Advanced Ceramics for Strategic Applications

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Lecture - 7
Defects in Crystalline Solids

In our earlier couple of classes, we have discussed in details various crystal structures, which are available in different kind of solids, ceramic materials, and others. Those are some the ideal things one can expect, ideal atomic arrangement the structure of the different solids, many different solids crystallizations in different kind of structures, in different geometric. Have a today, we are going to discuss some of the deviations from such as idles structures; of course, these deviations or the time being, it is respected to some the lattice points.

And these lattice points may be to some extend displaced or may not be there some lattice points, particular ions, may not be there are in the right place, so these are called the defects in crystals or defects in crystalline solids. There are different category of defects; today primarily will be discussing about what we called the point defects, point defects means these defects are very basically restricted to lattice points, they are kind of geo dimensional defects. So, they are primarily restricted to the lattice either individual one lattice points or couple of different types of lattice points, so that is what we are going to discuss today.

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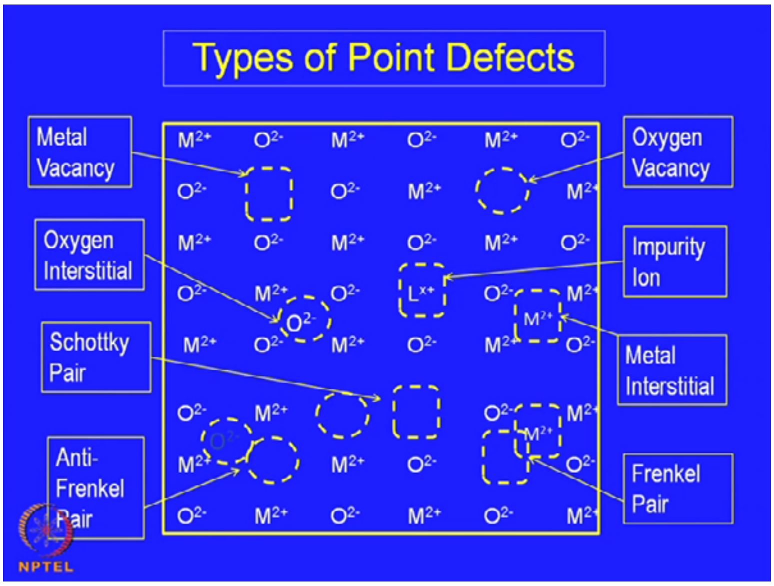

Types of Point Defects

Metal Vacancy

Oxygen Interstitial

Schottky Pair

Anti-Frenkel Pair

Oxygen Vacancy

Impurity Ion

Metal Interstitial

Frenkel Pair

The defects and this defect are really called point defects, because they are restricted to points, lattice points. Now, in this diagram it is little complicated diagram, it will be busy diagram, but very simple in a since once we know the principal, basically we have a lattice, a oxide M O type oxides, metal oxides, a diablo metal oxide; M is (()), oxygen is any way hydrogen. So, we have a array of such diablo ions, alternant ions, metals and oxygen, which is basically a cubic arrangement kind, and in these lattice points there may be different kind of distortions or deviations.

We have listed quite a few of them for example, this is basically the lattice M, O alternate sites of ideally, alternate sites of metal and oxygen of there in any direction. The first one is what we called the oxygen vacancy, vacancy is nothing but a missing lattice, medic missing meeting missing lattice point and in the oxygen sub lattice, so this is the missing oxygen. So ideally, they should have been oxygen ion, but for some reason rather that oxygen is missing and therefore, that defect is designated and oxygen vacancy.

Similarly, correspondingly we had metal vacancy, when a particular metal ion is missing, where exactly it is gone, is not at all concerned, but when we are looking at this particular area of the lattice, we have seen that that particular metal ion is not available, or is missing from that particular site. So, in addition with the vacancies, we can have interstitials that means, for example decision oxygen interstitial, oxygen ion should not have been there, but an additional oxygen ion has been introduced in between the normal lattice sites.

So, this is an extra oxygen ion in an abnormal site, and it is interstitially position between the normal lattice points, and that is why it is called oxygen interstitial. So, this is an oxygen interstitial point defect, oxygen interstitial. Similarly, we can have metal interstitial, so just like oxygen you have a metal in an abnormal site which is not suppose to be occupied by metal, but they will interstitial site it giving occupied by metal. So, it is a the position is not a regular position, that it is a defect and defect so for as the crystal lattice is concern.

We can have impurity ion, it can form a some impurity, very minute quantity of a impurity may be added or either intestinally added or accidentally it is there. So, that here of course, the impurity can go both into the interstitial site, as well as substitution site, because the we know about solid solutions where both substitutional interstitial solutions are possible.

But in this particular case we have just consider substitutional solid solution, and so the L, L is a for an atom or for an ion, metal ion which has substituted in the original metal M 2 plus. Now, here it has been written as x plus, now it not necessarily this for an atom can have the same valance as that of the original metal M 2 plus, instead of 2 plus it may be less than 2, it may more than 2, and that is the reason I written them as L x plus. So, normally if the different atom or the different (()) is there, we call it as (()) substitution, so it is that the terminology, but for our purpose it is only an impurity ion, so that is also a defects a defect in that crystal.

In addition, you can have three different kinds of pairs, pairs of defects, these are all single defects either in the oxygen sub lattice or in the metal, either the metal interstitial or metal vacancy, oxygen interstitial or oxygen vacancy. Now, we have, we are talking about not a single defect, but a pair of defects; the very first one is here in the middle, it is called Schottky pair where both oxygen is missing as well as metal is missing. So, they are forming as a pair together, earlier we have talked about single point defects or singular point defects, here is a pair of point defect they come together and that is how we call it as Schottky pair.

So, it is a metal vacancy and oxygen vacancy both the sub lattice has vacancies in that, and they come closer to charger impact they move also, if they want to move in the lattice they normally move in pairs. Then we have another type of defect called Frenkel pair, Frenkel pair is in the primarily in the metal sub lattice; so there is a metal vacancy and metal interstitial. So, this is a metal vacancy and that is a metal interstitial, that is one is the metal interstitial just like earlier, we have consider interstitial. So, but only difference here is we are coming in pairs, both of them have been form together and they will form in equal numbers.

So, that is called Frenkel pair and the last one is called the Anti-Frenkel pair, Anti-Frenkel pair is nothing but, here it is in the metal sub, involve in the metal ions, metal vacancy and metal interstitial. Whereas, Anti-Frenkel pair means oxygen interstitial and oxygen vacancy off course, this is not that common, but even then it is possible and there are cases, and there are situations when Anti-Frenkel pair is also available in the solids. So, these are the differed kind of possible point defects, which can occur in some of the ideal crystal of any type, either it is a high temperature material or low temperature material it does not matter, these kind of things do occur all the time.

It is in fact thermodynamically, it is a stable situation to have defects in solids, non of the no solids it is actually perfect, all solids will have some kind of defects all the time and they have a very important role to play. So, for as property for the materials are concern, just like the crystals structure important role, the defects of the crystal and defect also have a very important role to account for different properties.

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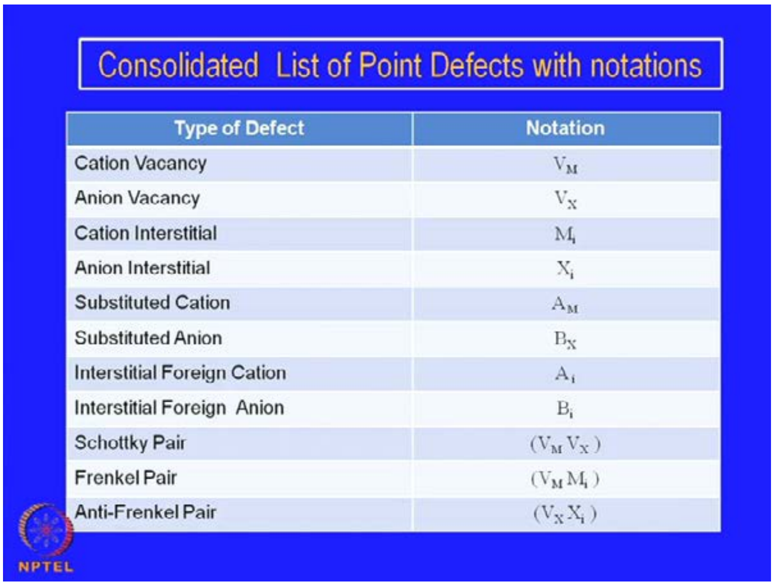

Consolidated List of Point Defects with notations

Type of Defect	Notation
Cation Vacancy	V_M
Anion Vacancy	V_X
Cation Interstitial	M_i
Anion Interstitial	X_i
Substituted Cation	A_M
Substituted Anion	B_X
Interstitial Foreign Cation	A_i
Interstitial Foreign Anion	B_i
Schottky Pair	$(V_M V_X)$
Frenkel Pair	$(V_M M_i)$
Anti-Frenkel Pair	$(V_X X_i)$

All these defects are normally denoted by some notation and these are standard notations, throughout this discussions will be using them. So, let us have a look at the these notations, these are like this cation vacancy, this is denoted by V M that is vacancy subscripts is the site; so B M is the notation for the cation vacancy. So, any vacancy actually is denoted by V, so either it is V M or the next one the anion vacancy is V X, so it is the V X and V M, cation interstitial in case of cation interstitial, it is not i M and with analogy to vacancy, it is not interstitial i M, but it is in M i, it is the reverse.

So, it is the interstitial i at the metal side, so that is how it is M i and not i M and anion interstitial X i same as that are, analogue it is to M I, the anion interstitial is X i. Substituted cation that is basically we have talked about the substituted solid solution of course, the notation has been use differently here, they are the atom was L, but here it has taken as A. So, A goes to the M side, in fact as per the earlier diagram it should have been returned as L M, but after and some reason it has been written as A M, substituted anion, if it is anion is at is a substitution just like metal is getting substituted.

So, A goes and sits M side that is why A M, if B goes to the x site that is the oxygen site, it would be B x, interstitial foreign cat ion that has not been considered in the earlier diagram. But, just like a substitution foreign atom, foreign cation, interstitial foreign cation can also coming in principle that is A i, interstitial foreign anion is B i and then we have sub Schottky pair it is a pair of vacancies. So, it is a V M and V X, Frenkel pair it is reversed, it is different not both of them are vacancies, one is vacancy, another is an interstitial. And both involving M or the metal, and that is why it is V M metal vacancy and metal interstitial, that is Frenkel pair and Anti-Frenkel pair.

Similarly, in the x sub x oxygen sub lattice, in fact there is been a little at mismatch between this, and the diagram x you have not considered the x, x actually oxygen and A M of course, image as A M and A instead of L, we have used a here. So, Anti -Frenkel pair is V X or B, you can call it B o and X o I, X is actually oxygen, so that is the, those are the notations used for different kind of point, defects, we have discussed just now.

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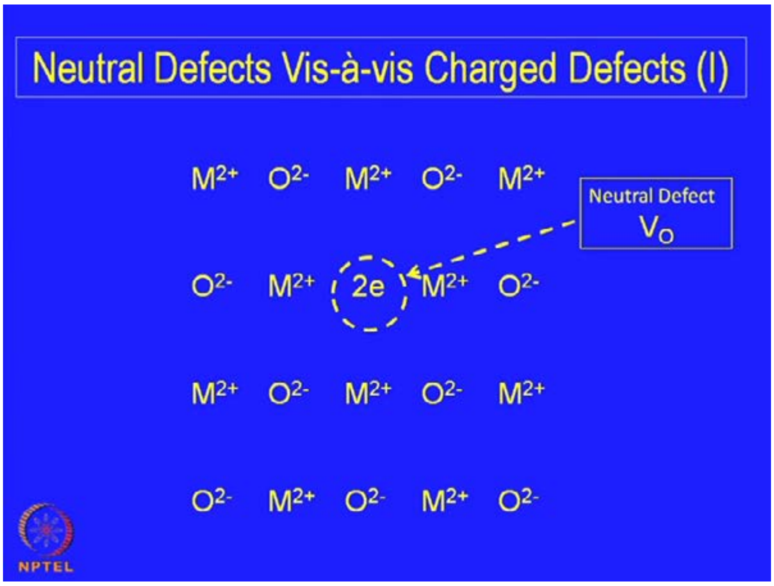
Neutral Defects Vis-à-vis Charged Defects (I)

And these notations should be quite important and useful for all later discussion, when we have since we are talking about ionic solids oxide. So, we have ions, these are not metals the metals also do you have similar kind of situations, only thing they do not have it is charge specious, they are neutral specious. So, they are things are slightly different, but when you are talking about ionic splices or ionic solids, we are considering two different ions and therefore, we have to, we have a situation when they can be either charge or neutral.

So, just like the metal can be are metal ions or charged ions or oxygen ions, is a charged ion other normal metal, a metal atom is not at all charged ion. So, similarly a defect in this case since, you are talking about a ionic lattice, so there is a possibility of what we call they charged defect and neutral defects. What is the concept, here we are talking about in oxygen vacancy, once again this is the lattice and here oxygen was supposed to be there, and oxygen has be removed, so it is created oxygen vacancy. The question is whether it is a neutral oxygen vacancy or a charged oxygen vacancy, and what is the difference, so for the charger distribution is consider.

Now, the oxygen and it is charge there are two parameters, two components one is the mass component another charge component. So, when oxygen is removed from this, it has been is no longer there in that site; so the mass has been removed, but the charge may not have been removed. In fact, the oxygen, oxygen comes out the lattice, it will come out in the form of an atom, it do not come out in the form of an ion, only within the lattice it will having a charge component. So, when it is coming out of the lattice, then it may release that two electrons associated with it, at the site where it was originally CD or it was supposed to be there.

So, this is the two charges, the two electronic chargers which is been left behind even the oxygen has come out in the form of an atom, because the charge, it cannot take charge and come out on its surface (()) in the atmosphere. So, when this to charges are left behind at the particular site where is this ion was supposed to be there, then this vacancy, this vacancy is a neutral defect means it does not disturbed, it has changed the mass distribution the mass is not there, but the charges still there. So, it was 2 plus a 2 minus originally still it is 2 minus, so in that particular site two electrons are floating; and if that two floating electrons are sitting in that place, then the vacancy that is created is called neutral defect.

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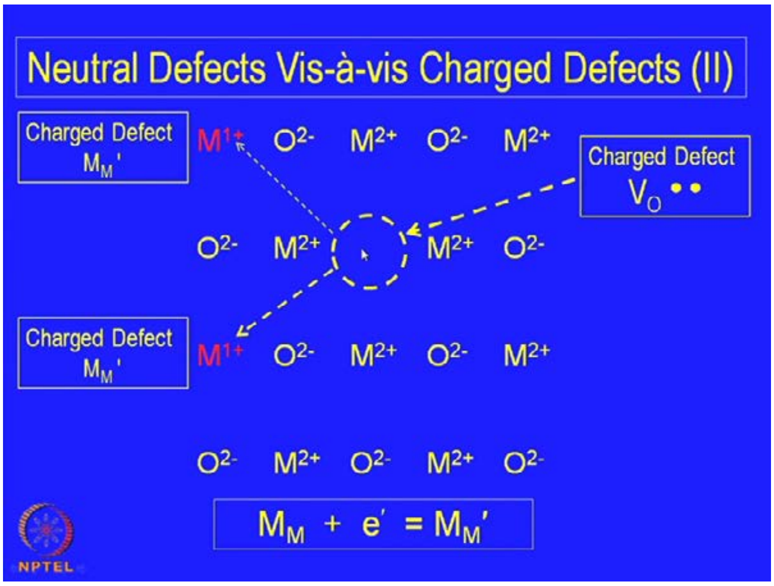

Neutral Defects Vis-à-vis Charged Defects (II)

Charged Defect M_M'

Charged Defect $V_O^{\bullet\bullet}$

Charged Defect M_M'

$M_M + e' = M_M'$

Then this is a situation when it is charged defect, these two electrons are no longer there, two electrons has gone away or seated away from this particular site, but it may be within the solid, it has not left the solid, it has not left the crystal, but it has left that particular site. So, when that particular site is no longer having that two negative charges it is absolutely vacant, then the charge distribution has changed at that point this vacancy, this particular vacancy now will be called a charge defect of having a two dots.

Two dots means an effective positive charge, a deficient of two native charger it was having two charges negative charges, oxygen ion in that form of an oxygen ion, you having to negative charges that negative charges at left that particular site; so far this site is consider, this is a effectively positively charge, double positive charge.

And that for a change it is not actual charge, it is really not 2 plus it is the deficiency just like holes, in case of semiconductor physics, this is effective positive charges and that is why it is not written as plus. We actually written in the form of at dots that the convection used by (( )) chemistry are defect chemistry, but what happen is these to electronic charges, 2 electronics were there 2 electronics has been released the system. So, these electrons has not left the site, a left the solid, so it is there in the solid, but may not be exactly in the same location.

So, this what is happen it has donated one electron to this metal ion and another may be to another metal ion, that is most likely not normally, two electrons goes to this a metal side. That depends of course, what is the variable valancy it has, so consequent that this as release two electrons to the system and when in as to there in 2 plus the M becomes in plus 1. Instead of plus 2 it will become plus 1, because one negative charge has been added and that particular metal is capable of changing its valancy from plus 2 to plus 1.

So, if that is the situation, then this kind of charged and neutral defective do occur, so one of the condition is the metal present here must have the variable valancy and it must be able to accept thus electron. So, otherwise that electron will be over in a around, and it may be energetically less favorable, so what happens the charge, this also becomes the charge defect. This is a charge defect, and consequently this is also a charge defect, it is a defect in the sense it is no longer in 2 plus it is M plus and this is also a M plus. So, this is another kind of defect which is created by M at the M site, but not its a regular charge, it does one less positive charge, one less positive charge it is suppose to be 2 plus, now it has only 1 plus.

So, they are the deficient one positive charge, so effectively it is a natively charge which is now, so in respect of the original lattice should it is created two different kind of charge M at the M site within one negative charge here, and another negative charge there. So, the reaction is like this change or the changeover is like this, M at M site means, M at M site, M subscript M means M at M site which mean two double charges are divalent that is the normal, that is the regular and that is neutral. And to that one electron had been added from released by the oxygen or creation of the vacancy, so creation of oxygen vacancy has there is two electrons, and these two electrons had been accepted by two different patterns present, original lattice.

And they have changed their valancy from 2 plus 2 1 plus and that can be written that M at M site with one less positive charge, so it is less positive charge can also be written as negative charge, effective negative charge. So, effective negative charge here is actually the prime, effective positive charge is denoted by dots for as effective negative charge is denoted by prime that is also another convention used in the defective chemistry.

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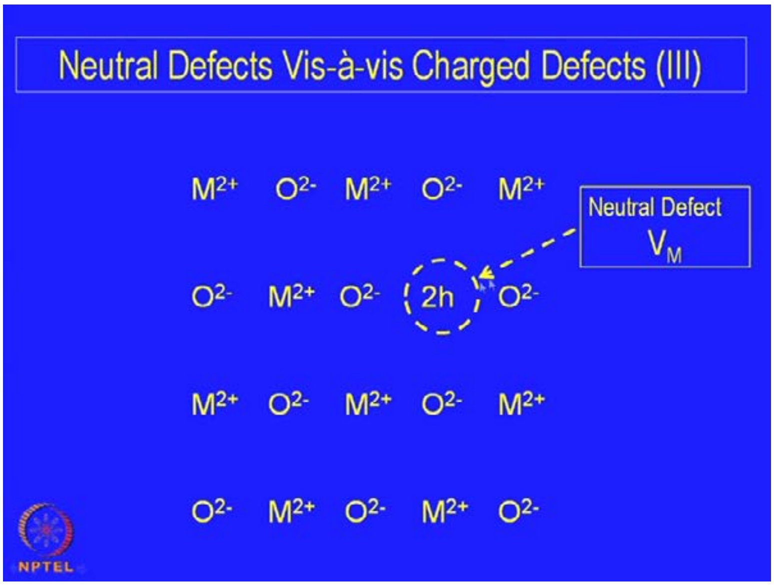

Neutral Defects Vis-à-vis Charged Defects (III)

M^{2+} O^{2-} M^{2+} O^{2-} M^{2+}
O^{2-} M^{2+} O^{2-} 2h O^{2-}
M^{2+} O^{2-} M^{2+} O^{2-} M^{2+}
O^{2-} M^{2+} O^{2-} M^{2+} O^{2-}

Neutral Defect
V_M

In the same manner it can be the other way also a vacancy, metal vacancy, neutral vacancy, this is a neutral vacancy, and it has left behind here two holes from the concept of semiconductor physics. We have electrons and holes basically, holes and nothing but, the deficiency of electrons, so here h means the hole has been is positively charge hole if the deficiency of electrons. So, two have been left behind that means two positive charges and neutral vacancy has been created.

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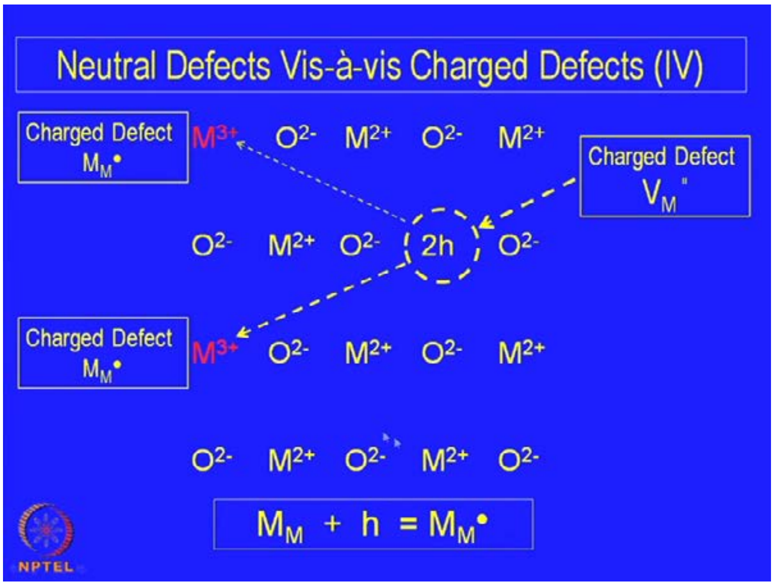

Neutral Defects Vis-à-vis Charged Defects (IV)

Charged Defect
$M_M^{\bullet}$

M^{3+} O^{2-} M^{2+} O^{2-} M^{2+}
O^{2-} M^{2+} O^{2-} 2h O^{2-}
M^{3+} O^{2-} M^{2+} O^{2-} M^{2+}
O^{2-} M^{2+} O^{2-} M^{2+} O^{2-}

Charged Defect
V_M''

Charged Defect
$M_M^{\bullet}$

$M_M + h = M_M^{\bullet}$

For exactly the same manner this two holes has now gone back to two different metals, so once that hole is no longer there at that particular site, the charge distribution will be changed. So, this is become effectively negatively charge plus, and this is the place where metal supposed to be there, so it is created by a oxygen metal vacancy with a 2 double prime with a 2 double prime, which means a negative effective negative charge, prime means effective negative charge.

So, this is effectively a negative charge species has been created here, and consequently to maintain the charge neutrality 2 holes have been added to the metal, now all this things, it is not getting added to oxygen it cannot, because oxygen has very stable diablo configuration. So, oxygen cannot be 1 plus or 3 plus or 1 minus 3 minus on the other metal can be, can change the variable valence, and only when such thing happens then the creation of the defect of becomes easier. If metal cannot change its valence then vacancy creation will become less energetically (()), so it can may not form the vacancy or may not from the particulate defect.

So, once again here it is day reverse is happening here, M 2 plus will have changing to M 3 plus, again there should be a possibility that the particular metal can change its valancy from 2 plus 3 plus. So, that happens then, they have against charge defect what are the different nature, M M not prime, but M M dot that means, an extra positive charge will be added here, earlier next a negative charge was added. So, the valancy was decreasing here, the valancy has increased and by adding an extra hole, and the reaction is written here in M plus h is M M dot which is again effectively positive charge.

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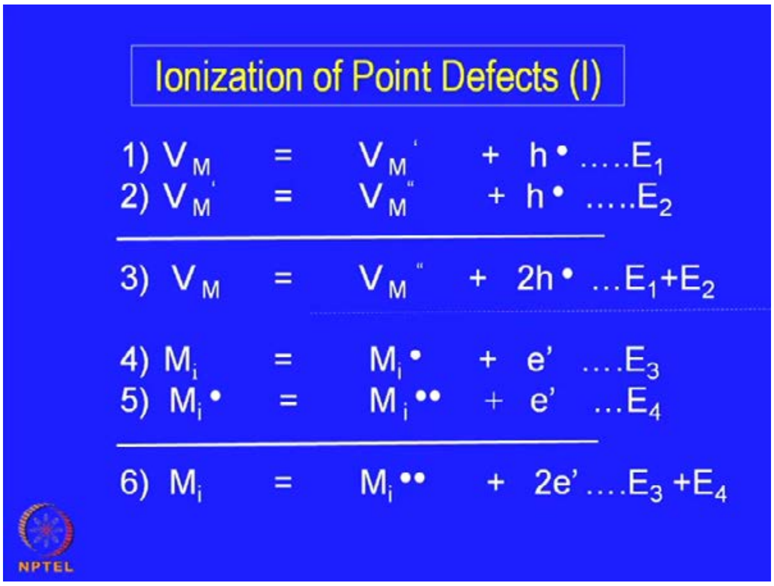

Ionization of Point Defects (I)

1) $V_M = V_M' + h^\bullet \ldots\ldots E_1$
2) $V_M' = V_M'' + h^\bullet \ldots\ldots E_2$

3) $V_M = V_M'' + 2h^\bullet \ldots E_1+E_2$

4) $M_i = M_i^\bullet + e' \ldots.E_3$
5) $M_i^\bullet = M_i^{\bullet\bullet} + e' \ldots E_4$

6) $M_i = M_i^{\bullet\bullet} + 2e' \ldots.E_3 + E_4$

So since you are talking about neutral defect and charged defects, so there is possibility ionization. So, that is what really happens, there are four situation we have discussed and all these things, no you are discuss actually two different situations, but in the early diagram we are talking about either, if say either two negative charges effective negative charges or two positive charges which was earlier in the oxygen vacancy. Oxygen vacancy was two positive charges, two effective positive charges where has here two negative charges, now it not necessarily mean that all the time it will be double charged or it may get double charged through a step, step wise process, and that is what is written here.

Initially M at M site will change over to M M prime, this belongs to lower and h dot is created and this ionization is there be a some ionization energy in involved, it may V, so instead of so instead of getting ionized simultaneously to both of them simultaneously, it can goes step by step manner one of together. So, that is shown there, there ionized can take place in a stepwise version and so each involves certain amount of energy, and that is what for this reaction the ionized energy this one and for the next one or next step E 2. And overall this is the summation of that this to and the overall energy E 1 plus E 2; same way of the metal interstitial; you can have this kind of ionization, and it may be E 3 and E 4, so by is adding together one metal goes ionization double dot and plus 2 electrons, so realizes to electrons, and the total energy involved is E 3 plus E 4, same thing happened the oxygen also.

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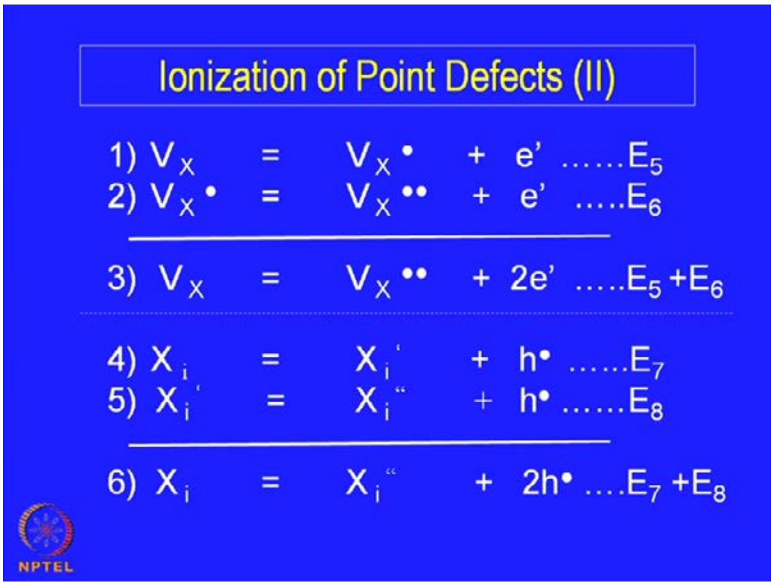

Ionization of Point Defects (II)

1) $V_X = V_X^{\bullet} + e'$ ……E_5

2) $V_X^{\bullet} = V_X^{\bullet\bullet} + e'$ …..E_6

3) $V_X = V_X^{\bullet\bullet} + 2e'$ …..$E_5 + E_6$

4) $X_i = X_i' + h^{\bullet}$ ……E_7

5) $X_i' = X_i'' + h^{\bullet}$ ……E_8

6) $X_i = X_i'' + 2h^{\bullet}$ ….$E_7 + E_8$

So, that was your metal sub lattice and here the oxygen sub lattice, the oxygen defects can also get ionized in this manner, either it will to realize some electron or holes. If you can go to through these things; it is quite clear, so instead of a said ionization, both the ionization taking plus simultaneously it will take place, normally it will take one after the other. And each one of them will in all certain amount of energy either realize of energy or acceptance of the energy.

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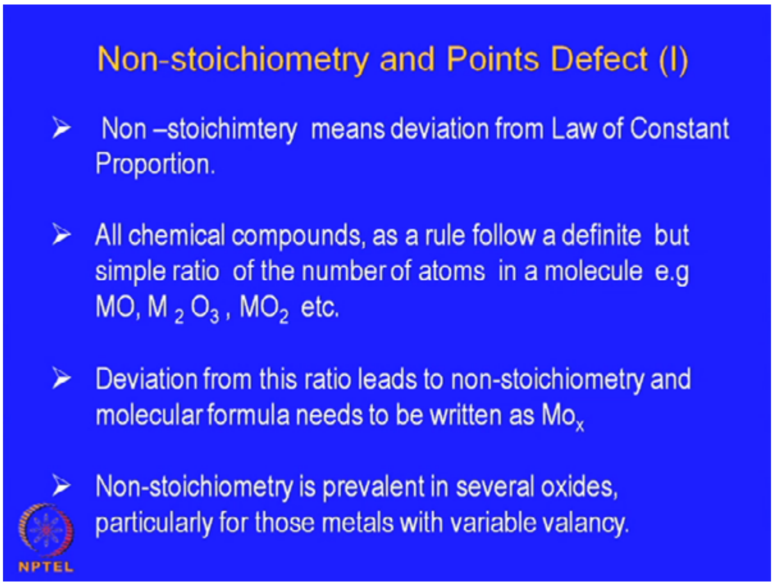

Non-stoichiometry and Points Defect (I)

- Non –stoichimtery means deviation from Law of Constant Proportion.
- All chemical compounds, as a rule follow a definite but simple ratio of the number of atoms in a molecule e.g MO, M_2O_3, MO_2 etc.
- Deviation from this ratio leads to non-stoichiometry and molecular formula needs to be written as Mo_x
- Non-stoichiometry is prevalent in several oxides, particularly for those metals with variable valancy.

Now, if this we cannot to another concept this is actually the consequence of defects, non-stoichiometry and point defect, so there is a strong co-relationship between non-stoichiometry and the point defects. What we really mean by non-stoichiometry basically, non-stoichiometry means deviation from law of constant proportion, for all compounds, ionic compounds in particular there is always a definite ratio in which the metal and the oxygen are bounded together. So, that is normally not deviated, but whenever the defects that deviation do take plus, all chemical compounds as a rule follow a definite, but simple ratio of the number of atoms in a molecule examples MO, M 2 O 3, MO 2 etcetera.

That means, metal oxygen ratio is a simple integral multiple or a factor, so either is 1 is to 1, 2 is to 3 or 1 is to 2 etcetera, etcetera. So, when that is deviate that is what we called the non-stoichiometry instead of 1 is to 1 it may be slightly some fraction, some fraction of 1 and that means that they are some defects in it. And that, because of the defect the ratio has been changed, deviation from this ratio leads to non-stoichiometry, and molecular formula needs to be written as M x, M instead of MO 1 is to 1, it has be return has M x, which means that actually denotes what is the exact ratio, between the cation and anion, it need not be an integer all the time.

And the the result is of course, the reason for this is basically the point defects, because the point defects it is present, if it is present in one particular sub lattice either in oxygen or the metal obviously, it will disturbed the ratio until, unless they are pairs formation. That it be Schottky pairs or Frenkel pairs or Anti-Frenkel pairs, if they form in pairs then of course, this ratio will not change, get changed and that is the reason these ratio, these pair kind of defects are known as stoichiometry defects. The others singular defects are called the non-stoichiometry defects and that is because, the cause non stoichiometry defect are the result in non-stoichiometry of the compounds.

Non-stoichiometry is prevalent in several oxides, particularly for those metals with variable valancy, as a mention whenever there is a ionization of defects we need a variable valancy metal, metal to represent there. So, variable valancy metals are the oxides, thereof do have a tendency to become non-stoichiometry.

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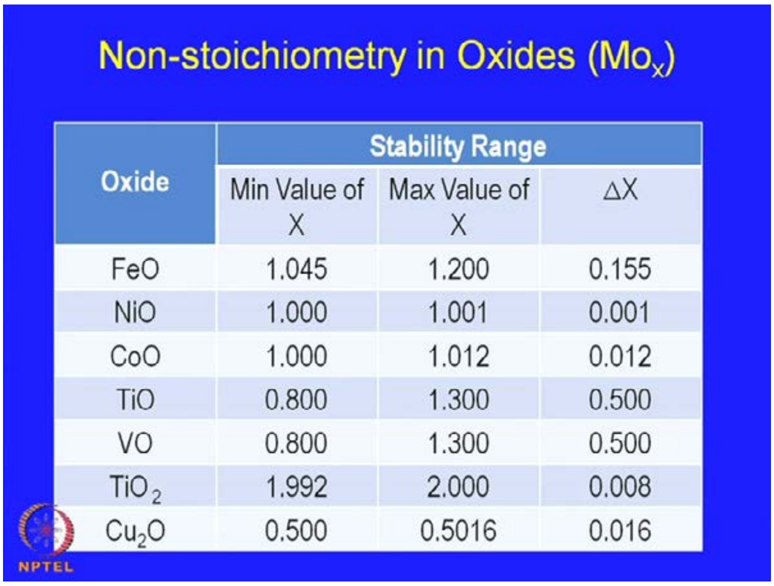

Non-stoichiometry in Oxides (Mo_x)

Oxide	Stability Range		
	Min Value of X	Max Value of X	ΔX
FeO	1.045	1.200	0.155
NiO	1.000	1.001	0.001
CoO	1.000	1.012	0.012
TiO	0.800	1.300	0.500
VO	0.800	1.300	0.500
TiO_2	1.992	2.000	0.008
Cu_2O	0.500	0.5016	0.016

Now, these are some examples what kind of non stoichiometry one can expect, in different oxides and as you can see all the oxides here basically, they are consumed metal oxide in that series. Because, they have the variable number of d electrons, and incomplete d cell, and that is why the ionization is easier. So that for they have a variable valiancy as well iron oxide FeO; you can see all though it the formula is 1 is to 1, actually, it is not 1 is to 1, if you take x Fe x, FeO x, FeO x, the x value changes of the minimum value of 1.045 to 1.2 that means, the amount of x is much larger than one 1.

Normally it should be as for the formula it should be 1, but actual practice it may add it may be adding from 1.054, a 045 2.2 which is required a large deviation. So, all the time all the time, it is the more than 1, which means which means x is more than 1 that means, oxygen is more than 1, so iron or the metal is less than 1. So, metal it is actually a metal deficient oxide, it is called metal deficient oxide, because oxygen is more or sometimes is also refer to as oxygen x x oxide. So, most of these, some of these transition metal oxides either metal excess or metal deficient, oxides normal in the form, nickel oxide, it is sometime it is 1, but many time it is a more than 1, but the deviation is little less its only 0.001.

Cobalt oxide the same manner like nickel oxide, and yes exactly like nickel oxide the deviation is also slightly more, but not too large 0.012. Titanium oxide is little different one can see here titanium oxide means is to 1 is to 1, so x is suppose to be one instead of that the x actually barriers from 0.8 to 1.3, so it can be less than 1 or it can be more than 1 also. So, that that is another situation where the non-stoichiometry changes from its middle position, or the accurate position or correct ratio in both ways; vanadium oxide is also exactly seen as titanium oxide, TiO, TiO 2 is slight is different it is suppose to be 1 is to 2.

So, only in some cases it is really two, but otherwise it is less, it is less than 2, 1.992 which is value low Cu 2 O, 0.5, 1 2 is to 1 actually, so instead of 0.5 it is 0.5016. So, basically this table means that there are large number of oxides, where this particular ratio is not maintain and normally of course, it depends on the nature of preparation technique, the history. And under what condition it has been equilibrator, what kind of (( )), whether what kind of oxygen atmosphere was there, whether it is reducing atmosphere or oxides is oxidizing atmosphere, all these things do depend, do control the exact value of x, but they have a tendency to deviate from it is original ratio or ideal ratio.

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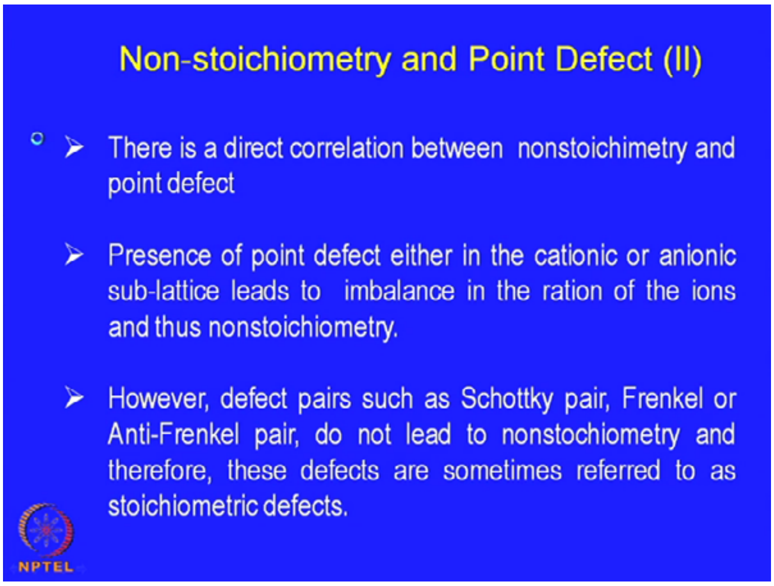

Non-stoichiometry and Point Defect (II)

- There is a direct correlation between nonstoichimetry and point defect
- Presence of point defect either in the cationic or anionic sub-lattice leads to imbalance in the ration of the ions and thus nonstoichiometry.
- However, defect pairs such as Schottky pair, Frenkel or Anti-Frenkel pair, do not lead to nonstochiometry and therefore, these defects are sometimes referred to as stoichiometric defects.

There is a strong correlation, direct correlation between non-stoichiometry and point defect it is quite obvious, presence of point defect either in the cationic or anionic sub lattice leads to imbalance in the ratio of the ions and thus non-stoichiometry. So, it is the point defect both in the cationic or anionic sub lattice, leads to imbalance in the ratio of the ions and thus the non-stoichiometry.

So, non-stoichiometry is nothing but the, basic the deviation from the expected ratio or the formula you see however, defect pairs such as Schottky pairs as I have already motioned. Frenkel or Anti-Frenkel pair do not lead non-stoichiometry and therefore, these defects are sometimes referred to as stoichiometry defects, that are also quite understandable, because they appearing pairs, so, they do not change particular sub lattice.

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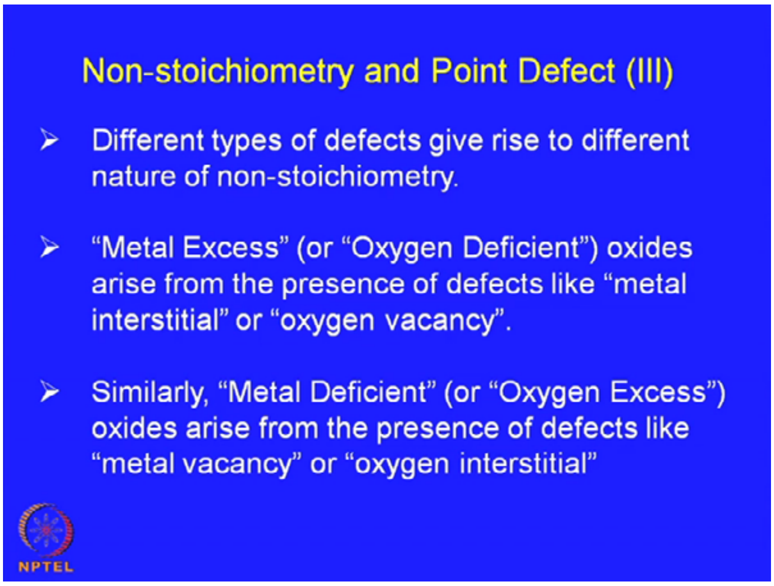

Non-stoichiometry and Point Defect (III)

- Different types of defects give rise to different nature of non-stoichiometry.
- “Metal Excess” (or “Oxygen Deficient”) oxides arise from the presence of defects like “metal interstitial” or “oxygen vacancy”.
- Similarly, “Metal Deficient” (or “Oxygen Excess”) oxides arise from the presence of defects like “metal vacancy” or “oxygen interstitial”

So, they change uniformly both the sub lattices and therefore, the ratio remains same, different types of defects give rise to different nature of non-stoichiometry, that also briefly I mentioned metal excess or oxygen deficient; oxides arise from the presence of defects like metal interstitial or oxygen vacancy. So, it is basically a ratio, so if it is one is metal excess, one can also express the same thing as oxygen deficient, and once again these can arise from both the parameters like metal interstitial or oxygen vacancy.

Oxide metal excess means, there can be metal interstitial additional metal, ions, introduced in to the inside the lattice or if oxygen vacancy has been created also that will lead to same effect. Similarly, metal deficient or oxygen excess reverse of that oxides arise from the presence of defects like, metal vacancy and oxygen interstitials, so these are very I think its quite common or common sense will be good enough to understand. Now, this background let us try to see whether, you can write some equations, defect equations and defect reactions, just like metal chemical species are denoted by certain formula certain symbols.

Here also we have already mentioned that the defects have their own symbols, and they can we put together to write some chemical reactions, and depending on what kind of physically reactions actually taking place, so we can write on papers how the reactions it taking place which is moving here, and which is reacting with what. So, just like chemical reaction one can write reactions, defect reactions and in the same manor we can have equilibrium constants and so on.

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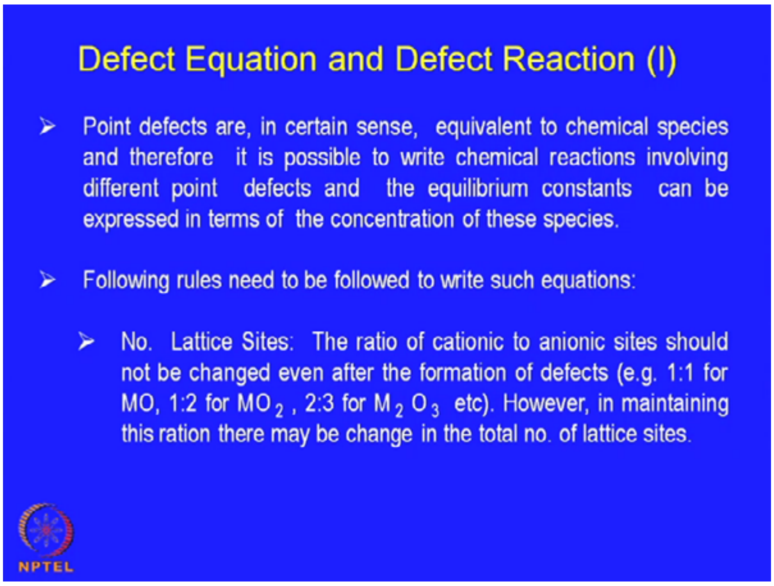

Defect Equation and Defect Reaction (I)

- Point defects are, in certain sense, equivalent to chemical species and therefore it is possible to write chemical reactions involving different point defects and the equilibrium constants can be expressed in terms of the concentration of these species.
- Following rules need to be followed to write such equations:
  - No. Lattice Sites: The ratio of cationic to anionic sites should not be changed even after the formation of defects (e.g. 1:1 for MO, 1:2 for MO_2 , 2:3 for M_2O_3 etc). However, in maintaining this ration there may be change in the total no. of lattice sites.

So, defect equation and defect reactions, writing such things you have to follow certain principles, these are some things are listed here point defects are in certain sense equivalent to chemical species. And therefore, it is possible to write chemical reactions involving different point defects, and the equilibrium constants can be expressed in terms of concentration of these defects, of these species right, just like you can have equilibrium constant.

In terms of the concentration term here also one can use the similar principal, following rules need to be followed to write such equations, 3 or 4 things have to be remember, lattice no lattice sites, number of lattice sites, I think this is no lattice sites number of lattice sites should be let me change it. Number of lattice sites the ratio of cationic to anionic sites should not be changed even after the formation of defects, as per example 1 is to 1 or 1 is to 2 and 2 is to 3, these defects, these ratio must be maintain.

Even if some of the lattice sites missing, but the ratio cannot be change, because even if the vacancy is created the particular element may be missing from there, but the lattice site is not going to change. So, lattice site is there and we have to say that it is vacancy site however, in maintaining this ratio there are may be changes in the total number of lattice sites. That means, the total number whether is 60 or 600 or 700 whatever you take that should not change, the total number should not change, but the ratio may change.

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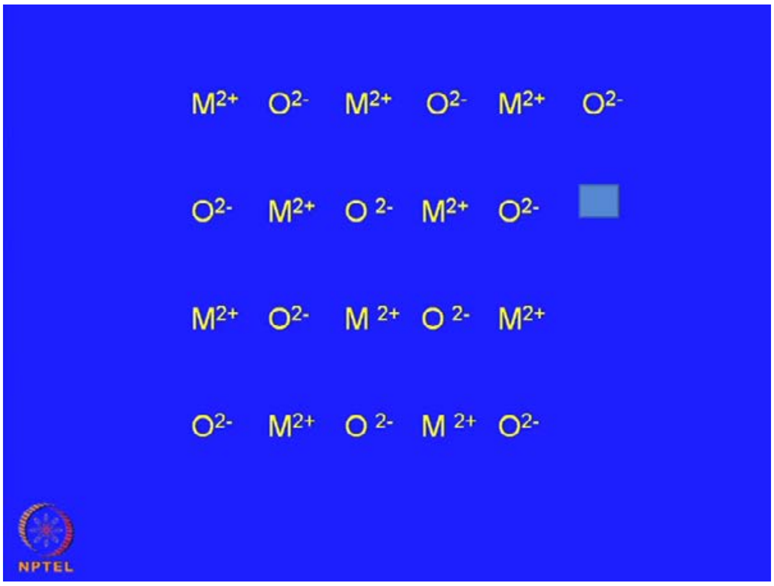

M^{2+} O^{2-} M^{2+} O^{2-} M^{2+} O^{2-}

O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} ■

M^{2+} O^{2-} M^{2+} O^{2-} M^{2+}

O^{2-} M^{2+} O^{2-} M^{2+} O^{2-}

This is what actually understood by that process that means, you see if you are making a begins here, actually the material is not there M 2 plus, suppose to be there it is not there, but the lattice site is there, and that is the reason why you talking about a vacancy. The other one lattice site is not there, and that is why this is not a vacancy, this place is not a vacancy this is a vacancy provided that lattice site, that ratio is equal to be maintained and that site has to be considered.

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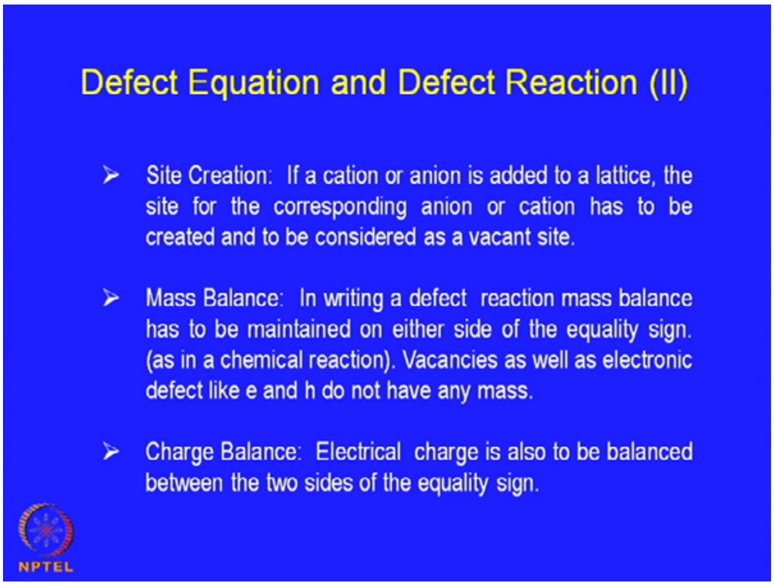

Defect Equation and Defect Reaction (II)

- Site Creation: If a cation or anion is added to a lattice, the site for the corresponding anion or cation has to be created and to be considered as a vacant site.
- Mass Balance: In writing a defect reaction mass balance has to be maintained on either side of the equality sign. (as in a chemical reaction). Vacancies as well as electronic defect like e and h do not have any mass.
- Charge Balance: Electrical charge is also to be balanced between the two sides of the equality sign.

Defect equation and defect reaction that is what the title we are discussing site creation, if a cation or anion is added to a lattice, the site for the corresponding anion or cation has to be created and to be considered as a vacant site. So, going back to that earlier diagram, let us say we have initially we have these, this was the boundary the solid sorry, this is the boundary, this is the boundary of the solid. These were not there, this oxygen was not there and we have from outside we have added that oxygen, so we have created lattice site, in the anion lattice site will be created.

As soon as the anion lattice site is created; a cation lattice site also have to be considered, because this is 1 is to 1, so one you add this oxygen; this as if this lattice site is also there, we need not consider these two until unless sorry these two, until unless another metal or oxygen has been added there. However, we have to consider this one, 1 is to 1 that means, if you have created one oxygen lattice we have to create a metal lattice site also, but since the metal is actually not there in reality that has to be considered as a vacancy. So, that is the reason here it was originally 16 lattice sites, now you have added one lattice site 17th one, so immediately you have to add 18th one also and consider it as a vacancy.

So, that is the reason it says, the ratio must be same, a ratio must be maintained, but the total number may change earlier it was 16 total lattice site, now it is 18 that is possible that is allowed, but the ratio has to be there. Mass balance, just like in chemical equation mass balance also maintain in writing a defect reaction, mass balance has to be maintained on either side of the equality sign as in a chemical reaction. Vacancies as well as electronic defect like, electron and hole do not have any mass, vacancies do not have any mass, so that is obvious and we have to take into account that.

Charge balance electrical charge is also to be balanced, between the two sides of the equality sign. So, whenever you trying to write an equation just have a chemical reaction or chemical equation, we have to maintain both the mass balance as well as the charge balance, and that is really very important.

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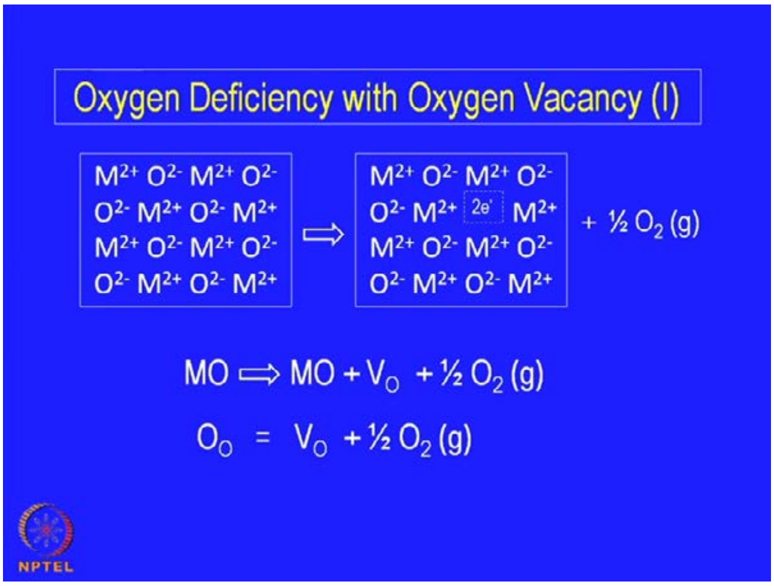

Oxygen Deficiency with Oxygen Vacancy (I)

M^{2+} O^{2-} M^{2+} O^{2-}
O^{2-} M^{2+} O^{2-} M^{2+}
M^{2+} O^{2-} M^{2+} O^{2-}
O^{2-} M^{2+} O^{2-} M^{2+}

$\Rightarrow$

M^{2+} O^{2-} M^{2+} O^{2-}
O^{2-} M^{2+} $2e'$ M^{2+}
M^{2+} O^{2-} M^{2+} O^{2-}
O^{2-} M^{2+} O^{2-} M^{2+}

$+ \frac{1}{2} O_2 (g)$

$$MO \Rightarrow MO + V_O + \tfrac{1}{2} O_2 (g)$$

$$O_O = V_O + \tfrac{1}{2} O_2 (g)$$

Now, you will be giving some diagrams, may not be able to explain each and everything in details, I think they are quite itself expander, I will consider few cases, in fact many of the possible cases for example, we are creating an oxygen vacancy, a oxygen deficiency with a oxygen vacancy right. In fact, when we are talking about non-stoichiometry oxides and there is a relation between non-stoichiometry and the defect, so there is a strong correlation, and quality between the non-stoichiometry and defect concentration.

So, all non-stoichiometry are actually the reserve talk creation of some defects; so we have two types of deviations, one is oxygen deficient or oxygen excess, which is equivalent oxygen deficiency is equivalent to metal excess, both are same basically. Because, we are only talking about the ratios, so oxygen deficient or oxygen excess or in other words metal vacancy metal deficient or metal excess, so these are the four possibilities. And all these possibilities can be again by two alternatives a oxygen vacancy can be created by oxygen sorry, oxygen deficiency can be created either by a oxygen vacancy, or it can be created by metal interstitial both of them are actually equivalent, so far as the ratio is concerned.

So, here one kind of situation where oxygen vacancy is being created by oxygen vacancy, so a oxygen vacancy this is a lattice, perfect lattice and then, some vacancy has been created here, a oxygen vacancy has been created, and two electron holes is been and two electrons is been left there, so a neutral defect has been created. And in fact, an oxygen has coming out, this oxygen must as come out in the form of a atom, it is atom because, it is in the coming out in the gas phase.

So, we look at it has half O 2, it is coming out as molecule, but actually one atom oxygen is coming out, so we write it as half O 2 that is a very common notation we use in defective equations. Here, you can see this is MO and then MO plus oxygen vacancy, this oxygen vacancy plus half O 2 g, it is quite simple that is how what is the reaction, but this is not a mass balance, this is not a mass balance. So, this is just showing what is happening, a perfect lattice is still a MO lattice is there, but all have together with some defects oxygen vacancy and releasing half oxygen.

Now, this can be written in this manor, oxygen at oxygen site we did not write the M, we can just write what is happening to the oxygen sub lattice, oxygen at oxygen site it was their and that basically you are looking at this site. So, originally it was oxygen at the oxygen site, now vacancy has been created, and together with that we are released one atom of oxygen that oxygen has gone out from the solid to the atmosphere. And therefore, this is a simplified the action, only involving the oxygen sub lattice there is no involvement of metal in this situation.

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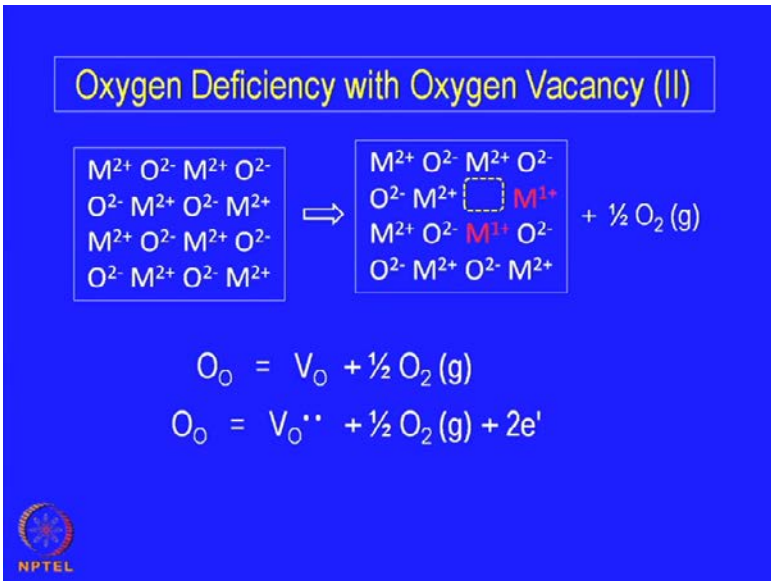

Oxygen Deficiency with Oxygen Vacancy (II)

$M^{2+}\ O^{2-}\ M^{2+}\ O^{2-}$
$O^{2-}\ M^{2+}\ O^{2-}\ M^{2+}$
$M^{2+}\ O^{2-}\ M^{2+}\ O^{2-}$
$O^{2-}\ M^{2+}\ O^{2-}\ M^{2+}$

$\Rightarrow$

$M^{2+}\ O^{2-}\ M^{2+}\ O^{2-}$
$O^{2-}\ M^{2+}\ \square\ M^{1+}$
$M^{2+}\ O^{2-}\ M^{1+}\ O^{2-}$
$O^{2-}\ M^{2+}\ O^{2-}\ M^{2+}$

$+ \frac{1}{2} O_2\,(g)$

$$O_O = V_O + \tfrac{1}{2} O_2\,(g)$$

$$O_O = V_O^{\bullet\bullet} + \tfrac{1}{2} O_2\,(g) + 2e'$$

Oxygen deficiency with oxygen vacancy same thing, now we are talking about a charge defect which was earlier a neutral defect electrons was released, are left behind at that particular site where is oxygen was originally there. Now, that electron has become mobile, electron has become free, it is not attached to that particular site, it is not relating to that particular site, it is more mobile and so add joining or any two metal sites, are metals has been accepted or metal has accepted those the electrons, and change it is valancy.

So, that is how what is happening here, so when it is we are talking about charge defects, this was the neutral defect situation and now when talking about charge defects, this has been happen, there is no question of charge on this site. However, this oxygen is balancing this oxygen, and that is why this oxygen, the regular oxygen, because on both sides mass balance as together as well as charge balance, these are the two very important aspects are writing defect equation. So, finally, charge also has been added there, so this has been charge this metal vacancy oxygen vacancy which was created, originally at the neutral defect and now it is been charge defect.

So, two positive charges, effective positive charges been created and two electrons have been released these two electrons have been free, when we write this kind of two electrons this electrons are free, and mobile electrons. Other electrons are the immobile electrons, there strongly attach to the (()), so they are not mobile, these mobile, these electrons which are been created by the different defects, they are (()) mobile, and that is why separately, and these electrons are actually a join here and there. One is gone there and another is gone there, these are the two electrons that is what we write here.

We do not write that this has already been accepted by the metals; this metal is not coming here, only the electrons are coming, because these electrons may not be sticking to this particular site, we will see later on. See the conductivity, how the conductivity behavior of this kind of metals, are non-stoichiometry oxides behave will find that, these electrons are not attached to this two metals only, after sometime they will go to their or they actually moving around, will be moving around from one place to another.

And that is call what we call hopping, hopping of electrons this can hop, because these are free electrons, these free electrons are almost equal or equivalent to the metallic free electrons are metals whatever we have metals, that is why it is has been written like that well.

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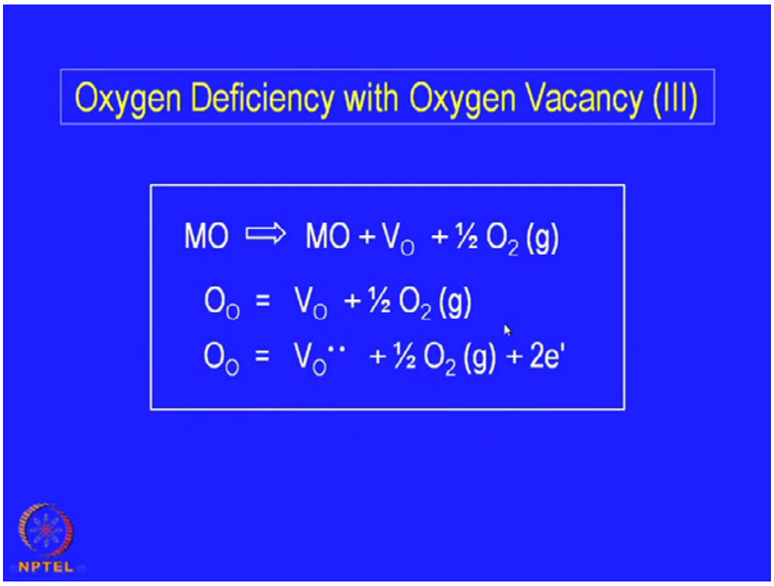

Oxygen Deficiency with Oxygen Vacancy (III)

$$MO \Rightarrow MO + V_O + ½ O_2 (g)$$

$$O_O = V_O + ½ O_2 (g)$$

$$O_O = V_O^{\bullet\bullet} + ½ O_2 (g) + 2e'$$

Finally, this is the overall reaction, we are writing this is a just to express what is happening the metal oxygen metal oxides perfect lattice, having still perfect lattice in addition oxygen vacancy has been created, and half oxygen has gone out in the form of atom. Living behind two electrons, then this metal site has been removed here and we simplify that equation like this, only oxygen just maintain the mass balance, here there is a one oxygen, and there is one oxygen here, that is why you have been maintain this oxygen, that means we are focusing on the oxygen lattice site and option vacancy.

So, this is of course, does not have a mass there is no charge here, all are neutral here a charge has been introduced, and there is two negative charges and then this is two effective positive charges, then utilize each other and this oxygen and this oxygen makes the mass balance. So, by that process, the whole reaction can be can be written in the form of very simple chemical reaction like, situation and we can also find out a equilibrium constant for this reaction, we will discuss that in the next class.

Thank you, Thank you for the attention.