Advanced Ceramics for Strategic Applications
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Lecture - 10
Two and Three Dimensional Defects

Welcome, today we are going to discuss in continuation to our earlier lectures, the defect in crystalline solids. Previously, we have already discussed two types of defects, two groups of defects impact; one was the point defects like vacancy in interstitials, Schottky defect, Frenkel defect and so on. And then, we have also discussed the one-dimensional defects that is or in other words line defects that like dislocations.

We have also discussed different types of dislocations and their importance in describing or understanding the mechanical behavior of solids. Today, we are going to discuss the third group of third or fourth group of defects, which we called two-dimensional and three-dimensional defects. Earlier I just mentioned, we have discussed the zero dimensional and one-dimensional defects, now we will be going to discuss the two and three dimensional defects.

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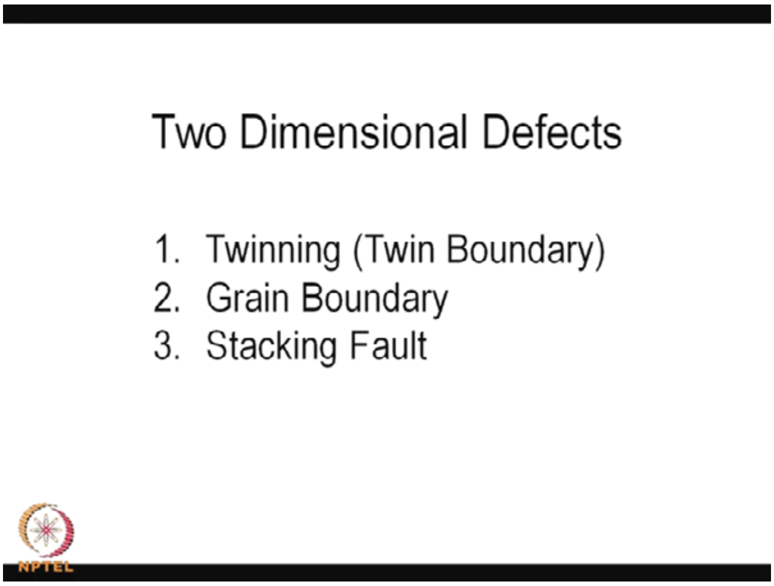

Two Dimensional Defects

1. Twinning (Twin Boundary)
2. Grain Boundary
3. Stacking Fault

So, we start with the two dimensional defects, there are three types of two-dimensional defects. And the first one is called the twinning, the process of twinning and by that process, we actually generate defects like twin boundary. Second one is a grain boundary and the third one is stacking faults, sometimes they are also called surface defects because basically, two-dimensional forms of surface.

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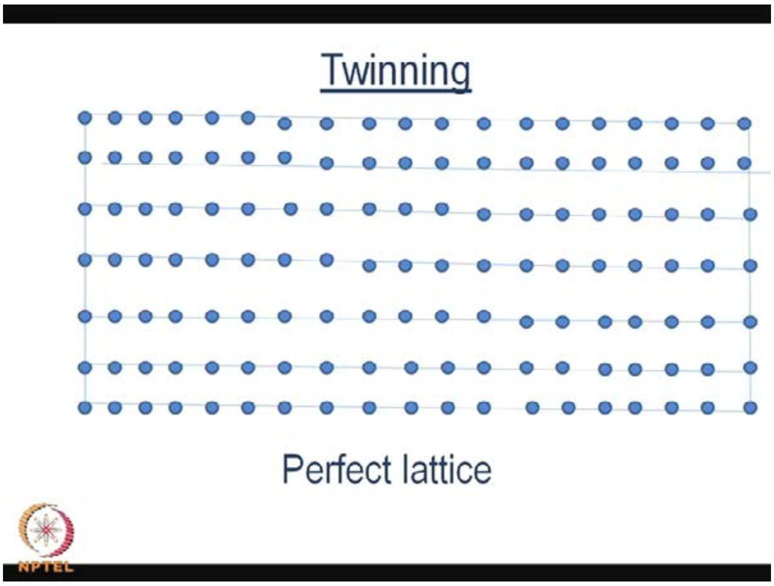

Twinning

Perfect lattice

Well the twinning, all these defects are relative to the perfect lattice, this is a perfect lattice, in which the atoms are arranged in the particular geometric fashion. And the horizontal lines are actually the planes, we can imagine one set of particular set of planes; and there is no defect in this particular case, either point defects or line defects or two-dimensional defects because of, twinning.

However, if there is a mechanical stress either internally generated or externally applied, depending on the nature of the crystal and it is energetic and energy equal to form different kinds of defects, a twinning (( )).

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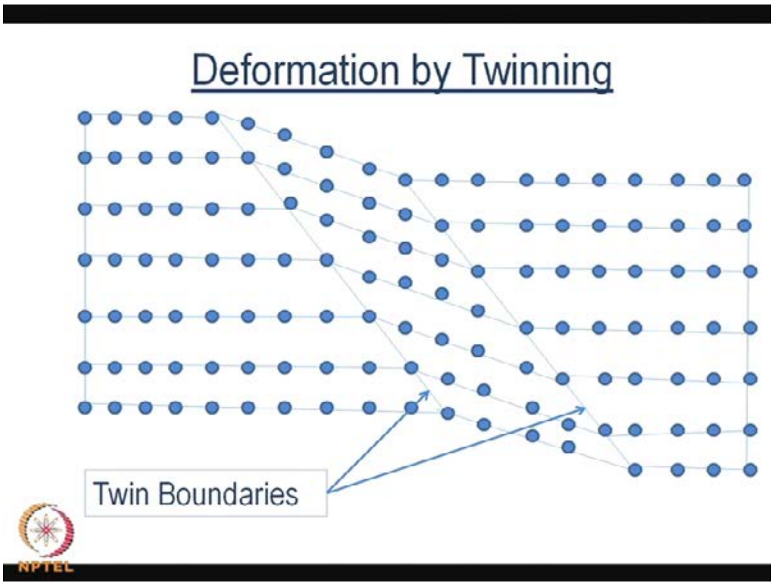

Deformation by Twinning

This is what we call a twinning; that means, a deformation, a kind of shear deformation; if we compare the earlier structure, the perfect lattice, and then goes to this twin crystal or twin planes, we find is a shear shear region, where this part of the crystal remains intact. This also have the same orientation, as it was originally present and however, in between we have a region a region where, the atoms are displaced atoms are displaced to some extend not very large distances.

But we will see the atoms are arranged or displaced in a particular proportionate manner that means, this atom has moved smaller distance, this atom has moves from this distance, larger distance and so on. And this particular atom is moved from its original position, the larger distance, and they have a relationship between themselves. So, they again form a set of planes, they are not randomly distorted, not randomly displaced. But, they displaced in such a manner, they form of plane.

So, this particular plane, which was a continuation plane with this, has now shifted downwards. And in between, a plane has come up, which having a different orientations, but it remains as a plane. So, it is a kind of cooperative movement of a set up atoms under a shear stress and they maintain certain orientation and relationship, they are not randomly displaced. But they have a particular nature of the displacements so that, they maintain the particular orientation, orientation among themselves.

But that orientation is different from their original orientation, it also one can look at this, if you look this boundary, either this boundary or this boundary. Once again, one can imagine a plane there and if you look, take the atoms across this particular boundary you will find this part of the boundary, this part of the plane is mirror image of this plane. This plane is a mirror image of or the deformed plane is the mirror image of the original image across this boundary.

So, all the planes, all the set of planes here, parallel planes forms a mirror image of themselves after the twinning has taken place and similarly, this is also another boundary where this is a mirror image of this one. So, twin boundary these are called the twin boundary and process is called twinning so, deformation there is displacement of this set of planes called compare to its original position. And so, there is a deformation mechanical deformation, displacement of the atoms.

So, there is a plastic deformation so, this plastic this is also plastic deformation not an elastic deformation. So, this twinning is another mechanism just by just like dislocation mechanism, by which plastic deformation takes place. Twinning is also another deformation, it is a different mechanism, by which if deformation plastic deformation takes place of a crystal. And these are called twin boundaries and they are back basically planes, a set of vertical planes and these also another plane.

So, normally two different twin boundaries appear simultaneously, as a result you have a mirror image of the original planes. So, this is what we called the twin boundary and it takes place almost instantaneously. It is not a lot of time dependent process, it is basically takes place within a fraction of second so, this was the once again if can look at once again, it is a perfect lattice and then, immediately it changes to a twined region of the crystal.

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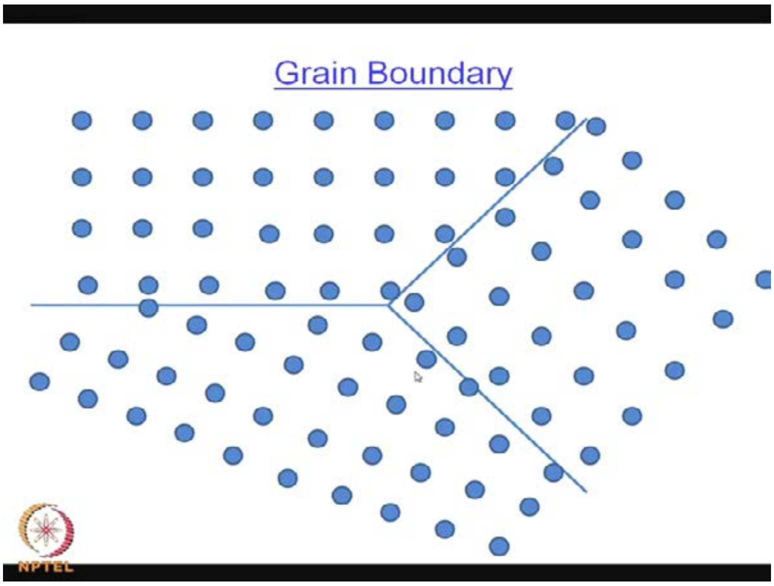
Grain Boundary

So, that is what we call it twin boundary and that is the definition and there are crystals going back there are crystals in which, twin boundaries are quite predominant. And particularly, we have discussed earlier about the ferroelectric crystals no we discussed later this frankly speaking discussed later. We will see these twin boundary, they are quite predominant in some ferroelectric crystals and many of the hexagonal kind of crystals.

The twinning boundary and twinning deformation is quite predominant well that is will not discuss much a lot it because, may be will come across the kind of the deformation at later stage, i will just introduce you and define what is twin boundary. The next type of surface defects or two-dimensional defects are known as the grain boundaries, in any polycrystalline material it is a combination of large number of single crystals and these single crystals are oriented in different directions.

So, particularly until unless you take very special precautions, it is very difficult to prepare a single crystals, mostly ceramics are available in polycrystalline material. And therefore, the boundaries between two different single crystals within a solid, within a polycrystalline solid, it is actually called the grain boundaries. So, this is one grain, this is another grain and that is another grain so, you have boundaries and this boundaries are called grain boundaries and once again it is a two dimensional surface.

And these boundary although we have drawn it in the form of a line, but actually their surfaces and they are not plain surfaces. One has to remember, they are not unlike twin boundaries, twin boundaries are plain surfaces, here grain boundaries are very irregular surfaces depending on, how the crystal have grown from its nucleation. And by nucleation and growth process, how the crystals are grown and finally, collided with the charger forming every irregular surface.

So, these boundaries are called grain boundaries this is one grain and this is another grain and this another grain. The characteristics of these grains are, this grain having a particular orientation for example, these are the these at the particular planes having orientation in this direction. But, you can see the planes are oriented in a different direction whereas, in this there are other directions. So, the orientations in these crystals are different and that is how, the boundary is a defined.

So, if it is a continuation of the same orientation then, the boundary would not have been there because, that is a change of orientation of the automatic arrange of the crystals that is why, there is a boundary. And sometimes, it is a combination of large number of dislocations, a large number of assembly of large number of dislocations can be give rise to this kind of a boundary. And there obviously, high energy site compare to the bulk of the crystal.

These are the bulk of crystal, has grains, the grains of the lower energy internal energy whereas, the grain boundaries at defective sides. And therefore, they have a much larger energy per unit area so, this is what we called grain boundary. They are quite prominent and predominant in any polycrystalline material with ceramics, metals or any other alloy.

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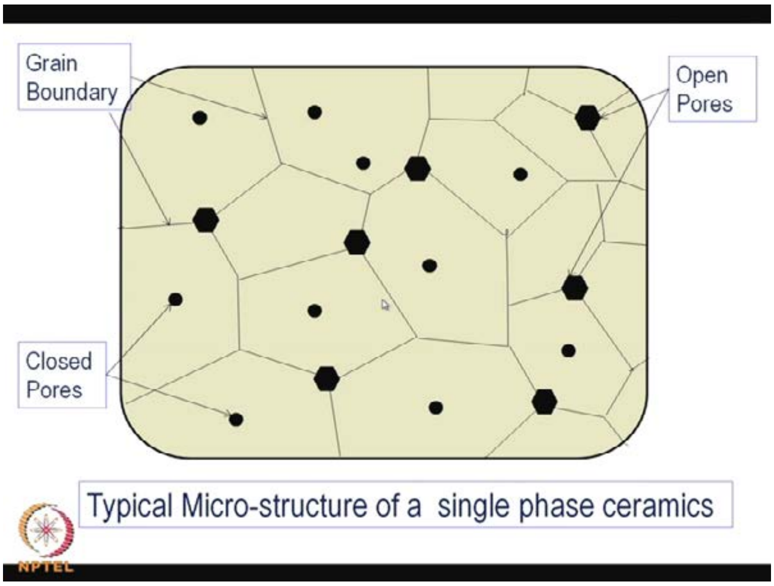

Typical Micro-structure of a single phase ceramics

This is a typical microstructure, a schematic schematic of a typical microstructure of a poly crystalline ceramics in particular. As you know, ceramics are always prepared from ion powders and then, the assembly of those powders or the compact powders are heated to high temperature and then, the chemical bonds are formed or (( )) takes place and finally, there is the grain boundary formed.

Now, to start with ceramics, what we called the green compacts or porous much larger pores. And slowly as we increase the temperature or (( )) or fire them at at at higher temperature, the porosity gets reduced, the grain to grain contacts, the solid to solid contact develops. And finally, you get a well developed grains, well developed single crystal grains.

So, these are single crystal grains that we have seen earlier but, any poly crystalline material or particularly ceramics, the way we prepared it, it is supposed to contain some amount of pores. So, the dark spots here are actually the pores, the voids these are voids. There are two different types of voids, you have marked here, these are the lines or grain boundaries and in the boundary junctions triple points, these are called triple points.

The inter boundary or inter granular pores are there so, these are the return pores or the remanant pores, which could not be removed even after (( )) originally limited scope temperature and time. So, these are inter granular pores, they are relatively large pores and normally, these inter granular pores are open pores what we call these open pores.

Open pores means, they are through and through pores that means, there is a permeability from one end of the surface to another end of the surface, it is open. So, if you try to put some gasses are liquids, we can go through depending on the size.

Whereas, there is another variety of pores, which is called closed pores or their intra granular pores. That means, these pores are within the grains, not at the corner junction of the grain boundaries. So, these are within the grains and these grains, these pores are normally called closed pores, these are called closed pores that means, they are not through and through pores and (( )) pores, they are closed from all the sides.

So, these are the two different types of pores, we will see later that, these pores are also one kind of defects; one kind of defects but otherwise, these are the boundaries, these boundaries are the two dimensional defects in a polycrystalline material.

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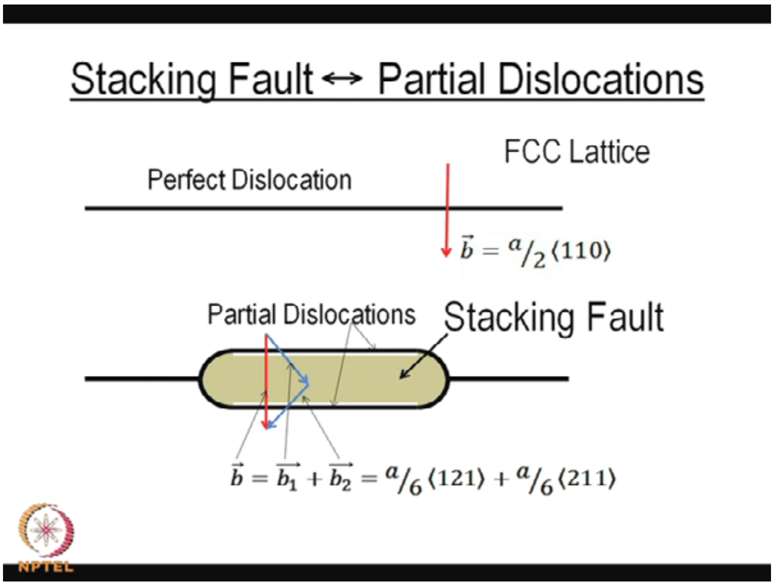

Stacking Fault ↔ Partial Dislocations

There are in addition to twin boundaries and grain boundaries, there is another type of defects, what we called is stacking fault. We have seen earlier that, the atomic arrangement or the atomic order, the way the atoms are arranged. Actually, you can consider a stacking of different layers of line layers of atoms, we have seen close packed layers A B C or A B A B packing or stacking. So, that remembering that FCC lattice for example, has a A B C A B C stacking.

Whereas, hexagonal close pack or HCP has A B A B stacking but it is possible; it is possible that these stacking arrangement may not continue throughout the crystal. In some part of the crystal there may be some kind of mismatch, some kind of a distortion or deviation from this stacking. And A B C A B C stacking can change over to A B A B stacking so, within the same crystal it is not necessarily that all through you have similar stacking.

It may have different kinds of stacking or the stacking sequence may change within a small region of the crystal, and that is what we call the stacking fault. Now, stacking fault may originate from different points (( )) it can originate from different regions, but one of the regions is, what we called formation of partial dislocations. Earlier we have discussed perfect dislocations having some Burger’s vector and that is the direction, in which the atoms move and distance by which, the atoms are moved that is defined as a Burger’s vector.

So, all dislocations are basically defined by a Burger’s vector so, this is here decide line we have discussed earlier that dislocation is a line defect. So, this is can be represented by a perfect line like this so, this is a perfect dislocation, single dislocation having a Burger’s vector provided is in the edge dislocation, the Burger’s vector is perpendicular to the direction and the tangent to that line.

And in this case, FCC lattice that a example we have taken and Burger’s vector in a FCC lattice is actually a by 2 1 1 1 1 1 0 direction. So, that is a close packed direction and a is a lattice parameter so, a by 2 1 1 0 direction is that, is what is called the Burger’s vector of the dislocation in FCC lattice. On a certain situations, it may happen this perfect dislocation, which is instead of continuing like this, they have separated out in two, what we called the partial dislocation.

And this partial dislocations actually arranges because, the displacement changes, the Burger’s vectors get resolved in two different directions, one particular Burger’s vector like b, which is now becomes b 1 plus b 2. So, this is that Burger’s vector director this is like this whereas, this partial dislocations have a Burger’s vector like this. This is the 1 b 1 and this is b 2 so, instead of the atoms moving from this position to this position according to this Burger’s vector, the atoms will move ultimately it will move to this position.

But, it will move via a different route, it will first move to this position and that is with a Burger’s vector of b 1 and then, this moves to another final position from an intermediate position to this final position, by Burger’s vector of b 2. So, b becomes a combination b 1 and b 2, although the ultimate result is same but, now because of the two different Burger’s vector we have 2 partial dislocations, what we called the partial dislocation.

When all the atoms are moved from this place to this place, it forms 1 dislocation and when it moved from this place to this place another dislocation. So, the line perfect dislocation has been resolved in 2 different dislocations, one is two different partial dislocations and in between this region, between space between these two region is also atomic arrangements are there. And this atomic arrangement is different from the rest of the crystals outside, outside this boundary and this is, what we, we call, and what we see as stacking fault.

So, this because of this partial dislocation because, the atoms are moved from a different position, which it was not supposed to be under normal condition. So, this has a different stacking compared to the outside so, this is the 2 Burger’s vectors b 1 and b 2, a by 6 1 2 1direction and a by 6, 2 1 1 directions. So, these are the miller indices of the directions I hope you are aware of the (( )).

So, these are the miller indices of the directions so, this is 1 1 1 1 1 0 direction, it has been resolved in 1 2 1 and 2 1 1 directions. So, because there are two partial dislocations the (( )) space is actually have a different stacking than the original A B C A B C stacking. So, this is what we call stacking fault so, a fault which spreads over a particular area.

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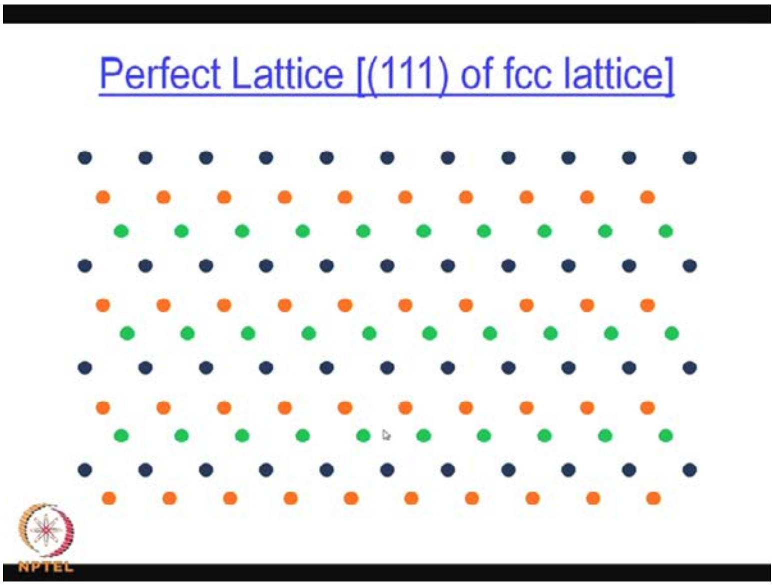

Perfect Lattice [(111) of fcc lattice]

This will be clear little in a different way, better way once again this perfect lattice of 1 1 1 plane. These are the different layers of planes and this may be I think this will be clear in the next one like this.

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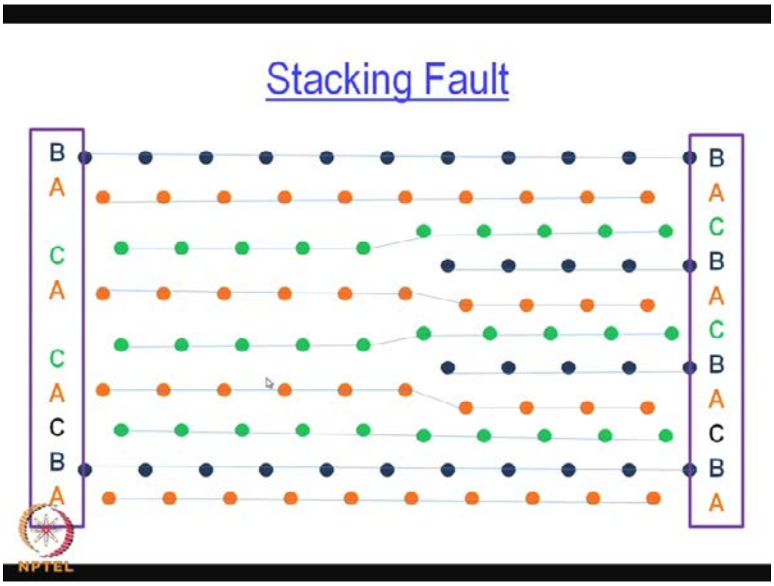

Stacking Fault

So, the perfect lattice has a A B C A B C in this direction this is the perfect lattice here, on this side this is this part we can see there is some deformation has taken place on this part of the crystal. And the left part of the crystal there is a some changes whereas, this is the perfect crystal and if you have notice the stacking sequence, you will see there is A B C A B C A B C A B lattice.

Now, you have a 2 dislocations, if you have remember the way we define dislocation the edge dislocation, here extra a is over there, another a is over there. And therefore, this are missing on this part of the crystal, as a result you will see this taking stacking has changed, in this part of the crystal stacking has changed. Instead of A B C A B C, which is on this side, on this side we can notice it is A B C then, A C A C and then, again A B C.

So, this part of the crystal we say, there is a stacking fault so, the atoms are not placed in the like positions as in the perfect crystal. But some of the atoms are missing because of, the formation of this dislocation and therefore, this part of the crystal has a stacking fault, rest of the things have a perfect crystal. So, within a perfect crystal there is a stacking problem or the stacking sequence gets changed and therefore, we call it a stacking fault.

So, this is the third type of two dimensional defect, sometimes it is also called a volume defect. Because, it extends over some volume in a three dimensional, it can extend a three dimension. In some reference we will see stacking fault has been defined as a two dimensional, in some other case you will find they also defined as three dimensional defects.

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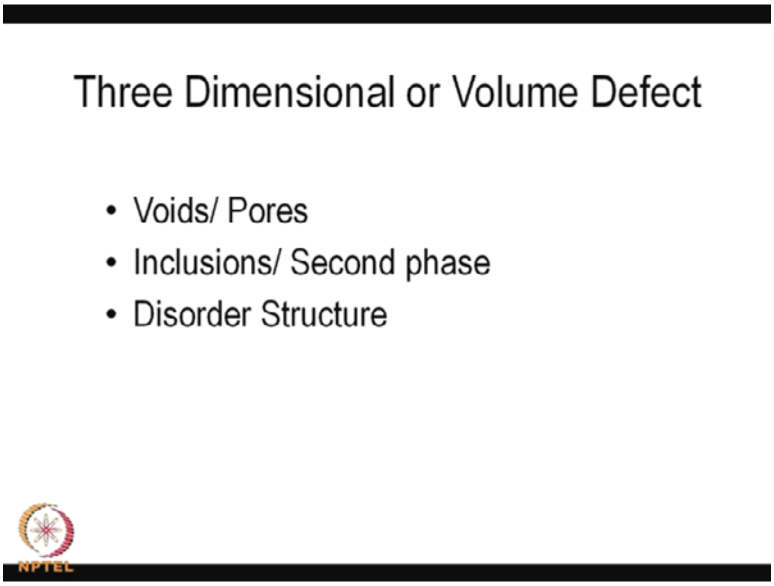

Three Dimensional or Volume Defect

- Voids/ Pores
- Inclusions/ Second phase
- Disorder Structure

So, these are the three different surface defects or two dimensional defects, we have mentioned earlier. Next, you come to three-dimensional or volume defects not surface defects but, the volume defects they are relatively simple to imagine. For example, voids and pores, inclusions or the second phase of course, provided the dimension, there is no particular critical dimension. But inclusions of the second phase either it may be impurity atom impurity phase or it may be a designed second phase.

If the volume percent of the size of those individual phase region are very small, we can call them defects within a single phase region. Looking at the same microstructure, this is what we called void because, the pores the pores are nothing but, voids. So, the large avoids are there so obviously, is three-dimensional defects whether it is a inter granular or intra granular. Both of them have some volume and therefore, this pores are always the three dimensional defects.

Inclusion, this can also a micro structure of this nature can also arise, if there is instead of pore, pore is in fact one can imagine as a pore as a second phase compact to if this becomes the first phase, this becomes second phase, a different material different kind of structure. In this case it is a void, instead of that this could be a different phase all together, a different phase in the sense having a different crystal structure, different compositions and so on.

So, depending on the overall composition nominal composition of the material, there may be second phase. So, second phase of this nature, not pores second phase of this distribution can also we call a three dimensional defect. So, that is what we call about three dimensional defects and right we sorry the third one, is what we called disorder structure, disorder structure also is a three dimensional defects.

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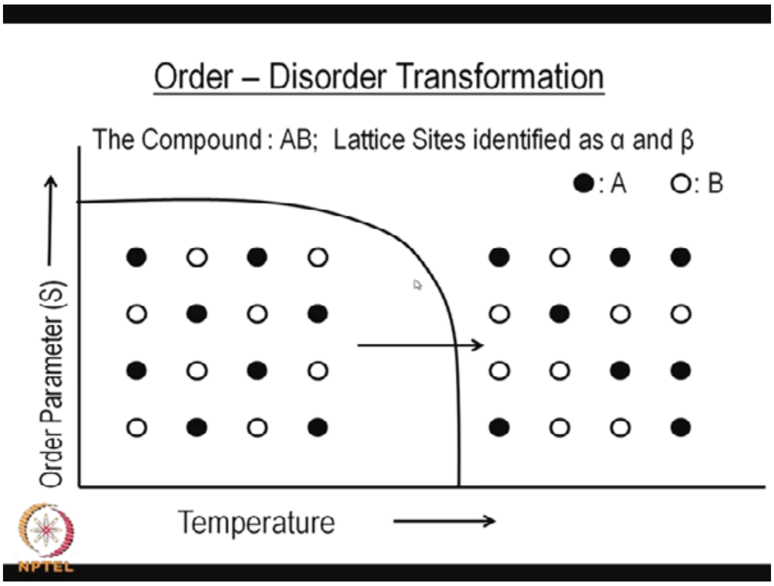

Order – Disorder Transformation

The Compound : AB; Lattice Sites identified as α and β

And the example of a disorder structure, a simple example of this, it is a of this nature, let us have a compound A and B whether A be one variety of atoms and B another variety of atoms. And it is a combination in which, sizeable fractions of A and B are present well since it is a B obviously, same number of A and same number of B will be present. If it is A to B, the ratio will be different but. in this case since 50 50 A and B so, these are A atoms and these are B atoms.

Now they are occupying different sites, different lattice sites now, in this structure if you look at from the left side this also A B, this also A B same compound. But, the atomic arrangements are different, the relative position of the A and B are different, here we call it an order structure. All the a and b atoms are alternatively placed and that is an order order arrangement of A and B atoms because, lattice sites may be indistinguishable but, the atoms are distinguishable.

So, the (( )) occupying the lattice sites that determines, what is the order, whether it is order state or in the disorder state. Here, the A and B atoms are not occupied in regular lattice site, they randomly distributed so, this is an disorder this is a disorder structure, disorder phenomenon where, this is in order phenomenon or order structure. So, this disorder is actually a defect compared to its normal thermodynamically equilibrium distribution, particularly at higher temperature.

Particularly at higher temperature, the disorderness increases and there is random distribution so, this is also a kind of defect, which which actually occupies a particular volume. So, over the whole volume or a particular region of the solid, this kind of disorderness comes and sometimes, this disorder is also in order way. For example, in some kind of a layered structure material and we see later on the layer structure material, some layers, some crystallography layers or some atomic layers are actually disorder, others are ordered structures or remains ordered.

So, disorderness may be restricted to a particular atomic planes or atomic volume or layers, two dimensional layers. So, that is also some kind of a disorder but here, we are considering the total volume.

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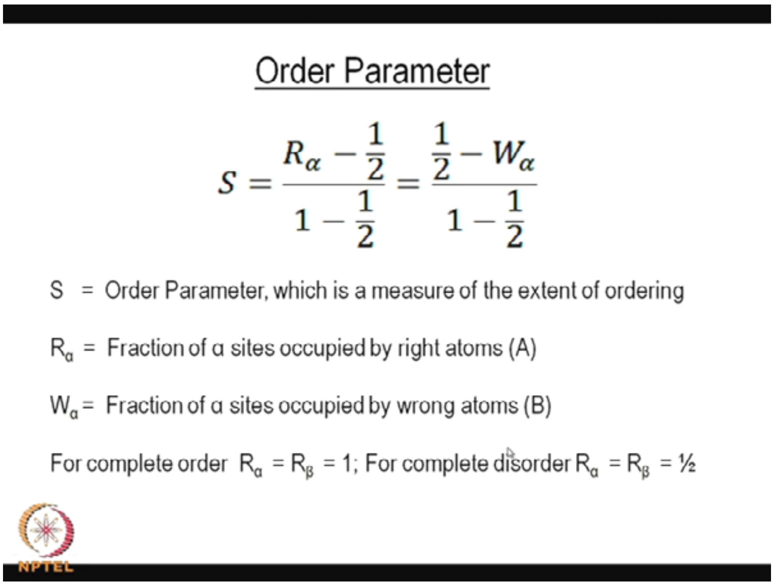

Order Parameter

$$S = \frac{R_\alpha - \frac{1}{2}}{1 - \frac{1}{2}} = \frac{\frac{1}{2} - W_\alpha}{1 - \frac{1}{2}}$$

S = Order Parameter, which is a measure of the extent of ordering

R_α = Fraction of α sites occupied by right atoms (A)

W_α = Fraction of α sites occupied by wrong atoms (B)

For complete order $R_\alpha = R_\beta = 1$; For complete disorder $R_\alpha = R_\beta = ½$

Now, we can define some order parameters, that is basically that is basically extent of order disorderness is called ordered parameter, which is a major of the extent of the ordering or alpha, the fraction of alpha sites looking back to that structure. There are A atoms and B atoms and also, the lattice sites identified as alpha and beta sites. So, some are identified as alpha sites and some are identified as beta sites particularly, in an ordered structures.

So, whether the alpha site is occupied normally, the normal circumstances as alpha will be occupied by A and beta site will be occupied by B. But if that does not happen then, the order parameter comes in, that is how, it has been defined S, the order parameters R alpha. R alpha is the fraction of a site, fraction of sites not the I think, it should be one minute these are fraction of sites occupied by the right atoms, that is A.

Alpha should have been occupied all the time A atoms and beta should have been occupied by B atoms. So, an alpha R alpha is the fraction of sites occupied by the right right atoms or the A atoms and W alpha is the fraction of alpha sites occupied by the wrong atoms, that is what it says. So, if R alpha is the right atoms and W alpha becomes wrong atoms So, for complete order, R alpha equal to R beta equal to 1 and for complete disorder, R alpha equal to R beta equal to equal to half.

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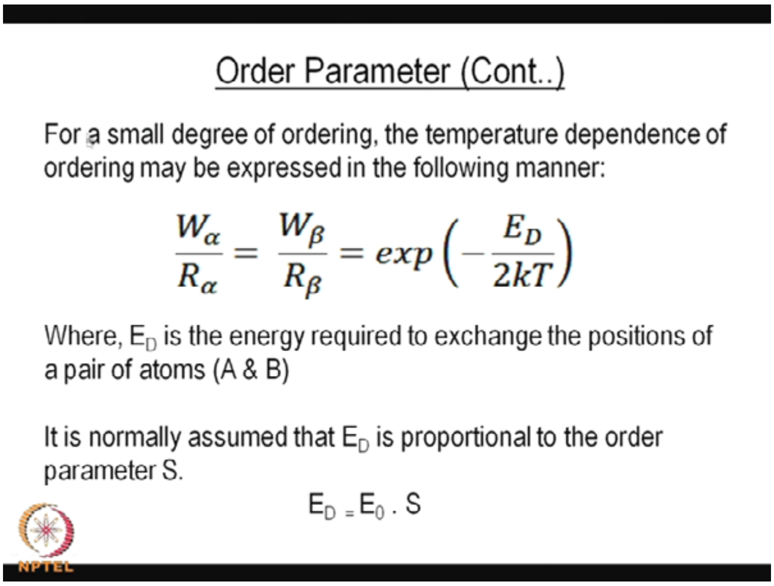

Order Parameter (Cont..)

For a small degree of ordering, the temperature dependence of ordering may be expressed in the following manner:

$$\frac{W_\alpha}{R_\alpha} = \frac{W_\beta}{R_\beta} = exp\left(-\frac{E_D}{2kT}\right)$$

Where, E_D is the energy required to exchange the positions of a pair of atoms (A & B)

It is normally assumed that E_D is proportional to the order parameter S.

$$E_D = E_0 . S$$

Well for a small degree of ordering, the temperature dependence of the ordering may be expressed in the following manner, which is a temperature dependence and this in exponential term and, there is a activation energy E D so the formation. So, here E D is the energy required to exchange the positions of a pair of atoms, A goes to the B sites and B goes to the A sites. And a energy requirement just like your point defects, formation of Frenkle defect or Frenkle pair or Schotty pair, would all you need certain activation energy.

Similarly, this E D is the action energy for the disorderness so, that is how this parameter or the extent of disorderness actually dependent on the temperature by an exponential term like this. We normally assumed, that the E D is proportional to the order parameter S so, this E D is proportional to the order parameter, which we have defined earlier. And the proportionality constant is a constant E 0 so, there is a relationship there is a relationship between the order parameter and the temperature.

And this order parameter remains more or less at one value, constant value till a transition temperature reaches, this is what we call the transition temperature, where suddenly this order gets changes to disorder structure or disorder structure comes back to the order structure. So, this is another kind of crystalline defects we crystalline defect we normally encounter in perfect crystals. So, that completes our discussion on the crystalline defects.

We have earlier classes we have discussed about the point defects, next we have discussed about the line defects and in today's class, we have also discuss the two dimensional or the surface defects and volume three dimensional defects, the volume defects. So, there are 4 varieties of crystalline defects zero dimensional, one dimensional, two dimensional and three dimensional so, that completes our discussion each on name of the course, different category different types of defects, each category has different types.

So, we have all discuss and they have they are influence we have earlier seen how point defects influence the electrical properties and then, we have the line defects influence the mechanical properties. Also the two dimensional defects like twin defects, twining related to the mechanical property and then, grain boundaries. Grain boundaries are integral part of polycrystalline materials and they have a very, very important effect.

So, for as various different properties are concerned, we will see whether it is mechanical property, whether it is electrical property, whether it is high temperature properties, all of them are controlled by this kind of defects. Having discussed all these and completed our discussion on crystal structures earlier, let us go to some question answer session at the end of this.

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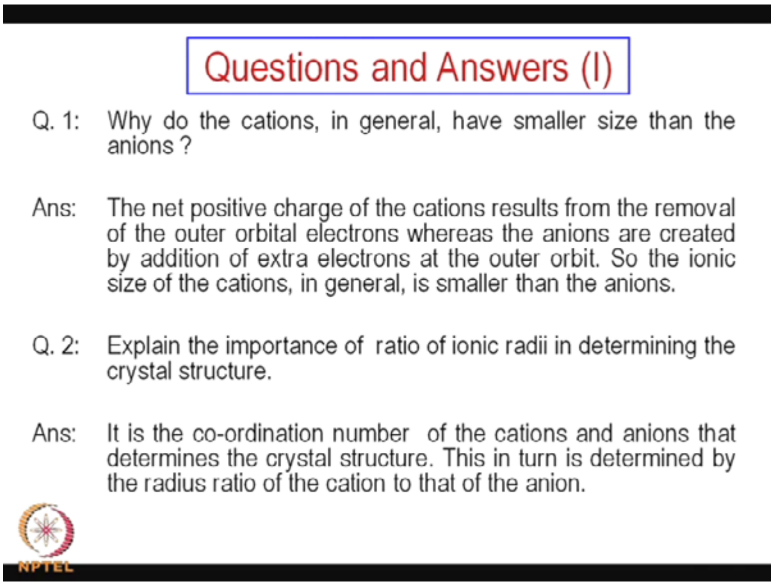

Questions and Answers (I)

Q. 1: Why do the cations, in general, have smaller size than the anions ?

Ans: The net positive charge of the cations results from the removal of the outer orbital electrons whereas the anions are created by addition of extra electrons at the outer orbit. So the ionic size of the cations, in general, is smaller than the anions.

Q. 2: Explain the importance of ratio of ionic radii in determining the crystal structure.

Ans: It is the co-ordination number of the cations and anions that determines the crystal structure. This in turn is determined by the radius ratio of the cation to that of the anion.

I taken some questions here and also discuss their answers given here, some are descriptive questions, couple of them are mathematical or numerical questions. The first question is, why do the cations in general, you have seen earlier that, with the atomic arrangement of any oxide or compound actually contains atom, cations and anion right. So, the question is, why do the cations in general have smaller size than the anions, we have also seen why i am discussing this question.

We have seen the size is very very important role to play in determining the crystals structures so, the answer to this question is very simple, the net positive charge, cations means positive charge. Charge of the cations results from the removal of the outer orbital electrons, either the outer orbitals or the next inner orbital particularly, transition metals are rarers so, outer either outermost or the next outermost orbital electrons are removed.

Whereas, the anions are created by addition of extra electrons of the outer orbit. So, the ionic size of the cations in general, is smaller than the anions, that is a normal thing but, there are maybe exceptions in there. We have seen in crystal structures that, in some cases the cations and anions more or less of the same size but generally cations are smaller than the anions are the reason is, in one case you are removing the outer electrons, in another case you are actually adding the outer electrons because, this is true for primarily for the ionic crystals.

The second question is, explain the importance of the ratio of the ionic radii in determining the crystal structures that is what I assume, mentioning just now. Because ionic radii of atoms are the ions the cation either the cation or the anions that actually, determines the exact arrangement of the atoms. And therefore that leads to the symmetric and various crystal systems, and the description of the crystal structures so, it is the coordination number.

So, it also determine the co ordination number of the cations and the anions that, determines the crystal structure right. This in turn, is determine by the radius ratio of the cation to that of the anion, it is a that is a very important role of the coordination number, either of the cation or the anion in determine the crystallographic symmetry. And this co ordination number is determine again by the radius ratio, what is the ratio of the crystal of the cation to that of the anion. And therefore, ionic radii or the ionic size is very important role to play in determining the crystal structures.

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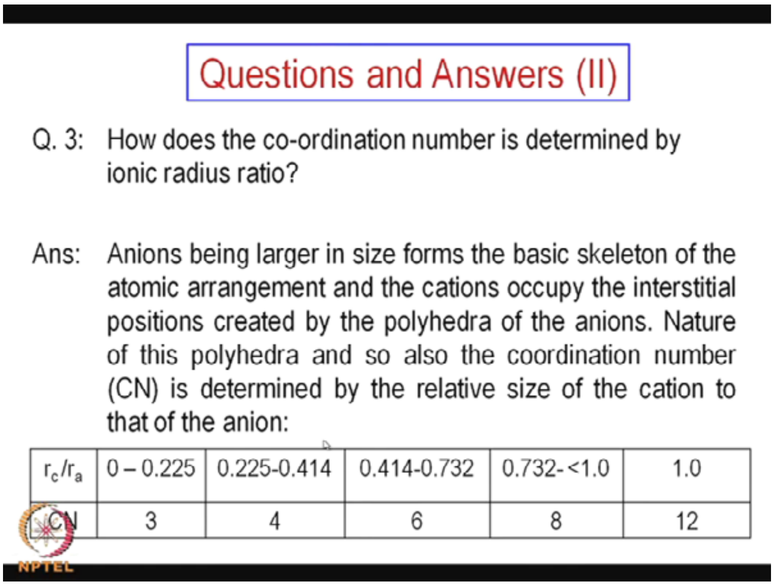

Questions and Answers (II)

Q. 3: How does the co-ordination number is determined by ionic radius ratio?

Ans: Anions being larger in size forms the basic skeleton of the atomic arrangement and the cations occupy the interstitial positions created by the polyhedra of the anions. Nature of this polyhedra and so also the coordination number (CN) is determined by the relative size of the cation to that of the anion:

r_c/r_a	0 – 0.225	0.225-0.414	0.414-0.732	0.732-<1.0	1.0
CN	3	4	6	8	12

The third question is, how does the coordination number is determine by ionic radius ratio, it has the important role no doubt but, how exactly it is determined. That is what you have do, one has to remember these limits, the answer to this question is the anions being larger in size forms the basics skeleton of the atomic arrangement. So, since atoms of the anions are larger, they actually form the skeleton, they come they cannot come closer, too closer to complete to form the complete compacts structures.

But they touch each other earlier, if you are talking if you consider the equilibrium distance of separation then, the anions will touch each other earlier than the cations. So therefore, the anions being larger in size forms the skeleton whereas, cations even after the touching each other or coming to the closest at position, they have some voids. They form a voids and those voids are sufficient for the cations to be accommodated there and that those are the interstitial sites.

So, the exact coordination number or the exact polyhedra surrounding a cation is determine by the cation to anion ratio, this is r c by r a and this is the coordination number. So, if this is between 0 and 0.225, this becomes a 3 fold coordination, if it is between 0.225 to 0.414, it forms 4 fold coordination. Then it still larger that means, the cation size is larger relatively larger to the anion, then it goes to the 8 fold 6 fold coordination then, 8 fold coordination.

And when it is exactly 1, both are equal it forms a 12 fold coordination so, that is the situation, that is why the cation to anion ratio is so important for determination or consideration of crystal structures.

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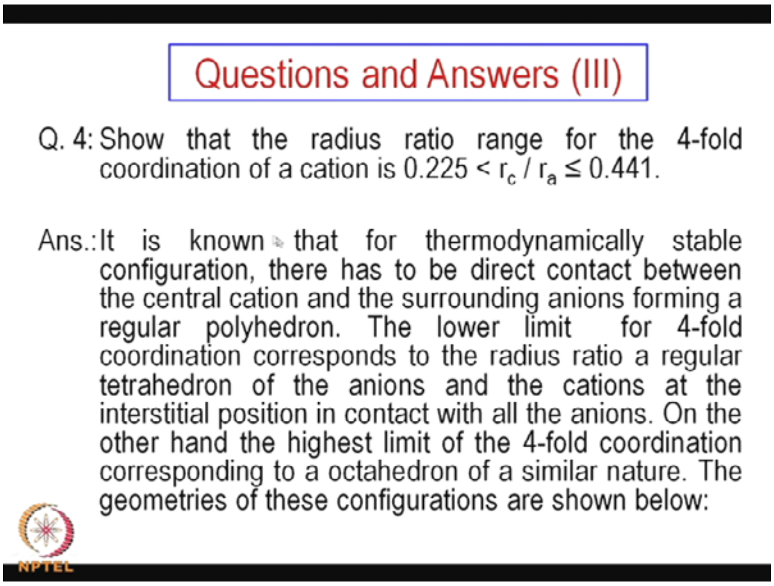

Questions and Answers (III)

Q. 4: Show that the radius ratio range for the 4-fold coordination of a cation is $0.225 < r_c / r_a \le 0.441$.

Ans.: It is known that for thermodynamically stable configuration, there has to be direct contact between the central cation and the surrounding anions forming a regular polyhedron. The lower limit for 4-fold coordination corresponds to the radius ratio a regular tetrahedron of the anions and the cations at the interstitial position in contact with all the anions. On the other hand the highest limit of the 4-fold coordination corresponding to a octahedron of a similar nature. The geometries of these configurations are shown below:

The fourth question is, so that, the radius ratio range for the 4 fold coordination of a cation is 0.225 that means, if it is between 0.225 and 0.414, that we have seen earlier that, we have listed earlier. But we have to we have to justify why this number comes, this is the next question how do that justify the d s. If the r c by r a ratio is between

0.2254 and 0.415 0.414, it becomes the tetrahedral coordination or the 4 fold coordination and that comes from the geometric basic solid geometric.

This is our next consideration, it is known that for thermodynamically stable configuration, there has to be a direct contact between the central cation and the surrounding anions, forming a regular polyhedron. The cation cation must touch the surrounding polyhedron surrounding anions, if it is smaller than the interstitial sites, it is not a stable chain, it is not a stable configuration. It can be slightly larger so that, the anions can be pushed apart a little bit then also its stable beyond but, beyond certain point once again is not stable, it goes to next higher coordination that we have discussed in earlier classes.

So, this is what we are trying to do it is a try to consider or try to mention here, it is known that the thermodynamically stable configuration, there (( )) thermodynamically stable configuration, there has to be a direct contact between the central cation. But the interstitial cation and the surrounding anions forming a regular polyhedron, the lower limit for the 4 fold coordination corresponds to the radius ratio of regular tetrahedron, radius ratio of tetrahedron, radius ratio of of a regular tetrahedron of the anions and the cations at the interstitial position in contact with all the anions.

So, it just touches the cations when the anions are in the tetrahedral configuration, on the other hand the highest limit of the 4 fold coordination corresponds to a octahedron of a similar nature. Then, the geometries of these configuration are given below. I am just going to the next slide so, from 4 fold the tetrahedron that is the lower limit, higher limit is, when the atoms anions are little pushed apart. But you have still the tetrahedron is valid, which is, where the atom anions are not touching themselves, there is no contact between the anions they are pushed apart because, cation is slightly larger but, the limit is until unless is goes to a regular octahedron so, the up to that point the 4 fold coordination is stable.

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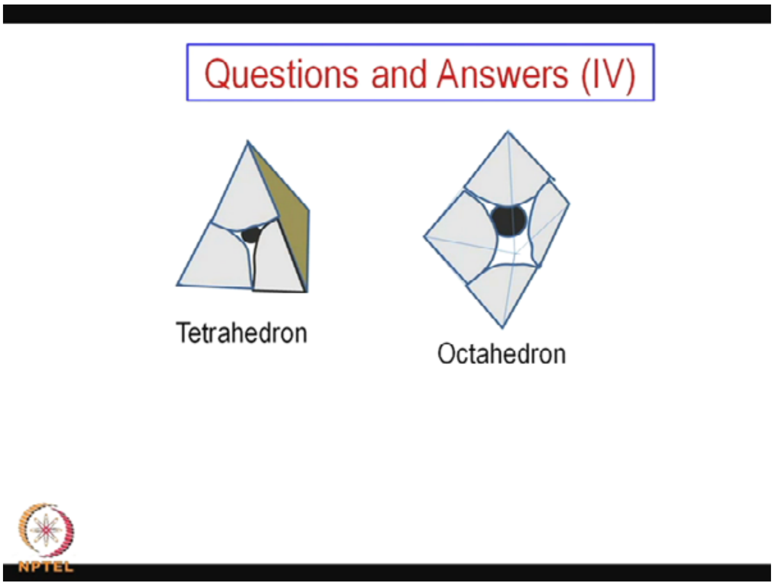

Questions and Answers (IV)

Tetrahedron

Octahedron

This is what a kind of cut a few of the three dimensional picture tetrahedron, here is on the corners of each tetrahedron each corner of the tetrahedron is occupied by a anion. And you have a small cation at the center of the octahedron of the tetrahedron so, that is a (( )) of the three dimensional three dimensional structure, a tetrahedron. So, there are 4 atoms, 4 anions and the center we have a small cation so, you want to find out what is the critical size of this small cation.

Whereas, the other limit is octahedron, this is the lower limit of the 4 fold coordination and the higher limit of the 4 fold coordination is an octahedron, where you have a square by pyramid. That means, the one particular atom is not shown here but there are 4 anions on the horizontal plane, same plane and then, another anion in the top, another one in the bottom. So, that forms a 6 anions 6 anions and then, that the center of the bipyramid will have a small interstitial site, which has to be occupied by a cation. So, these are the two three-dimensional pictures, they are not drawn very regularly but, I hope the illustration is understand away.

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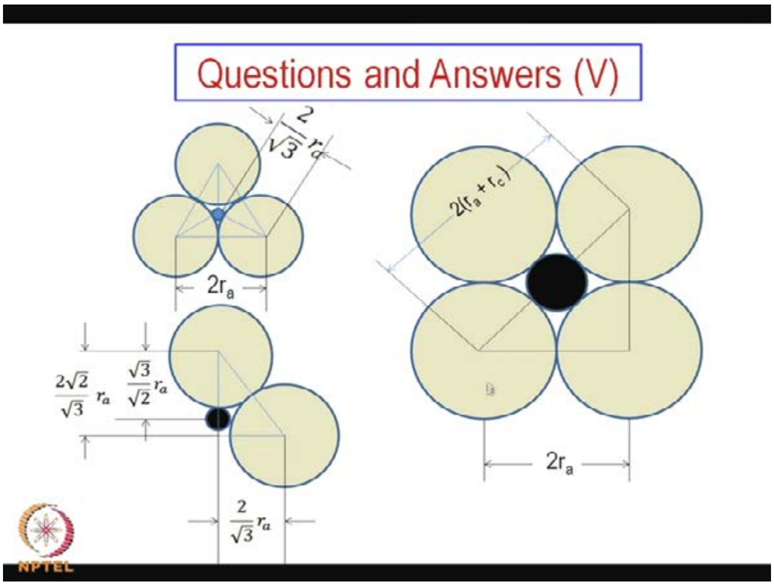

Questions and Answers (V)

Now, here we are taking some sections here we taking some sections, this is for the tetrahedron now, for the first this is the base of the section, base of the pyramid. They are the tetrahedron and this is a vertical plane, the vertical (( )) or vertical section of this same pyramid. Now, if r a, r a is the radius of the anion here it is large ions then, this is of course 2 r a, this is touching along this line. So, at the base and the distance between this and that, that is the center median of this regular isosceles triangle is 2 by 3, not isosceles triangle is equilateral triangle of course, 2 by root 3 r a.

So, these distance is two-third of this distance so, it find this is 2 by root 3 by r a and if we take the vertical line, the details are given in the next slide how it is been calculated, is quite simple. The basic solid geometry consideration this is your 2 by root 3 r a, this distance and this is a vertical line, this is the vertical section. That is this is the apex, these are the 2 base 3 base anions and this is one of the base ions and that apex ions, this is the highest point.

So, then these distance is 2 by third r a 2 by root 3 r a and this is the height from this right angle triangle. One can find out this height is 2 by 2 into root 2 by root 3 r a and this is three fourth three fourth of this total distance. So, this height is actually root 3 by root 2 r a, three-fourth of this and this is nothing but r c plus r a. r c is the diamond radius of the cation and this is the radius of the anion, so this distance is equal to this one.

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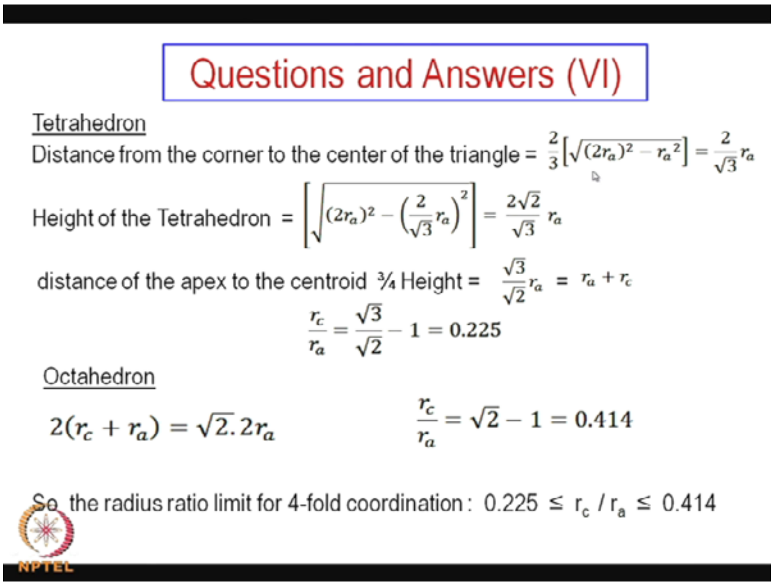

Questions and Answers (VI)

Tetrahedron

Distance from the corner to the center of the triangle = $\frac{2}{3}\left[\sqrt{(2r_a)^2 - r_a{}^2}\right] = \frac{2}{\sqrt{3}} r_a$

Height of the Tetrahedron = $\left[\sqrt{(2r_a)^2 - \left(\frac{2}{\sqrt{3}} r_a\right)^2}\right] = \frac{2\sqrt{2}}{\sqrt{3}} r_a$

distance of the apex to the centroid ¾ Height = $\frac{\sqrt{3}}{\sqrt{2}} r_a = r_a + r_c$

$$\frac{r_c}{r_a} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = 0.225$$

Octahedron

$$2(r_c + r_a) = \sqrt{2}.2r_a \qquad \frac{r_c}{r_a} = \sqrt{2} - 1 = 0.414$$

So the radius ratio limit for 4-fold coordination : $0.225 \leq r_c / r_a \leq 0.414$

So, in the, this is what the details of the calculation for the tetrahedron particularly, the distance from the corner to the center of the triangle. Center of the triangle means basically the median, along the median. And so, this is already shown there in the diagram. Height of the tetrahedron will be this one, from the right angle triangle so called Pythagorus theorem and the distance of the apex to the centroid is three fourth of the height.

And that is already shown there and we will find this one, from this one to this one, three fourth of this value is this one and then, will be equal to r c by r a. And then, once again looking at this values will see r c by r a equal to root 3 by root 2 minus 1, which is nothing but, 0.225 so, the critical this critical radius ratio for the tetrahedron is 0.225. And similarly, of course this calculus is much simpler, the consideration of the analysis is much is quite simply in this case.

For the this is the base this is the base of the bipyramid here so, these are touching along this corner, if this is 2 r a this will be equal to root 2 root 2 r a. And that will be equal to 2 r a plus r c, this distance 2 r a plus r c is the this distance so, so 2 r c by r a equal to root 2 into 2 r a and that gives rise to r c by r a is root 2 minus 1,0.414. So, the radius ratio limit for 4 fold coordination is 0.225 for the tetrahedron and 0.414 for the octahedron.

Similarly, one can find out the other radius ratio limits, which at presented earlier in connection to another question. So, we have derived this particular limit, one can very simply derive the other limits in the same consideration of the geometric.

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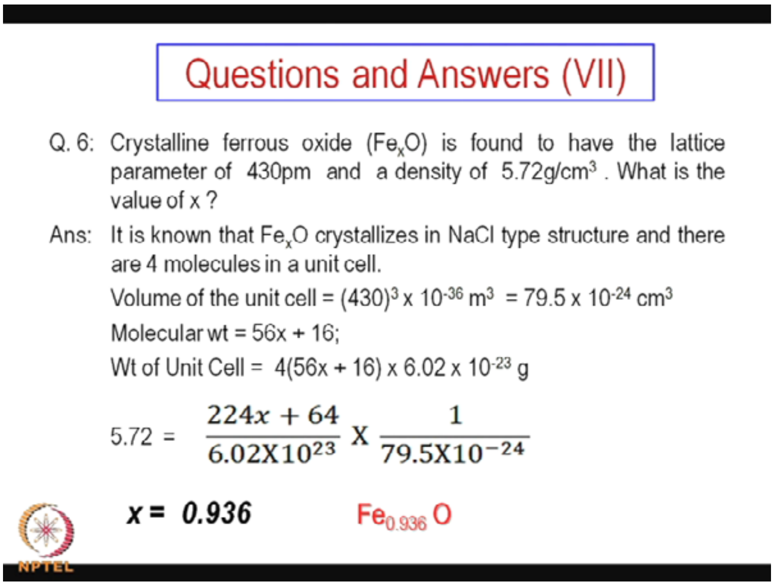

Questions and Answers (VII)

Q. 6: Crystalline ferrous oxide (Fe_xO) is found to have the lattice parameter of 430pm and a density of 5.72g/cm^3 . What is the value of x ?

Ans: It is known that Fe_xO crystallizes in NaCl type structure and there are 4 molecules in a unit cell.

Volume of the unit cell = $(430)^3 \times 10^{-36}$ m^3 = 79.5×10^{-24} cm^3

Molecular wt = 56x + 16;

Wt of Unit Cell = $4(56x + 16) \times 6.02 \times 10^{-23}$ g

$$5.72 = \frac{224x + 64}{6.02X10^{23}} \text{ X } \frac{1}{79.5X10^{-24}}$$

$x = 0.936$ $Fe_{0.936}O$

My last question, which I want to discuss is related the point defect; the question reads like this, the crystalline ferrous oxide F e x O; we have discussed earlier that it is (( )) oxide, which you can represented at F e x O is found to be have the lattice parameter of 430 pm is picometers or 4.3 angstroms and density of 5.72 gram per center meter cube. What is the value of x, this again not a very difficult question to answer, it is known that F e x O crystallizers in sodium.

This is very important, this is must be known F e x O crystallizes in the sodium chloride rocks salt type structure, and there are 4 molecules in a units cell. These information must be known for most of the structures, how many what is the crystal type, type of the crystal and how many molecules are there in 1 unit cell, that is very important requirement, which must be remember as much as possible. You will see in a spinal structure there are 8 molecules in a unit cell, there are many others where there are only 1 molecule per unit cell.

So, the volume of the unit cell because, the lattice parameter has been given; and this is a cubic cell, cubic structure FCC kind of structure; so this is 430 cube and that is nothing but, 79.5 into 10 to the power of minus 24 centimeter cube, that was picometer and this is, if you convert them, it will come to 10 to the minus 4 minus 24 centimeter cube. Molecular weight F e x O so, 56 is the atomic weight so, 56 x plus 16 and so, the weight of the unit cell is 4 multiplied by that into the Avogadro's number so, that becomes gram.

So, this is the weight of the unit cell and that is the volume of the unit cell so, density is simple. So, that is what is 5.72 equal to 224 x from here plus 64, 4 into 16, 64 and this is equal to 6.02 into 10 to the power 23 into this 79.5 into 10 to the power of 24 minus this. I think there is a mistake over there, this 6.02 must go no here is the mistake, it should be divided by divided by the Avogadro number, it is not multiplied by the Avogadro number.

So, that then it becomes like this so, anyway if you can change this it is a simple thing, if there is a mistake if there is a mistake you can rectify it and it will be ultimately the x will come from this equation, x will come as 0.936 0.936. So, x becomes F e 0.936 O so, that is how that is in principle you can find out from the density and the the lattice parameter what is the value of non stochometry, I am sorry there is a little mistakes here please correct it. So, that completes basically our discussion on the crystalline defects, already we have discuss the crystal structures and also, we have discuss few questions and their respective answers. So, with this we come to the end of this discussion, and.

Thank you very much for your attention.