesium or chloride. The nearest neighbors are the green ions and for the green ions the nearest neighbors are blue ions ok. So, the number of closest ions of the opposite kind is 8, in both cases ok. You could also ask questions about a number of closest ions of the same type ok. And that would be a different answer, and you can easily work that out also ok. So, next I will go to a different problem ok.

(Refer Slide Time: 05:25)



This is on this has to do with a with a thermodynamics of defects. The statement is the enthalpy of Schottky defect formation in NaCl is 2.30 electron volts and that of Frenkel defects in AgCl is 1.60 electron volts. In each of these two cases what is the ratio of fraction of defected sites at 1000 K to that at 300 K ok. So, we recall this both these are both these are, they have 2 ions these have ionic compound with 2 with two different ions. So, you have sodium chloride and silver chloride ok. And in both these cases we saw that we could write the fraction of defects using this as e to the minus delta H by 2 R T times e to the minus delta S by 2 R that was the expression.

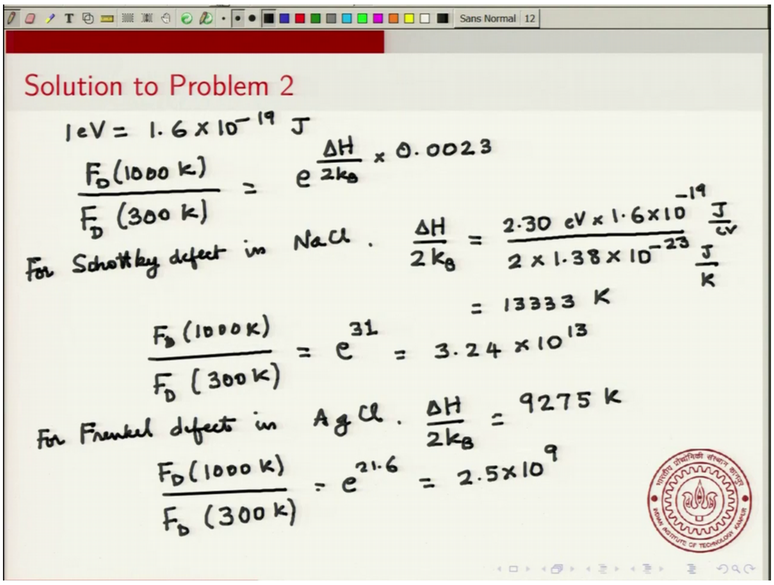
Now, let me call this F d, F stands for fraction. I will just use this notation just to make ok. Now what we have to calculate is F d at 1000 Kelvin divided by F d at 300 Kelvin ok. So, this ratio is so, so so, what we have to do is we have to take e to the minus delta H by 2 R into 1000 times e to the minus delta S by 2 R divided by e to the minus delta H by 2 R into 300 times e to the minus delta S by 2 R ok.

So, as usual we assume that delta H and delta S do not change with temperature, which is a fairly good approximation ok. And so and so what you can see is that this term will cancel on both sides ok. And I can write this ratio as in the following form I can write this I can I can take this up to the numerator and make this a plus sign. So, we will have e to the minus delta H and then I take minus delta H by 2 R common and I have, I will make it a plus delta H by 2 R then I have 1 over 300 that comes from the denominator and minus 1 over 1000 ok.

So, we use this is the expression that we will use. So, the fraction of defects 1000 Kelvin to the fraction of defects at 300 Kelvin it is given by this expression ok. And now and now let us so let us by 2. Now there are a few things that you have to keep in mind, this is written in terms of R ok. When you write delta H in per mole ok delta H has to be written in per mole, because this is written in terms of gas constant ok. Then you use then you use gas constant R ok.

When you use when you give delta H per defect so, this per mole of defect. So, if you give per individual defect then you should use Boltzmann constant k B ok. So, this is an important thing to keep in mind and you should always you should always check.

(Refer Slide Time: 10:33)



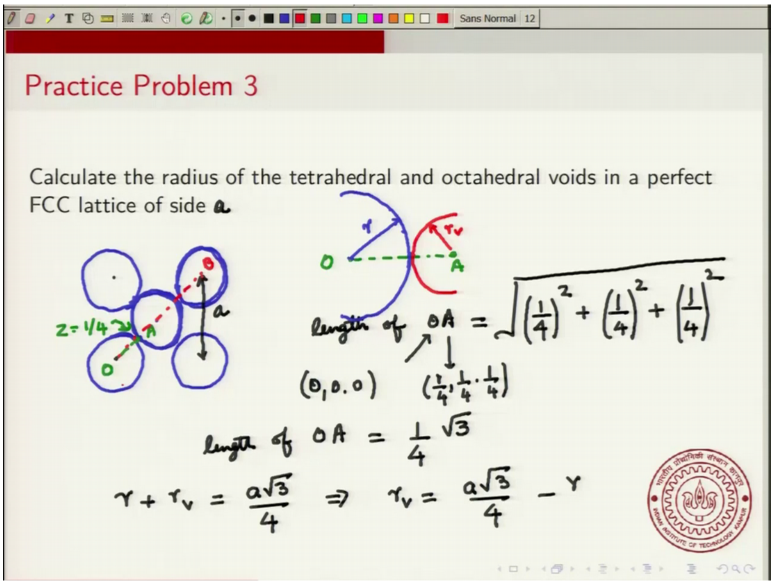
Now, now here the energy is given in electron volts the defect formation energy is given in electron volts ok. So, 1 electron volts, 1 electron volt is equal to 1.6 into 10 raise to minus 19 joules ok. So, clearly it is given in this corresponds to the formation of 1 single defect ok. So, this is the formation of 1 single is 1.60. So, you have to use Boltzmann constant ok. So that means, you have to use Boltzmann's constant.

Now, let us calculate this ratio. Let us calculate delta H divided by 2 k B ok. This ratio yeah before that let me just emphasize that you know if you want to calculate F D at 1000 Kelvin, divided by F D at 300 Kelvin. Then you should use e to the delta H by 2 k B ok. And you had the factor, you had this factor of 1 over 300 minus 1 over 1000. 1 over 300 is 0.0033333 and 1 over 1000 is 0.001.

So, this differences 0.002333 ok, I will erase 0.0023. So, so let me calculate this delta H by 2 k B. This is for Schottky defects 2.30 electron volts, into 1.6 into 10 raise to minus 19 joule per electron volt divided by 2 into 1.38 onto 10 raise to minus 23, this is the this is the value of the Boltzmann's constant joule per Kelvin ok. And so and so delta H by 2 k B will have units of Kelvin, and this works out to that is the unit of this and if you substitute in that expression you will get this F D at 1000 Kelvin. This comes out to, this comes out to so, this 13333 into 0.0023 ok. So, that that gives you e raise to 31 ok. Which is 3.24 into ten to the power 13. So, you can see that if you go to 1000 Kelvin the fraction of the number of defects is much larger than what you have at 300 Kelvin. But actually this 2.30 electron volt is a fairly large energy. So, at 300 Kelvin you do not have too many defects. In the first place; however, if you go to 1000 K then you have enormously you 10 raise to 13 times as many defects as you had at 300 Kelvin.

Now, now for Frenkel defect in AgCl you have delta H by 2 k B ok. Now in this case this 2.30 in 2.30 in this expression is replaced by 1.60 and if you do that, then this number comes out to you can you can work out that number. If you work out this number it comes to about 9275 Kelvin ok. And now the fraction F D at 1000 Kelvin to F D at 300 Kelvin is about e to the 21.6 ok which is 2.5 into 10 power 9 ok. Again, again there is large increase in the number of defects with temperature ok.

(Refer Slide Time: 16:23)



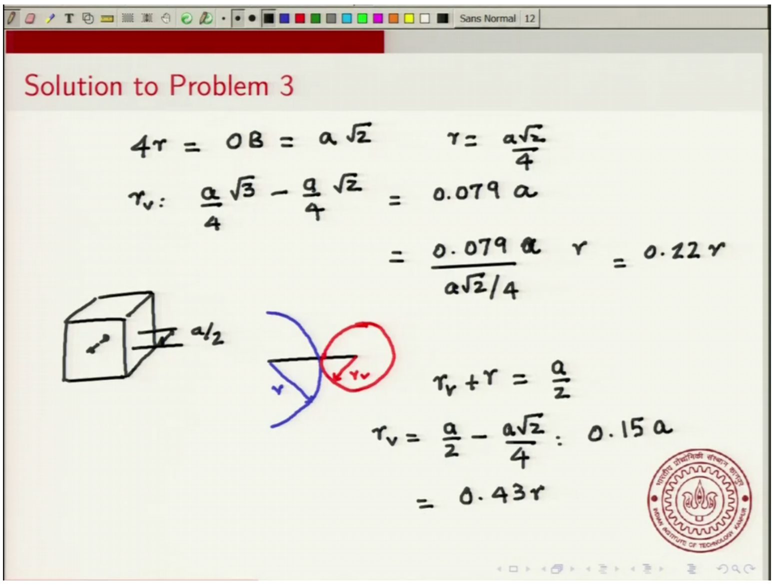
Now, next we will do another problem ok. This is to calculate the radius of tetrahedral and octahedral voids in a perfect FCC lattice of side a ok, we will write this in a the script a ok. So, a is the size of this lattice and you have to calculate the radius of tetrahedral and octahedral voids ok. Now, to do this you have to again let us let us recall a few things about the FCC lattice ok. So, in an FCC lattice or the center atom is in contact with each of the 4 corner atoms ok. So, the atom at the center at the face center is in contact with each of the 4 corner atoms. But the, corner atoms are not touching each other. So, this what I think this came a little big just make it smaller ok.

So, this is what it looks like in one plane ok. So, the face center atom is in contact with the corner atom ok. But the atoms at 2 adjacent corners do not touch each other ok. And now you recall the tetrahedral void ok, is located right here at z is equal to 1 by 4. So, that is the location of the tetrahedral void. So, the coordinate is x equal to 1 by 4 y equal to 1 by 4, z equal to 1 by 4. So, this is a tetrahedral void location. So, you can ask what is the distance of the tetrahedral void. So, along this, along this let me call this O A, A is the location of the void and along this O A direction, O A direction ok. So, now how this length of O A is equal to so, that is the coordinate of, coordinate of A ok.

So, I will write it in the following way. So, you can look at the coordinates of a coordinates of a are 1 by 4, 1 by 4, 1 by 4. So, it will be, so this will be 1 by 4 square plus 1 by 4 square, plus 1 by 4 square ok. And O is 0, 0, 0. So, you keep in mind that O is 0, 0, 0 and the coordinate of A is 1 by 4, 1 by 4, 1 by 4. It does not matter which way you see basically the distance and this whole thing under the root sign. So, this a length of O A. So, the length of O A is equal to 1 by 4 root 3 ok. And now and now along OA what you have is, you have this you have this, 1, 1 atom 1 face center atom ok. And so, this is the radius of the face center atom ok.

Now so, clearly the tetrahedral void if it is sitting at A, then the radius of the tetrahedral void ok. Clearly you have the relation radius of this face center atom plus radius of void atom equal to a root 3 by 4. And so this implies that the radius of the void is equal to a root 3 by 4 minus radius of the atom ok. Now, the radius of the atom can be related to a ok. a is the side. So, the radius of the atom can be related to a because as we said along the face center they touch each other ok. So, clearly this from O to this point B ok. So, this length is equal to is 4 times the radius so we can say that the 4 times radius is equal to O B is equal to a root 2 Therefore, r is equal to a root 2 by 4 ok.

(Refer Slide Time: 22:21)



So, then the radius of the void is equal to a by 4 root 3 minus a by 4 root 2 and. So, root 3 is 1.73 this is 1.41 and you have divided by 4 ok. So, this works out to about 0.079 times a. And equivalently you can also see that that since r equal to a root by 4 ok. I can just divide by a root 2 by 4 ok and multiply by r. So, I can write this as 0.079 divided by a root 2 by 4 and into r ok, into a into r ok. So, I will just multiplied and divided by r and what will happen in this case that the a will cancel and you will get, so you will get this as basically 0.22 R ok.

So, in other words the radius of the tetrahedral void is about 22 percent that of the ion. So, the size of the tetrahedral void is about 22 percent that of the ion ok. What about the octahedral void in FCC? Now the octahedral void is at the center of the cube ok. So, and now if you go, again take the let us go back to the planar view. So, the octahedral void is located right at the center of the cube ok and now if you go from this point at from the center at. So, the center of the cube is located at z equal to half, x equal to half, y equal to half and if you just go along this line going starting from the starting from the face center that is in the plane of the screen to the center of the cube which is located at z equal to half.

So, along that line if we go then, then you will get the relation for the octahedral void. So, again just to clarify what I mean is that if you take this point that is in the plane of the screen, and then you go you come directly up along this to z equal to half ok. So, then along that line what or may be maybe I will show it in a slightly different way, yes ok. So, I am going from the center of this face, I am going from the center of this face to the center of the cube ok. So, clearly this distance that have travelled is a by 2 and. So, along that line you can clearly see that a by 2 should be equal to the radius of the radius of the void plus the radius of the atom ok. So, clearly for the tetrahedral void r v plus r is equal to a by 2. So, r v equal to a by 2 and now we use the expression for r minus a root 2 by 4 and this works out to about 0.15 a.

So, it is actually nearly twice that of the tetrahedral void ok. And you can also work it out it comes to about 0.43 r. So, with fairly simple coordinate geometry you are able to calculate the radius of each of these voids, you have to visualize this thing ok. So, initially it take time, but after some time it will become very easy. So, with this I will conclude week 7 of this course some of the lectures have been quite long in this week ok. But part of it is because it takes it take a little while to draw and explain those the those structures ok. But otherwise the content for this week is not is not that difficult. So, I will conclude this lectures and we will start the 8th week after this.

Thank you.