Defects in Crystalline Solids (Part-I)
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Lecture – 08
Defect Reaction + Kroger-Vink Notation

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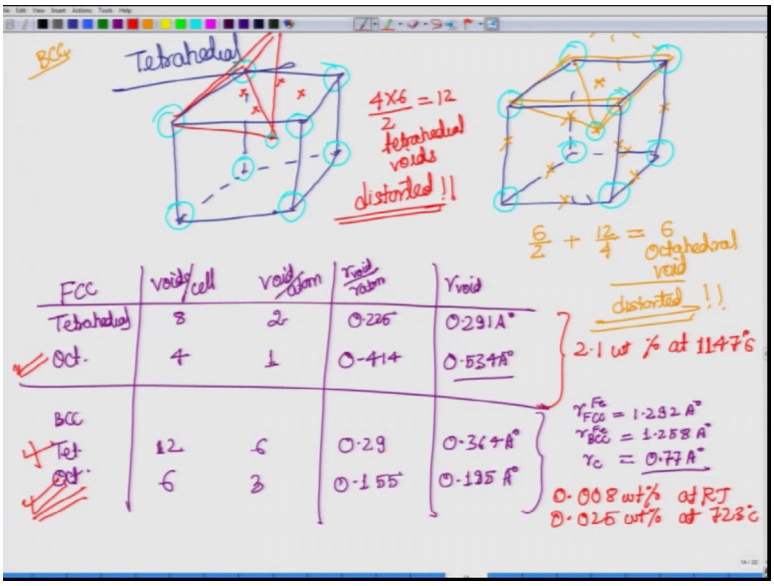

BCC

Tetrahedral

$\frac{4\times 6}{2} = 12$ tetrahedral voids

distorted !!

$\frac{6}{2} + \frac{12}{4} = 6$ Octahedral void

distorted !!

FCC	voids/cell	void/atom	r_{void}/r_{atom}	r_{void}
Tetrahedral	8	2	0.226	0.291 A°
Oct.	4	1	0.414	0.534 A°
BCC				
Tet.	12	6	0.29	0.364 A°
Oct.	6	3	0.155	0.195 A°

2.1 wt % at 1147°C

$r^{Fe}_{FCC} = 1.292$ A°

$r^{Fe}_{BCC} = 1.258$ A°

$r_C = 0.77$ A°

0.008 wt% at RT

0.025 wt% at 723°C

So, like I said that, although on paper when you look at it, it would seem like tetrahedral void in BCC would be preferred by carbon atoms, but it is not really the case. Octahedral voids are the once where carbon atoms 6. Now at this point let us also look at what will be the radius of these voids, I have shown you the ratio, now, let us look at the actual value. Radius of void, so, this comes out to 0.291 angstroms, this comes out 0.534 angstroms, for this one it comes out 0.364 angstroms and for here it comes out point ok, and at this point let me also give you what is the radius of FCC Fe, it is a little different. So, the radius of FCC Fe is a little different from radius of BCC Fe and but not by much thankfully for us and what is the size of the carbon atom that has to set over there? So, the carbon atom is equal to 0.77 angstroms.

So, the first thing that you have to realize let us first look at this even the simple one where we everything is going as per we expect, as per our expectation. So, the carbon is sitting at the octahedral void and here the octahedral void radius is 0.534 angstroms while the real size of the carbon atom radius of the carbon atom 0.77 angstroms. So, a larger atom is fitting in a smaller size just what I told you earlier that the presence of interstitials causes are lot of strain in the matrix around it.

So, our such a large 0.77 meaning it is more than 20 percent larger in size than the available void over here and it still it goes into that site it has to go in that site it prefers for the reason of thermodynamics because it leads to lower free energy the presence of these atoms in that place leads to lower free energy and therefore, the carbon atoms goes there and all the strain energy that is caused is included in that enthalpy of formation.

Because some amount of energy will have to be put in into the system to accommodate that strain and is spite of all that because of the configurational entropy we are able to achieve the system is able to get lower energy by addition of this carbon atom. So, this is something that would appeared quite counter intuitive on the first encounter.

Now, let us look at the second aspect we are saying that here the radius of the octahedral void is 0.195 which is like maybe approximately one-fourth of the radius actual radius of the carbon atom and still the carbon atom sitting over here instead of a much larger size which is 0.364 and what is the reason for this, the reason for this is hence now we looked at the fact that tetrahedral void and octahedral void are distorted.

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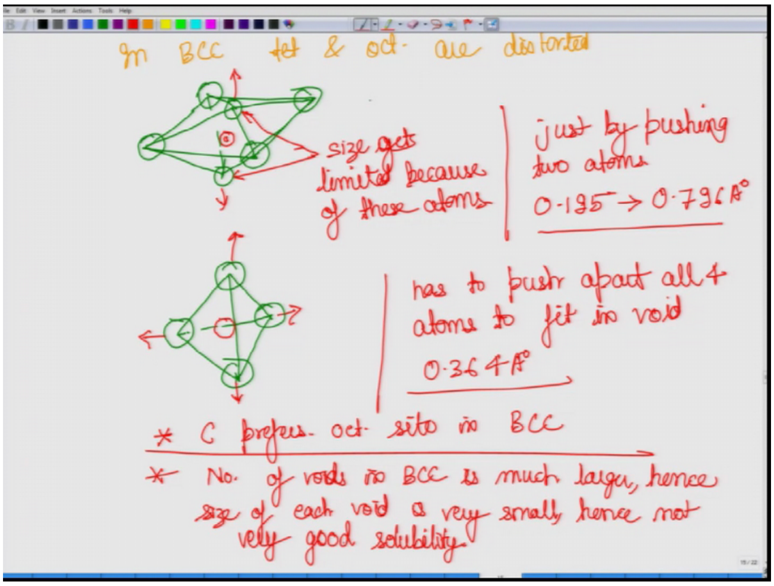

In BCC tet & oct. are distorted

just by pushing two atoms
0.195 → 0.796 A°

has to push apart all 4 atoms to fit in void
0.364 A°

* C prefers. oct. site in BCC

* No. of voids in BCC is much larger, hence size of each void a very small, hence not very good solubility

So, how are they distorted because we saw that all the lengths are not equal. Now let us look at it in a little bit more clarity. So, first let us look at the octahedral void. So, the octahedral void if you look at it is something like this what I am trying to show here is that that these 2 atoms are much closer. So, these 2 atoms are much closer, the atoms on the plane they are far apart and the size of the void is limited primarily because of these 2 atoms, the size gets limited because of these atoms.

Now, what is the easiest way to increase the size push these atoms apart. So, just by pushing 2 atoms this void can be increased in size from 0. 195 to 0.7696 angstrom. So, you will have to cause the little bit of strain. So, that will in cut included in the enthalpy formation some and by pushing those 2 atoms these atoms whatever is the interstitial over here which is carbon.

In this case the carbon can increase the size from 0.195 angstroms to 0.796 angstroms which is a big deal. Now if we look at over here in the tetrahedral void this is also distorted; however, in this particular case if this atom has to increase the space it will have to push apart all the four atoms. So, has to push apart all 4 atoms to fit in void. So, you remember this even this 0. 3 its original size is 0.364 angstroms. So, even 0.364 angstroms is very small it is almost half of what is less than half of what is actually needed.

So, this is still very small and one and the atoms have to push the atoms of the corner atoms apart and here it has to put push 4 atoms apart here it has to just push the 2 atoms of apart and it will be able to accommodate or increase the void size from 0.195 to 0.796 angstroms and therefore, this can easily fit inside this. So, this is the primary reason why carbon prefers octahedral site in BCC. Now let us come back to which one so, we have understood one aspect which is when we said that octahedral voids would be preferred, so now, we understand why.

Now, the second aspect we need to understand is which one will the carbon atom set more preferentially. So, here let me give you some information about what is the real solubility. So, the solubility of carbon in BCC is 0.008 weight percent at room temperature and if you if you go too much higher temperature which is it reaches 0.025 weight percent at 723 Celsius.

On the other hand solubility of FCC can be as high as 2.1 weight percent, although it is at a little higher temperature which is 1147 degree Celsius. So, now, what is the reason that even though BCC is the more open in structure, but it still the carbon atoms are more soluble in the FCC and the reason for this is when you look at the number of voids per unit cell or the number of void per unit atom.

So, what you see here the total number of void has only three per associated with each atom, here the number of void associated with each atom is 9. So, although the structure is more open in BCC, but the size of each because of the large number of voids the size of each void is very small.

And hence so we can write it like this. So, this is one our one understanding, second understanding is that number of voids in BCC is much larger hence size of each void is very small hence not very good solubility. So, this helps us to understand the interstitial impurity point defects.

So, you can see that there are so much intricacy involved in understanding us simple point defect which is, but in this particular phase the interstitials. So, you have more open structure like BCC and still the carbon is more soluble in FCC you have a larger tetrahedral void, but carbon atom preferred to set in the octahedral void why because here just by in octahedral by distorting just 2 atoms it can increase the size.

On the other hand in the tetrahedral void it will have to push away or distort for more atoms to be able to accommodate and therefore, the total space is available in octahedral void is larger. So, the in both FCC and BCC its so, happens that carbon sits in the octahedral void ok. So, with that we complete our understanding for this impurity defects which is the interstitial as well as substitutional. So, we have looked that the vacancy defects, we have look that interstitial and substitutional defects.

Now, what we need to do is we looked at this whole understanding again from the point of view of a defect reaction ok. So, you would see that these defect formation can also be written like a reaction and hence if it is a reaction you can find a rate constant equilibrium constant and from that equilibrium constant again you can find what will be the equilibrium concentration and you would see that it is a much more direct way of obtaining the equilibrium concentration.

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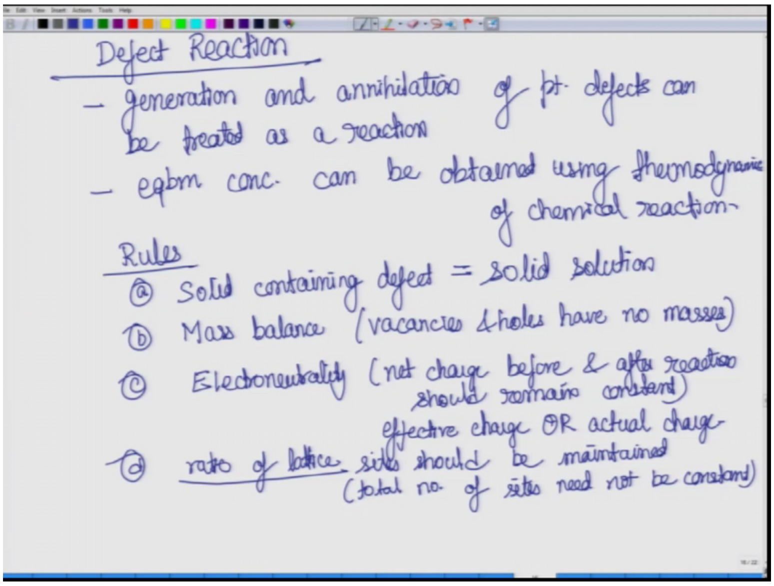

Defect Reaction

- generation and annihilation of pt. defects can be treated as a reaction
- eqbm conc. can be obtained using thermodynamics of chemical reaction.

Rules

ⓐ Solid containing defect = solid solution

ⓑ Mass balance (vacancies & holes have no masses)

ⓒ Electroneutrality (net charge before & after reaction should remain constant)

effective charge OR actual charge

ⓓ ratio of lattice sites should be maintained (total no. of sites need not be constant)

So, our next topic is defect reaction. What is the defect reaction how would you define defect reaction generation and annihilation of point defects can be treated as a reaction, equilibrium concentration can be obtained using thermodynamics. So, now, that it is a reaction, so equilibrium concentration in can be obtained thermodynamics of chemical reaction.

So, now when we treat it as defect as a reaction then there are certain rules. What are those rules that we have to follow that we must ensure that they are taking care of before we can call it reaction? So, first one is that a solid containing defects should be treated saying as a solid solution. So, whether you have a plus b 2 different atoms or you have a plus on defect both of them are like a solid solution. So, solid containing defect is equal to solid solution. So, it has to be treated like a solid solution and that we have already seen even when we were trying to get the configuration entropy that it has to be treated like a solution.

So, that is one thing mass balance when you write it as a reaction then on the left hand side and right hand side you should have same masses of course, here vacancies and if you are talking about charges then holes vacancies and holes have no masses. So, you can you did not worry about the mass balancing of these entities.

Electro neutrality the one of the primary purpose of treating these as defect is that we can understand how the charges are being distributed and therefore, it is much more useful for electronics and ionics solids. So, net charge should before and after reaction should remain constant. Now this is also something very difficult to achieve or difficult to write as equation.

So, first to maintain electro neutrality or to write a equation where the charges remain same, it is a little difficult and therefore, you have to adopt certain you can say protocol or naming system nomenclature. So, it can be either effective charge where you show, but should be the effective charge on a particular site.

So, you go by that effective charge maintaining that effective charge before and after or you can go by actual total charge. So, that actual charge, but whichever you choose you must maintain the same set of system, you cannot mix between effective charge system and actual charge system and expect to get electro neutrality on left hand side and right hand side.

So, we have to in most of these particularly what we call as Kroger Vink effective charge is used and it is found to be much more easier to understand and write down equation, now like I said we are talking about ionic solids. So, the ratio of lattice sites for example, if you are talking about MO. So, there is 1 M 1 O. So, the total number of sites for M and the total number of sites of o should remain equal.

And similarly if there is some other system M 2 O 3 then the site for M and O should remain in the ratio 2:3. So, that is what I mean when I say ratio of lattice sites should be maintained. So, if it is 2:3 then it must remain 2:2 otherwise it will also while at the total principle of electro neutrality for the whole system.

However we have only saying ratio of lattice sites, the total number of lattice sites need not be kept constant meaning that if you add if you are talking about MO site type of system if you add A site for M atom there is one site that has been added then that you should also add one site for O atom. So, the ratio would still remain constants. So, the ratio is constant although the number of sites for M and n the total number sites in the system is not constant.

Now, that we are looking at this like I said we have to adopt at a certain procedure a certain protocol and one of the protocol on nomenclature that is very effective to use is Kroger Vink. We will understand this notation system using NaCl.

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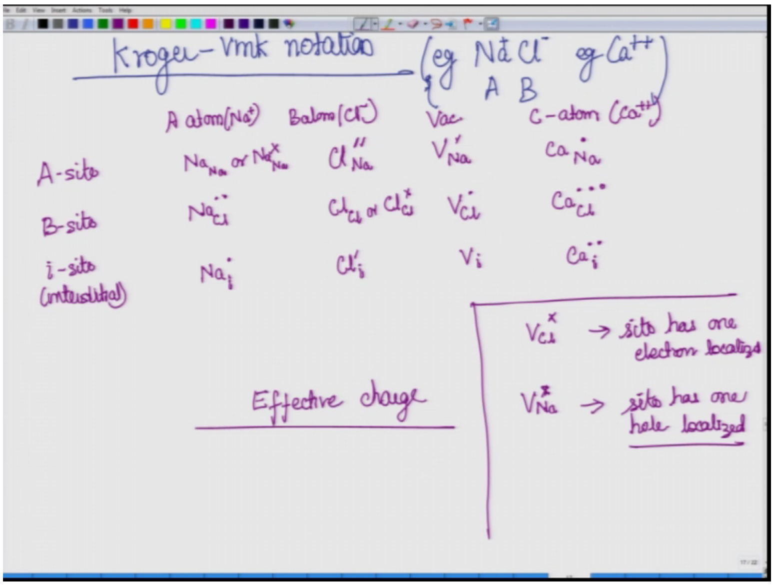

Kroger-Vink notation (eg Na^+Cl^- eg Ca^{++})
A B

	A atom (Na^+)	B atom (Cl^-)	Vac	C-atom (Ca^{++})
A-sites	Na_{Na} or Na_{Na}^{x}	$Cl_{Na}^{''}$	$V_{Na}^{'}$	$Ca_{Na}^{\bullet}$
B-sites	$Na_{Cl}^{\bullet\bullet}$	Cl_{Cl} or Cl_{Cl}^{x}	$V_{Cl}^{\bullet}$	$Ca_{Cl}^{\bullet\bullet\bullet}$
i-sites (interstitial)	$Na_i^{\bullet}$	$Cl_i^{'}$	V_i	$Ca_i^{\bullet\bullet}$

Effective charge

V_{Cl}^{x} → sites has one electron localized

V_{Na}^{x} → sites has one hole localized

So, NaCl is our system where Na can be considered where the place where Na sets which will call it at A site where the chlorine atom sits we can call it B site and let us assume that as impurity we have Ca calcium plus. So, this is a system that will use in order to explain this Kroger Vink notation and here as I said that calcium has 2 plus charge and NaCl as we know already that Na has one positive charge and chlorine has one negative charge.

So, now let us look at now there are 3 different kind of sites A site, B site and interstitial site. A atom which is Na plus B atom which is Cl minus and when we are talking about atoms then there is absence of atom which is vacancy and then there is C atom which is Ca double plus.

Now, when A atom which is Na sits at it own place then we denote it by Na subscript Na and when Na sitting as its own place we use in this particular system the case of effective charge. So, although Na has A plus 1 charge it should be Na plus, but Na is at its own sites. So, how different is it from 1 plus 1 charge that it should be there it is 0. So, it is it will be called neutral in that sense and hence it is represented just like that or Na subscript Na and the cross means there is no charge over there.

Now, let us put Cl atom at Na site now where there should have been plus one charge, but now chlorine minus atom is sitting over there without its minus charge which means it is too less than what it should be and therefore, it will be represented as 2 minus and the way to represent 2 minus s like this. So, they have 2 dash meaning it has too less positive charges than what it should be keep in mind we have in this particular system we use effective charge.

Let us go to vacancy. So, let us say vacancy sitting at a sodium site and it vacancy in use in general will not have any charge on it and therefore, it is 0 charge but it is sitting at the sodium site and there should have in a plus one charge. So, it is one less than what it should be and therefore, it is one negative charge.

Now, let us let us say that calcium atom is sitting at the sodium site, now calcium like I said as plus that is 2 plus charges. So, it is more plus than what does that particular site is supposed to have and therefore, it will be represented as one plus and the one plus is given by dot. So, this dot means plus dash means minus. So, this is how the different atom sitting at Na site would have effective charge remember again these are the effective charge.

Now, let us come back to B site now let us B site is for the chlorine. So, let us say we have sodium sitting at chlorine should have minus 1, but sodium is actually sitting with plus 1 charge. So, it is too more positive than what it should be that for it is plus if Cl is sitting on its own site then there is no effective charge therefore, you as a show it like this or like here you will put a cross.

So, we will way inter changeably using this. So, do not get confused we can this both of these represent that there are no charge on this plus and minus are very different. So, it will not get you should not get confused with that now vacancy sitting at chlorine site it should be minus 1, but it is 0. So, it is one more than one positive compare to chlorine. So, it will look like this calcium is plus 2 when chlorine should have minus 1 which means it is 3 more positive than what it should be, so it becomes 3 positive like this.

Now, let us come to the interstitial site because we are talking about impurity. So, impurity like we saw it can be substitutional as well as interstitial. So, let us say that sodium atom is sitting at interstitial, interstitial is not suppose to have any charge, so this is one positive because Na is with 1 positive charge. So, whatever with that charge is more than what is expected. So, it is shown as one dot chorine sitting at this place is 1 minus charge, this chlorine has 1 minus charge, but it is not expected to have any charge interstitial is not supposed to any charge vacancy now all these sites are actually vacant.

So, this is just a simple notation just to keep track of interstitials otherwise it means nothing and therefore, there should be no effective charge on this, calcium sitting in the sitting in the interstitial again it has 2 positive charge and it is not expect this interstitial site is not supposed to have any charge therefore, this is Ca double dot.

Now, if you understand this then try to guess what will be the meaning of C chlorine cross, now you have seen v chlorine plus which means that vacancy that there is one positive effective charge now let us say that I have put it as a cross meaning vacancy with chlorine vacancy sitting at chlorine site with no effective charge it would mean that this site has one electron localized now if the if chlorine where there then chlorine would have already had one negative charge when you electron over there.

Now, if there is no chlorine, but its still there is one electron over there that is why the effective charge is still nil meaning it is it is still has as much charge as it was expected to have, similarly if V Na is shown as like this sodium was supposed to have positive charge and vacancy in that place is it if where vacancy without any charge then it would have been one negative like they are shown over here, but here I am asking you this notation where it is shown as effective charge as zero nil it would mean that vacancy is having one deficient electron meaning something like a hole. So, site has 1 hole localized.

So, with this we can move on too and look at some of the simple equations that we had written earlier.

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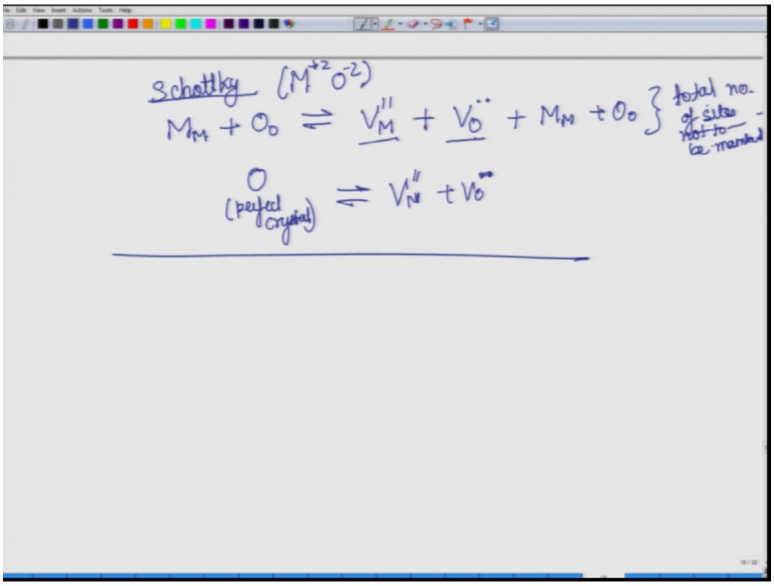

Schottky $(M^{+2}O^{-2})$

$$\underbrace{}\; M_M + O_O \rightleftharpoons \underline{V_M''} + \underline{V_O^{\bullet\bullet}} + M_M + O_O \Big\}$$

total no. of sites not to be maintained

$$\underset{(\text{perfect crystal})}{0} \rightleftharpoons V_M'' + V_O^{\bullet\bullet}$$

So, if we go back and say how Schottky defects should look like in something like M plus 2 O minus 2. So, it is a MO system where it has M with plus 2 charge and O with minus site. So, M sitting at M with no effective charge O sitting at O with no effective charge and since this is a reaction which can go in either way, now let us say this is a Schottky defect. So, there is a vacancy at cation site and that and vacancy at the anion site, so, vacancy at the cation site.

Now, there is no atom at this particular metal site and it has no charge associated with it which means now real charges associated which means effective charges minus 2 minus then there is V o there is oxygen site where there is nothing no atom present there with no charge no real charge which means effective charge is 2 positive.

And then there is still other atoms with M M plus O O which means that we can also write it as 0 meaning perfect crystal in this is not trying to maintain the total number of sites ok, we are not trying to show the total number of sites. So, the total number of sites like I said need not be maintained only the ratio.

So, now this is that is why here the total number of sites are not been maintained, but this vacancy ratio has remain same and therefore, we can write it as V N. So, this is how we can write as a defect reaction are Schottky defect. So, we will look at more examples on this in the next class and in the mean time you can try how you will write say Frenkel defect. So, see you in the next class.