Materials Science

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Lecture 12

Crystal Imperfections

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Crystal Imperfections

So far we have seen the short range arrangement of atoms in a solid and when this short range arrangement which is dictated by the nature of the bond does not continue in the solid in all the three dimensions over long distances, the solid becomes non-crystalline. However if it continues in three dimensions all through the long range, solid is crystalline. Having had a look at the crystal structures or this kind of arrangement in crystalline and non-crystalline states, now we shall talk about real crystals and real crystals are having imperfections in them, what I refer to as crystal imperfections.

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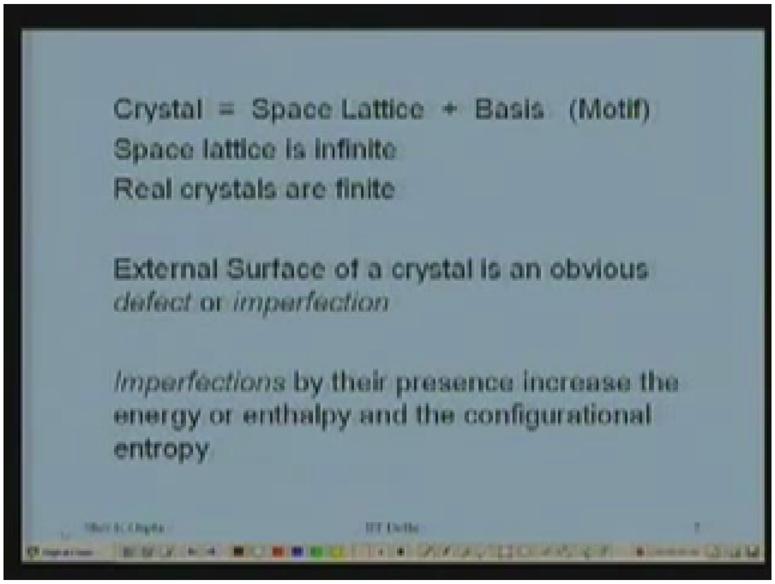

Crystal = Space Lattice + Basis (Motif)
Space lattice is infinite
Real crystals are finite

External Surface of a crystal is an obvious *defect* or *imperfection*

Imperfections by their presence increase the energy or enthalpy and the configurational entropy

So today we shall look at crystal imperfections. As we define crystal this course, the space lattice which is an infinite array of points in three-dimensional space, plus the basis which is a motif which consists of some number of atoms or molecules which form a group and that arrangement, that orientation of the group continues in three dimensions at each lattice point. That is what we call the motif.

From these definitions, space lattice which is an array of points in infinite area of points, the definition of the crystal should be infinite because on every lattice point a group of atoms which is motif is situated and this arrangement of points in three-dimensional space is infinite. So ultimately what should I end up with the crystal which is infinite. I do not have any solid or a crystal which is infinite in nature. They are all very, very finite and that are the real crystals.

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Now when I talk about a real crystal, let us say a cylindrical crystal like this, you can just this pen you can consider a cylindrical crystal. If you look at the cylindrical crystal, the cylindrical surface, the atoms, whatever the lattice points were there, on those lattice points the atoms or group of atoms is sitting but it is not continuing beyond the cylindrical surface. So what happens to those atoms which are there on the cylindrical surface? They have neighbors and the bonds formed inside the crystal but outside they do not have anything.

That does not mean the space lattice does not exist, space lattice exists. But that motif is not sitting on those lattice points. As a result these atoms which form the surface or which are on the exterior, they do not have bonds continued or they do not have neighbors continued this space. They have neighbors within the crystal inside. And you know that whenever a bond is formed, energy of both the atoms is lowered. That is the bond energy.

In this case you can say that you had an infinite crystal from where in this region you have removed the neighbors. Once we have removed the neighbors from the cylindrical surface of the crystal, all these atoms on the surface have higher energy as compared to those which are inside the cylinder. And this constitutes an obvious imperfection of the crystal because in a crystal I have a region which is the exterior, which is its exterior and as all the atoms which I have higher energy than the atoms which are inside. So therefore it is an imperfection. Right. So that is what I mean by the imperfection. Now we shall see that therefore the external surfaces of a crystal become the obvious imperfections. Something….

The external surface of a crystal becomes an obvious defect, an obvious imperfection. In other words, I can now also say that what I have discussed about this external surface, it could be, could have been a flat surface, not a cylindrical surface. These by their presence what I am calling the imperfection, they are like the external surface increasing the energy of the system, energy of the crystal, other words enthalpy of the crystal, a bond formed lowers the enthalpy. Bond broken, therefore increases the enthalpy.

At the same time it is likely to add to the configuration entropy. So these imperfections are increasing the enthalpy, they are increasing the configuration entropy. It all depends now whether the combination of the two can lower the free energy or not. If it can lower the free energy, I shall have the stable (imper) configurations or imperfections in the material. If not, if the imperfection is present, it would like to get out of the crystal and lower the free energy of the crystal in case it is present. Right.

Like the external surfaces we also have imperfections in the interior of the crystal. Like we have seen just the, what has happened to the atoms on a surface, they do not have neighbors and therefore the energy is gone up. Like that there could be regions inside the crystal where the energy of the system goes up. And because of that the configuration entropy can also go up. So therefore we have to see those situations inside the crystal.

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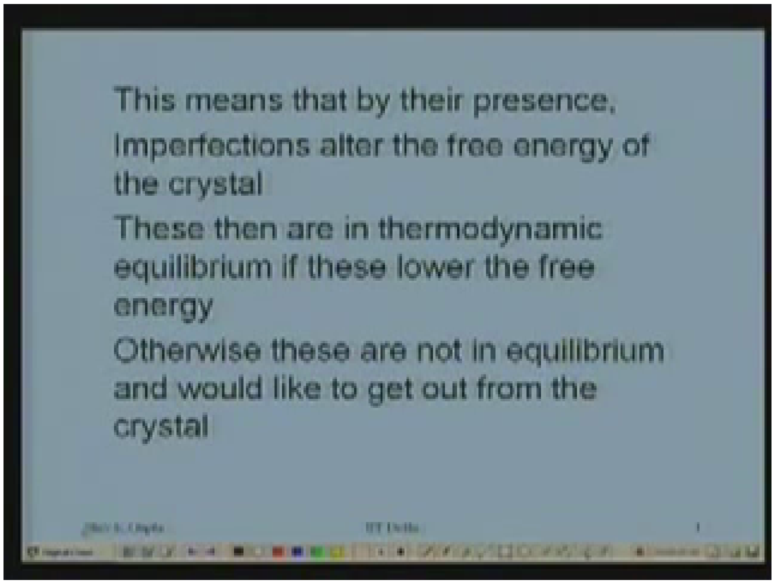

This means that by their presence, Imperfections alter the free energy of the crystal

These then are in thermodynamic equilibrium if these lower the free energy

Otherwise these are not in equilibrium and would like to get out from the crystal

That is what I was trying to discuss. By their presence there is, once there is enthalpy increase, at the same time there is configuration entropy increase. The delta G which is delta H minus T delta S, it could be less than 0, it could be more than 0. If it is more than 0, by their presence imperfections are increasing the free energy. If it is less than 0, it is lowering the free energy. So if the lower and bring it to a situation where the, for that configuration I have the minimum free energy, it is stable equilibrium.

And these imperfections are in thermodynamic equilibrium. Otherwise these imperfections will not be in thermodynamic equilibrium, and therefore would always have the tendency wherever they get a chance or whenever they get a chance to get out of the crystal. Okay.

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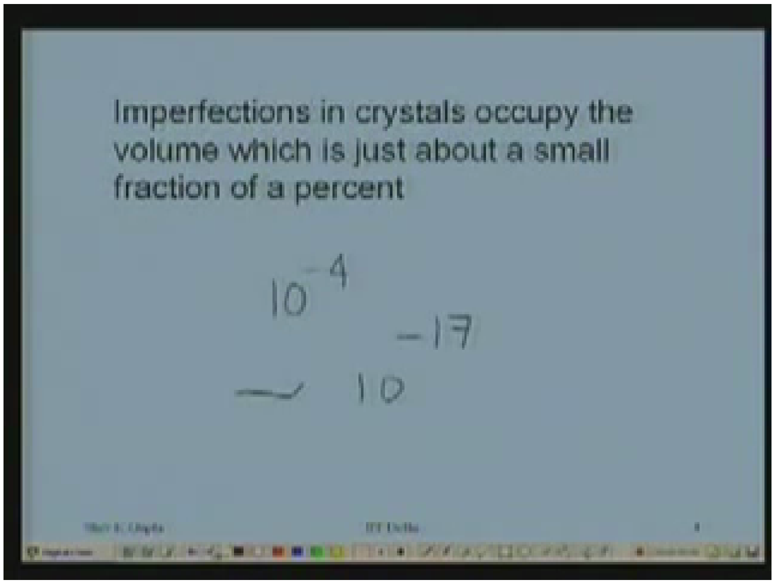

Imperfections in crystals occupy the volume which is just about a small fraction of a percent

10^{-4}

$\sim 10^{-17}$

Now another thing which is in observation that the imperfections which I have talked about, like I talked about the surface of a crystal. If you work out the area of these atoms which are there on the surface, record the word, that means and the thickness they occupy of the crystal, you can work out the volume. So that volume of the crystal is in defect region or in imperfect region. If you consider this as the fraction of the total volume of the crystal, it shall turn out to be fraction of a percent. It shall turn out to be a fraction of a percent, so very small volume.

Even if I consider those which are going to be, I am going to talk about inside the internal defects, internal imperfections or interior of the crystal, they also do not constitute a huge amount of the volume of the crystal as imperfection. These are usually a small fraction and this fraction can be very high, 10 to the minus 4, is a very high fraction. And such high fractions sometimes we do see around just before the melting point.

Low temperatures, I may have less of them. But there are certain other kinds which are low temperature, unable to go out. So in other words what I am trying to say is the fraction of a percent, of a particular imperfection or fraction of volume occupied by imperfection is very small. At room temperature I might have the fraction of the order of 10 to the power minus 17, that is one out of 10 to the power 17 is the volume which is defective or imperfection.

So very small which we are talking about, small volume. If such a small volume as I said earlier as engineers we are interested in the working of the material, not in the regress of these properties and these things, so why am I concerned about such small imperfection or such small volumes of imperfections in the crystals? I am concerned because of the reason they are properties of the material which are sensitive to the structure.

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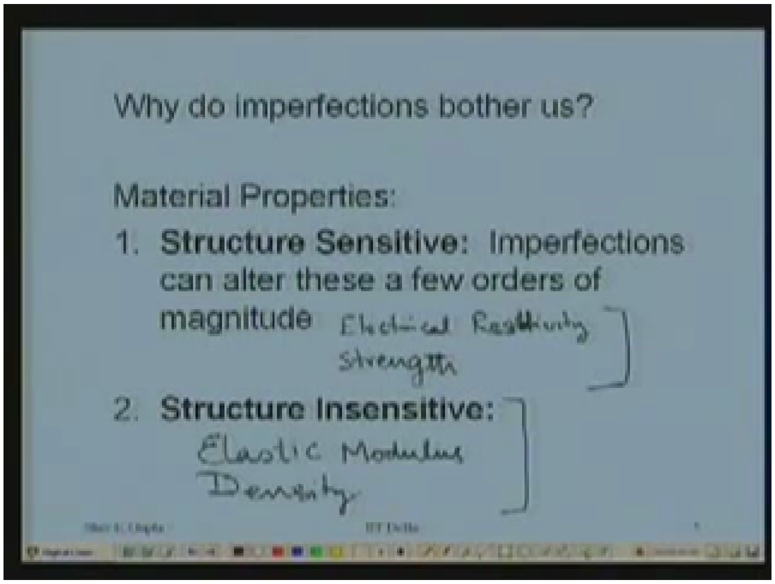

Why do imperfections bother us?

Material Properties:

1. **Structure Sensitive:** Imperfections can alter these a few orders of magnitude
   Electrical Resistivity
   Strength
2. **Structure Insensitive:**
   Elastic Modulus
   Density

The material properties in general can be classified two kinds: one are structure sensitive, that is why I am worried about. In these the imperfections can alter a few orders of magnitude the value of the property. Say volume fraction of the order of 10 to the power minus 2 or 10 to the power minus 5, in that range the volume fraction or the defect can enhance the property by two orders of magnitude.

Like let us say for example, electrical resistivity is 1, right. And then strength of the crystals is another one. Electrical resistivity, the strength, these are structure sensitive properties, right. But then there are other properties which are structure insensitive. Say for example, elastic modulus. If the defect is present in the order of half a percent, modulus might get affected to that extent, that is all or the density of the solid.

Within copper you add 10 percent zinc, density might get shifted towards zinc about 10 percent or may not be. So that is, what I am trying to say is the effect on the density of the solid or the crystal, elastic modulus, some properties where effect is marginal of the same order. And therefore we are not really concerned so much about the defects there but we shall have to look at the role of these defects there as well. But in here it is very important.

Talking about the electrical resistivity, talking about the strength of the solid, it is very, very essential for us to understand because the presence of the defects can affect them a few orders of magnitude. You understand, suppose I have a material like which has its strength of the order of 250 megapascal. It is possible for me by introducing these imperfections to make it to 2,000 megapascal and order of magnitude change, it is possible.

Aluminum alloys, it is possible for me to change their strength from, to the tune of 70 megapascal to maybe 550 megapascal. So this is what the imperfections are doing to the strength. Similarly the electric resistivity, like a semiconductor which may have its resistivity in the range of 10 to the power minus 4, minus 5 on meter can be made to go up to the order of 10 to the power minus 2, minus 1 on meter. Right. So that is, these are the things which can be a taking place in the properties, this change in property a few orders of magnitude.

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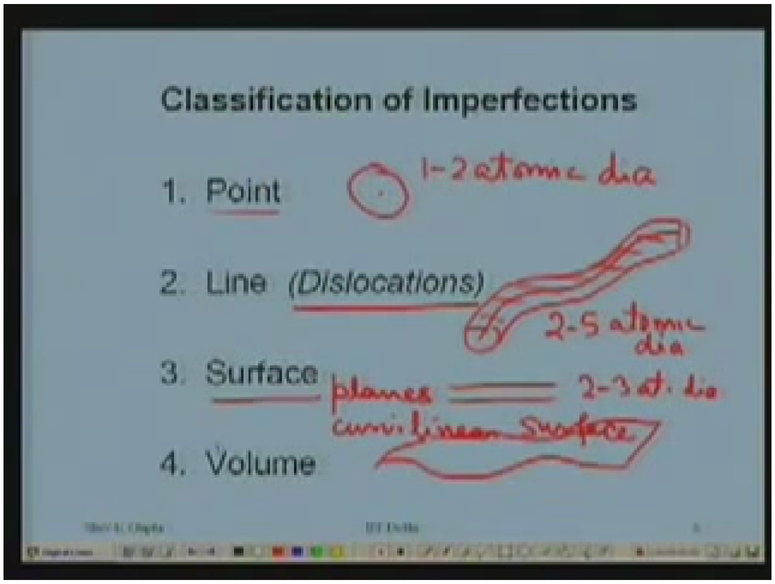

Classification of Imperfections

1. Point
2. Line (Dislocations)
3. Surface
4. Volume

Now before we go to look at the interior defects, rather the exterior defect which I refer to the external surface, the inside, the geometry of these defects can be talked about like we talk about in geometry a point, a line, a plane or a surface and then the volume. So when talk about this geometry of imperfection which is a point imperfection, point imperfection is a volume. This is a small volume centered around a point which could extend from 1 to 2 atomic diameters.

It is that way not just a mere geometrical point. It is a small volume around it. Right. But we call it a point defect because is geometrically localized at that point. Similarly there could be lines,

lines could be straight lines, line could be curved lines, is a curvilinear line usually and we give them a special name. These are called dislocations. Again around a line, let us say this is some line, there would be a volume which is a defect region.

This volume or this diameter of the cylindrical region could extend from 2 to 5 atomic diameters. Again it is a volume. Okay. Similarly a surface, interior surface, there are two types, we shall see them. They are planes, means crystallographic planes but they will have certain thickness. This could also be about 2 to 3 atomic diameters. Or this could be a surface, curvilinear surface. Like the cylindrical surface we talked about, it could be just something like this, some surface extending like that.

So there could be surfaces and there could be volumes. Volume usually we will not be devoting much time but those of you who have gone through the manufacturing process course, they must have shown you in the castings, the voids, pores what you call, the porosity in the solid. There is no material there, there is no atoms there. It is on lattice points, now they are there but atoms are not there.

It is a volume extending into few millimeters or a fraction of a millimeter if it is a very fine pore. So this is what I mean by volume defect or in a crystalline solid I may have an impurity like a slag included like in steel or in copper. That is a glassy phase, it is a glassy material, a small volume which could be irregular shape and that is a slag inclusion. It is a hard and brittle material, another voice a tough, ductile material. Okay. That is a volume imperfection.

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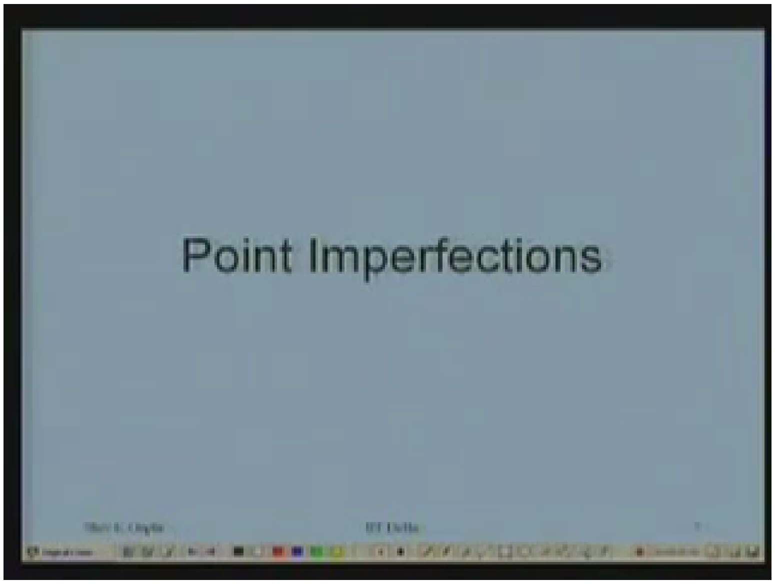

Point Imperfections

Beyond that we will not be talking about the volumes but we shall talk about the three and we start today with the first one, the point imperfections. That is what we shall try to look at today, the point imperfections which are geometrical points.

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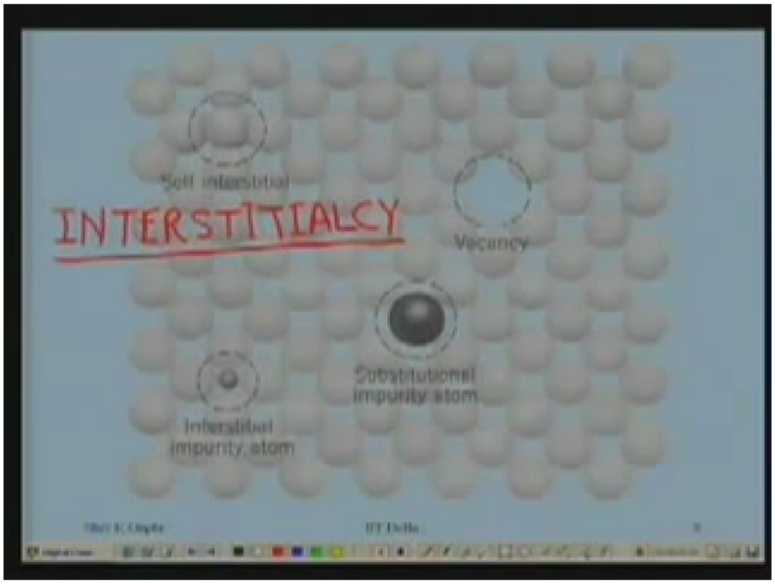

And I am showing you some of these here. This is let us say a kind of a metallic crystal. In this metallic crystal, first of all let us look at this point where no atom is sitting. There is a site for the atom to sit but atom is not sitting. As a result, this bond length has gone up. Distance between the second neighbor, here is gone up. So all these atoms which are here around a circle, they have a higher energy, their neighbors are disturbed, bonds are broken, so enthalpy has gone up here in this region.

Because the enthalpy going up, we shall also see there is an increase in entropy as well. Right, configuration entropy particularly if I am maintaining the constant temperature. This since it is not there or this atomic site is vacant, I simply call it by the name vacancy. Sometimes people do call it vacant site or it can be called simply the vacancy. Okay. That is the name we give to this. Then I have already talked about solid solutions. One, the interstitial kind, other the substitutional kind. It is a different kind of an atom sitting in the matrix.

Interstitial impurity atom, now I am calling it an impurity, if it is not wanted. Sometimes they add it purposely, even then you can call it impurity because not the matrix atom. And it is sitting in the interstitial void, right. Thereby they are compressing all the neighbors here, the electron clouds. And in this volume which I have shown here, the energy of the material has gone up because the electron clouds are compressed, so the enthalpy has gone up. This is called an interstitial defect or interstitial impurity atom.

This is a crystal imperfection, here you see the crystal is prefect but right not here. Same way the substitutional impurity atom which could be bigger or could be smaller. If it is bigger, it causes compressions in this volume. If it is smaller, it causes tensions in this volume because electron clouds have to extend to form the bond with it, a smaller one. And for a bigger one, they get compressed. So again there is an increase in enthalpy here. This is a substitutional impurity atom. And this can be, as I said already two kinds, bigger one and the smaller one.

Then we have a self-interstitial, little less likely though but it is possible. The atom of the same matrix is sitting into the (vaca) rather the lattice, sorry, the void space, interstitial void space. If you recall the closed-pack structures when I talked about, interstitial void space is tetrahedral and octahedral. Bigger one is the octahedral with 0.14 size. That is 41.4 percent size. But this is the 100 percent size which is squeezed in 41.4 let us say. It is going to squeeze the neighborhood very much and this region would be little more volume where the bonds are strained.

And therefore there is an extra enthalpy here because of that. Enthalpy caused by this, increase caused by this is very large. It is called self-interstitial. Self-interstitial defect is also named as interstitialcy defect. ti-ti comes twice, so interstitialcy defect. Okay. So that is the self-interstitial.

So these are the kind of defects we generally see in metallic crystals or the alloys. In covalent crystals where the sharing of electrons is taking place, we may see some defects like this. We can see it is quite possible.

“Professor-student conversation starts.”

Student: Sir….?

Professor: Yes, please.

Student: In the substitutional, atom is smaller now, and the even atom is the difference between data and interstitial impurity atom?

Professor: What is the difference between interstitial and the substitutional atom? This is the question he is asking. An atom is interstitial if it is sitting in the interstitial void space which is not the regular atomic site in the given matrix crystal. If the impurity atom or the substitute atom is going to substitute for the matrix atom, it is the substitutional atom. Now bigger and smaller, when I talk about the interstitial atom, interstitial size is just I said 41.4 percent. I can have 60 percent or 70 percent of the size.

But when I talk about substitutional impurity atoms, sizes may not be differing by 15-20 percent or maybe 30 percent more. That is all. I cannot have much more difference there. The size becomes more, the size difference becomes more, it is more likely smaller one will go in the interstitial only. Okay. It is because the tendency to have as many electrons you have to must orbit as possible because no way they are going to make it 8 metallic crystals.

“Professor-student conversation ends.”

In covalent crystals this vacancy is possibility. But it will create lot of enthalpy because SP3 bonds are not going to be there. There are no neighbors to form the bond. Enthalpy increase will be tremendous. Right. It is so high that it may be very difficult for me to see a vacancy in a diamond crystal but not so high in silicon and germanium which are down the particular group. And as I go down in a group, its covalent nature of the bond is decreasing. Okay. And therefore that is not so difficult there.

But in diamonds it is going to be very large enthalpy increase and I may not see many of these there. I may not see many at room temperature. But this kind of defect is quite possible, substitutional impurity atom which we shall see in semiconductors like silicon where I dope it with phosphorous or I dope with it boron, I dope it with gallium and things like that. So this doping which I do, it will be a substitutional impurity atom.

SP3 bonds are still satisfied. What is not (satis), what is going to be affected is the number of electrons around this may not be 4 or may not be 3 or may not be 4. Maybe 3 or it may be 5 or it may be 6. So that is depending upon what impurity I am adding, that is going to make the difference. But 4 bonds can still be formed. However this interstitial defect is rather very difficult to have in covalently bonded crystals like diamond, silicon, germanium. Why it is difficult to have, not possible to have?

More than 4 SP3 bonds are going to be there if it goes and sits in the interstitial void space. That is just not allowed. 4 SP3 bonds is low, it is sharing take place and it is localized sharing, it is not delocalized sharing like metals. So therefore this is not possible, rather improbable to have this kind of defect in covalently bonded crystals. Same is true about the self-interstitial. You are not likely to see these. Most likely you will this kind of defects or you can see these in covalently bonded crystals. So vacancies could be there. Substitutional impurity atoms can be there.

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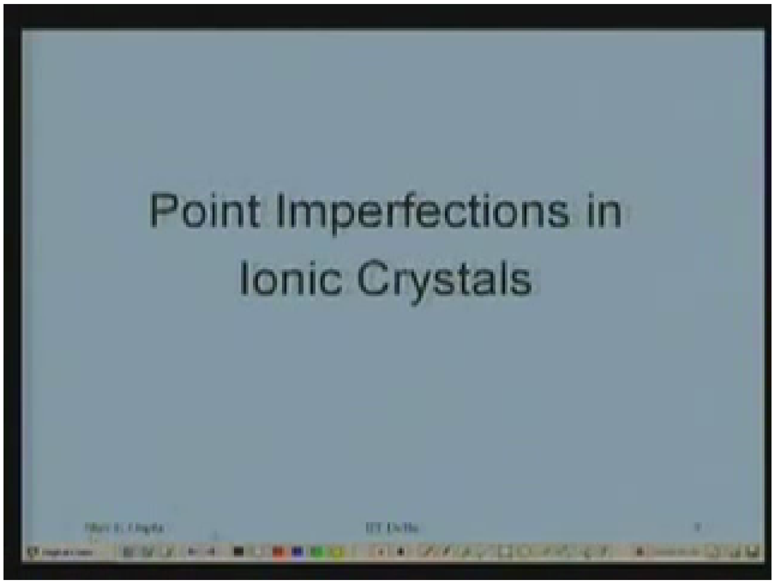

Point Imperfections in
Ionic Crystals

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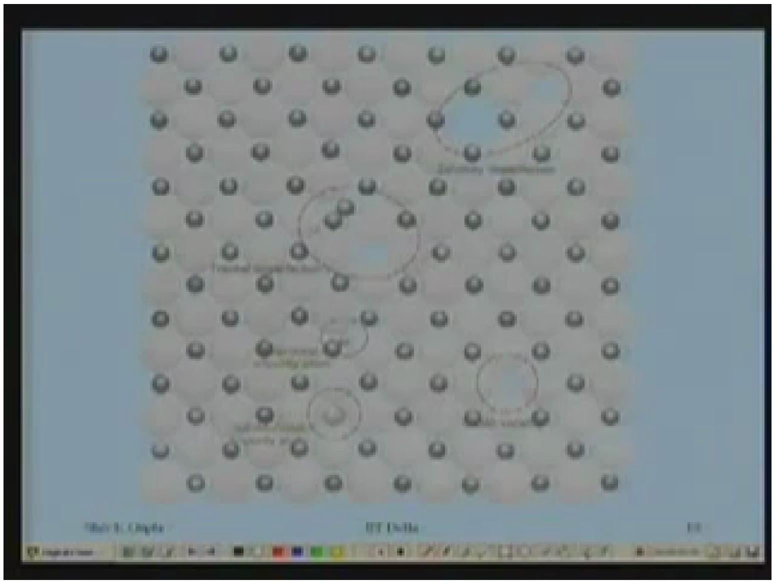

Now let us look at the point imperfections in ionic crystals. I try to make arrangement of an ionic crystal by having two different kinds of spheres, smaller ones, the dark ones and the lighter ones, the bigger ones. The anions and the cations, okay. In this it is possible for us to have a cation missing from its site. But once the cation goes out from its site, it takes with it the charge, positive charge. To make the crystal electrically neutral, I must also remove the negative charge, the anion, not necessarily in the neighborhood it could be from far apart, somewhere in the crystal.

So and when a cation is gone, anion is also gone. And the combination forms a pair. This pair of vacant locations of cation and anion is called the short-key imperfection or short-key defect. Now it is all right, like the structure I showed like for sodium chloride, it is I say that one sodium ion is missing, one chlorine ion is missing. And one positive charge and one negative charge, both are gone. Crystal is electrically neutral, no problems.

But if I have calcium chloride, CaCl2, one calcium ion is missing. I must have two chlorine ion missing simultaneously. So the pair would consist of two chlorine vacancies and one calcium vacancy. In other words, when I talk about the pair, it is a formula unit. Sodium chloride, one sodium, one chlorine. Calcium chloride, one calcium, two chlorine. One formula unit is not there sitting on its site, that is what is short-key imperfection. Is that clear?

The other most commonly seen defect is Frenkel imperfection whereby a cation displaces itself from its regular site and goes and sits on another interstitial void. This is its regular site and this is not its regular site. So it goes and sits another interstitial void. Now that it is going and sitting close to the next cation, but some of the interstitial void space (nearby) in the neighborhood is going and sitting there. I am talking about the three-dimensional structure.

So this displacement of a cation from its regular site to an interstitial site is what is called a Frenkel imperfection. In here there is no problem of the charge neutrality because cation has to be there in the crystal, it is there. But it is there somewhere else, not its regular site. So that this periodic repetition is what is disturbed by its displacement from this location to a neighboring interstitial void or some other void space. So that is what is called a Frenkel defect.

Now the other kind of defects, it is also quite likely, is a substitutional impurity atom like this. Say for example in sodium chloride I add potassium chloride. So chlorine goes to replace the chlorine but potassium goes to replace the sodium, that is what it is. It substitutes for the sodium. That is a substitutional impurity add term of the cation. Right. That is another possibility. The impurities can be present like that.

Now then there could be merely a cation vacancy and the crystal is still electrically neutral. Cation vacancy, crystal is still electrically neutral. This kind of a defect in ionic crystals is a defect structure, is caused by the fact cations have more than one valencies. Such are the cases when we have cations from the first long period or the second long period or the third long period, (())(35:21) where the atoms showing more than one valency.

Say for example, ion can be seen in valency 2, can be seen in valency 3. If I have FeO, iron oxide where all the ions are supposed to have double valency, valency 2 plus, but if say I have two ions introduced which are the valency 3, to make it electrically neutral one of the bivalent ion should be missing from its location. One of the bivalent ion should be missing from its location, that is what it is, so that it becomes electrically neutral.

But a crystal, the material you have is no more the formula FeO. If it is Fe 1 minus xo, is less than 1. That x can be very small fraction of 1. Okay. So that is possible, that happens in ionic crystals. That happens in all these compounds or (())(36:37) matter usually. Okay. I can also have an interstitial impurity atom like this, a small interstitial impurity, it goes and sits in the interstitial, is again some kind of a smaller cation having some charge on it.

That is going to go inside, the impurity can be there. If again the valencies of these is not same everywhere, they are showing more than one valencies, it is possible for something else to come in additionally. So that is again to make it electrically neutral. Okay. So these are the kind of defects which we have but most commonly if I talk of a pure crystal, I would have this or that. Either I shall have short-key imperfections or I shall have Frenkel imperfections.

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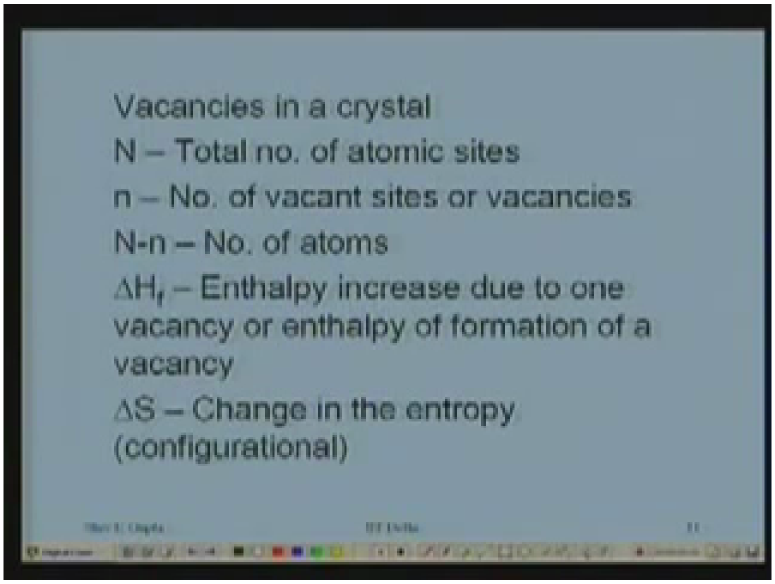

Vacancies in a crystal

N – Total no. of atomic sites

n – No. of vacant sites or vacancies

N-n – No. of atoms

ΔH_f – Enthalpy increase due to one vacancy or enthalpy of formation of a vacancy

ΔS – Change in the entropy (configurational)

Now I will show the how increase in enthalpy and corresponding increase in configuration entropy and what is result of this on the free energy of the material. Let us say I consider the situation of vacancies in a crystal. A simplest thing to understand and do, okay, because these vacancies could come about in the material without any external assistance. If there is atom not sitting in a place, I do not have to do anything for this. If a substitutional atom is sitting there and copper and zinc atom is sitting, zinc atom has to be added from outside in a pure copper crystal.

Where does it come from? On its own it cannot come. But vacancies can be there, vacancy can be present on its own. Atom for example, can just oscillate and oscillation can jump over the face. And wherever it has come from, there it becomes a vacancy, it is all close to the surface only. Then from something from inside can come and jump into that location during oscillations.

Then vacancy can go down further. So vacancies can be there in the crystal. I will show that how the vacancies get created or they can get annihilated from the crystal.

Number of ways it can happen. But no external assistance is required. Nothing has to be added from outside. That is why I am considering vacancy. It is a very simple situation. Let us consider N as the total number of atomic sites in the crystal. Out of these total number N, let us say n is the number of vacant locations or the vacancies. So I have total N minus n, number of atoms in my system. And n is the number of vacancies. We will show you that n is much much greater than N usually. So n is the number of vacancies, N is total locations, N minus n is the number of atoms.

And I showed you that there is going to be either increase in bond. Usually in this case bond lengths will increase near about there in that region. And therefore the bond energies go up and enthalpy increases of the crystal because of one vacancy, let me call this delta S at some f, that is enthalpy increases due to one vacancies or we simply call the enthalpy of formation of a vacancy. When a vacancy is formed in a crystal, delta Hf is the energy increase of the neighboring bonds and that is the enthalpy increase.

And correspondingly number of configuration is the system can go up and that change in the entropy is configuration entropy. Okay. Let us call that delta S, I am not putting the subscript c here. Only delta S let us say because I am trying to see that at a given temperature. The vacancy is there, vacancy is not there. So thermal entropy is not coming into the picture.

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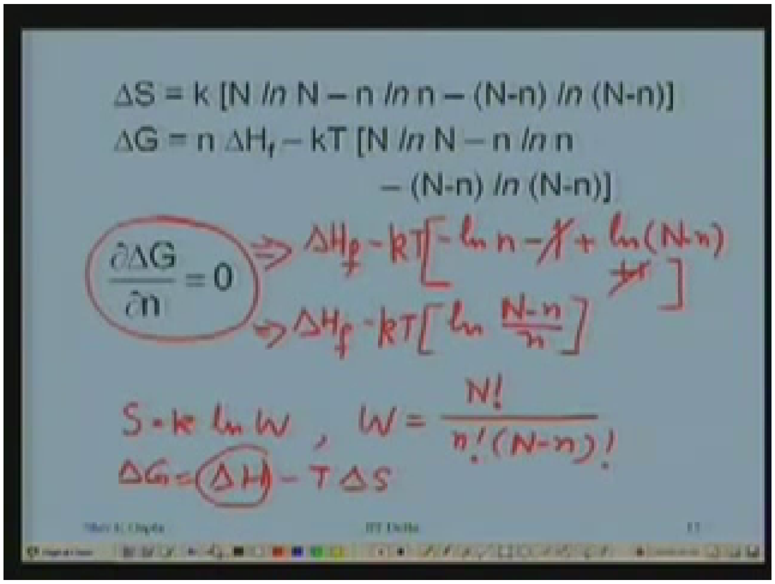

$$\Delta S = k\,[N\,ln\,N - n\,ln\,n - (N\text{-}n)\,ln\,(N\text{-}n)]$$

$$\Delta G = n\,\Delta H_f - kT\,[N\,ln\,N - n\,ln\,n - (N\text{-}n)\,ln\,(N\text{-}n)]$$

$$\boxed{\frac{\partial \Delta G}{\partial n} = 0} \Rightarrow \Delta H_f - kT\left[-\ln n - \cancel{1} + \ln(N-n) + \cancel{1}\right]$$

$$\Rightarrow \Delta H_f - kT\left[\ln \frac{N-n}{n}\right]$$

$$S = k \ln W, \quad W = \frac{N!}{n!\,(N-n)!}$$

$$\Delta G = \boxed{\Delta H} - T\Delta S$$

So I can write delta S, we have done this before. k times, k is the Boltzmann constant, times N log N minus n, natural logarithm of n minus, N minus n, logarithm of N minus n. See this has come from where, this has come from the configuration entropy of the mixture. Mixture of atoms and vacancies which we have talked about earlier, k log W, and W is equal to N factorial, this total number of sites, divided by n factorial which is number of vacancies, and N minus n factorial which is the number of atoms.

And when I take the log of this, use the Stirling's approximation, I can write that. n is very small but in terms of numbers when I talk about 10 to the power 23 atoms, it is a very large number. Okay. Even if it happens to be a fraction of 10 to the power minus 17, out of 10 to the power 23 atoms, how many vacancies will be there? 10 plus 6, and 10 plus 6 is much much greater than 1. I can use the Stirling's approximation.

All right. Then I can write down the free energy, delta G which is delta H minus T delta S. Delta S I have already got, so delta H is what I have to work out. Delta Hf is the enthalpy of formation of one vacancy. Since I have n vacancies, so it is n into delta Hf minus delta S into T, so k into T, within bracket N log N minus n minus n, log N minus n.

If it is reducing or making it to for certain number the minimum, I can find that or by differentiating this with respect to n and putting that derivative to 0. We do that, let us see what do we get. All right. Start here only, when I differentiate this with respect to n, I get delta Hf minus, first term shall give me 0 because N is a constant. Then I differentiate the second term, I get minus logarithm of n. And second term when I differentiate, I will get minus n by n, that is minus 1.

Similarly if I differentiate this, I shall be getting plus because minus n I have differentiated, it will become minus minus 1 and logarithm of N minus n. Similarly when I differentiate this, it will give me 1 upon N minus n which will cancel with this. But the derivative of this will be again minus 1. So I shall be getting plus 1. All right. This minus 1 cancels with this plus 1, and the bracket gives me delta Hf minus kT logarithm of, all right, that is what I get delta G. And this I have put equal to 0. If it is going through a minimum, let us do that what do get.

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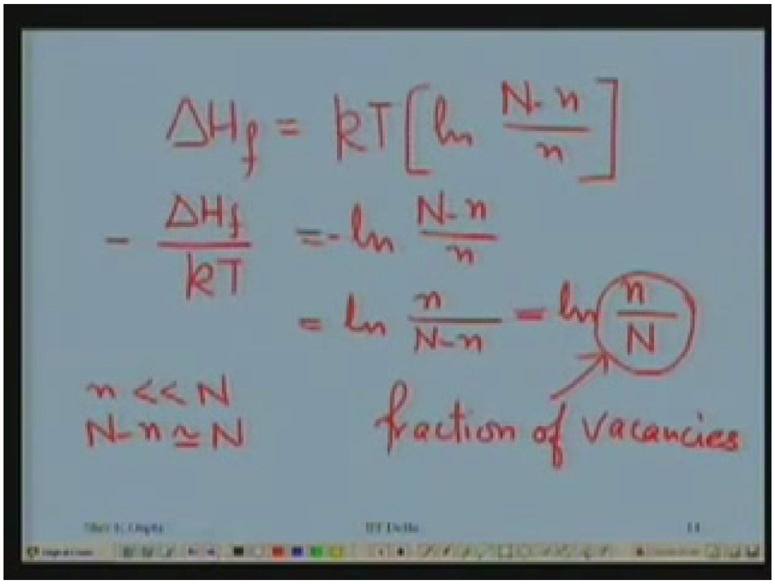

$$\Delta H_f = kT\left[\ln \frac{N-n}{n}\right]$$

$$-\frac{\Delta H_f}{kT} = -\ln \frac{N-n}{n}$$

$$= \ln \frac{n}{N-n} = \ln \boxed{\frac{n}{N}}$$

$n << N$

$N-n \simeq N$

fraction of vacancies

All right. Let us rewrite this. All right. Let me take minus on both sides. So this would become logarithm of n upon, now if I assume that n is less than N, so then I can take N minus n approximately equal to N. If I do that, this becomes logarithm of n upon N. And this I refer to as fraction of vacancies. All right. So we got this natural logarithm of fraction of vacancy is equal to minus delta Hf by kT. Again, rewrite this whole term again. All right, it is causing problem for me.

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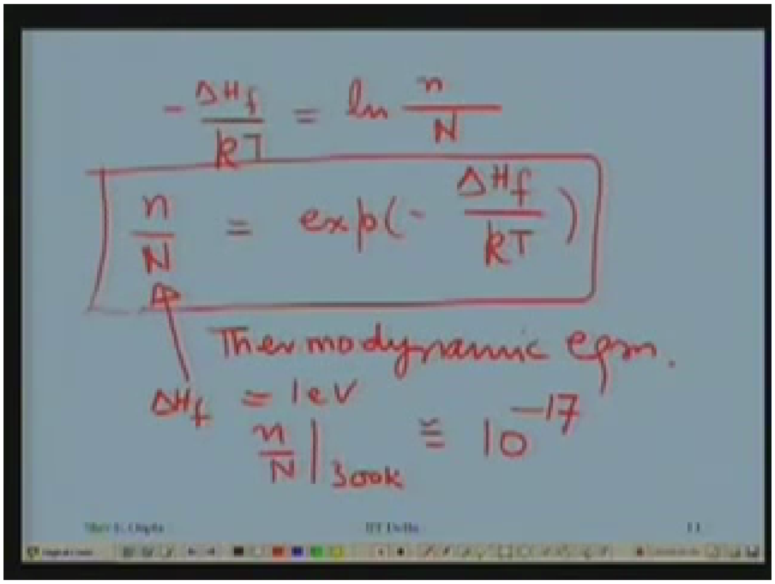

$$-\frac{\Delta H_f}{kT} = \ln\frac{n}{N}$$

$$\boxed{\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)}$$

Thermodynamic eqm.

$$\Delta H_f = 1\,eV$$

$$\left.\frac{n}{N}\right|_{300K} \cong 10^{-17}$$

Okay. Right. So we can rewrite this. We have got some minus delta Hf by kT is equal to, I take exponential on both sides, then I can write n upon N equal to exponential of minus, you can find out the second derivative and see that, that second derivative is positive. In other words, this is the minimum. This makes the delta G minimum. There is a fraction of vacancies present in a crystal which shall make it minimum, the free energy to be minimum. Therefore it is in (thermodyn), this fraction is in thermodynamic equilibrium.

Now just to show you that, as I talked about n is the very small number. This fraction you work out, usually Hf is in the range of about an electron volt, it is 0.8 electron volt to about 1.2 electron volt. And kT at room temperature, 300 kelvin is about 1 upon 14th of an electron volt. So exponential of minus 40 is of the order of 10 to the power minus 17. So this number for delta Hf equal to 1 electron volt, n by N at 300 kelvin is equal to approximately 10 to the power minus 17. So you can see that n is much smaller number at room temperature. Most crystals are in this range at room temperature.

“Professor-student conversation starts.”

Professor: For diamond this delta Hf is 2 electron volts because of a very strong SP3 bond. When delta Hf is 2 electron volt, what shall be this number?

Student: 10 to the power minus 34.

Professor: 10 to the power minus 34, very right. That means to see one vacancy, you must have 10 to the power 34 carbon atoms in a diamond crystal. Work out the size of the crystal, how many tons of diamonds you should have to see one vacancy at room temperature? 10 to the power 34 atoms of carbon. 6 into 10 to the power 23 atoms just weigh 12 grams. Okay. So you can see how many grams you need. I leave it to you. It is turn out to be in tons, okay.

"Professor-student conversation ends."

All right, having had a look at these, are the defects which are in thermodynamic equilibrium, by and large point defects are in thermodynamic equilibrium. As I said, already I showed the point defects, so they are in thermodynamic equilibrium. They are there in all real crystals. Now on what defects I talk of, whether I talk of the line defects or I talk of the surface defects, the dislocations at the surface defects are the various names we will give them.

They are never in thermodynamic equilibrium, let me tell you that. That is the enthalpy increase by their presence is not getting compensated by the increase in the configuration entropy. Like it was happening in the point defects. So they are not in thermodynamic equilibrium but in real crystal they are present, they are there. And we cannot get rid of them. We try but they can be minimized, they can be reduced but they come out in the crystal at various occasions while handling, while using, while manufacturing. But we are not able to get rid of them, so therefore we have to understand these though they are not in thermodynamic equilibrium, let us understand that.

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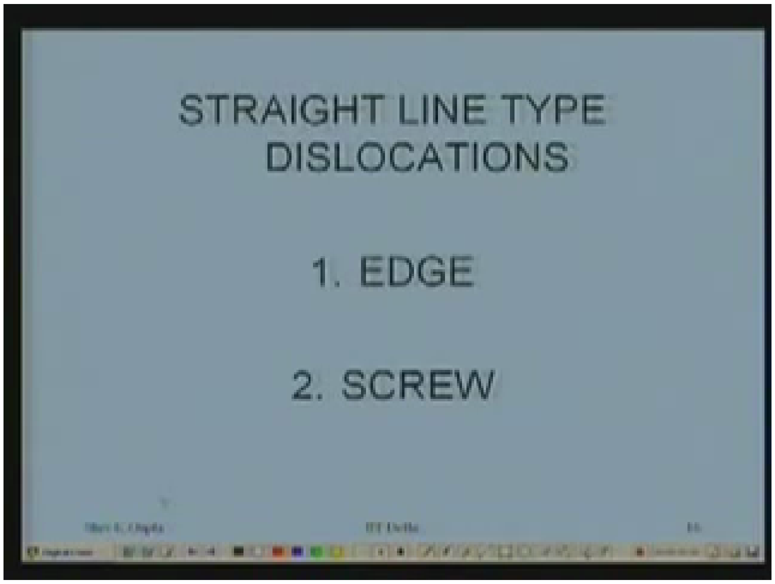

STRAIGHT LINE TYPE
DISLOCATIONS

1. EDGE

2. SCREW

Dislocation is said, the line defects. To understand these line defects, we shall start with straight lines first and then we shall move onto the curvilinear lines which are the general situation in the crystal. Two straight lines are named, one is edge, another is screw. We shall try to look at the edge and then we shall move onto the screw. Okay. First thing we shall look at is the edge.

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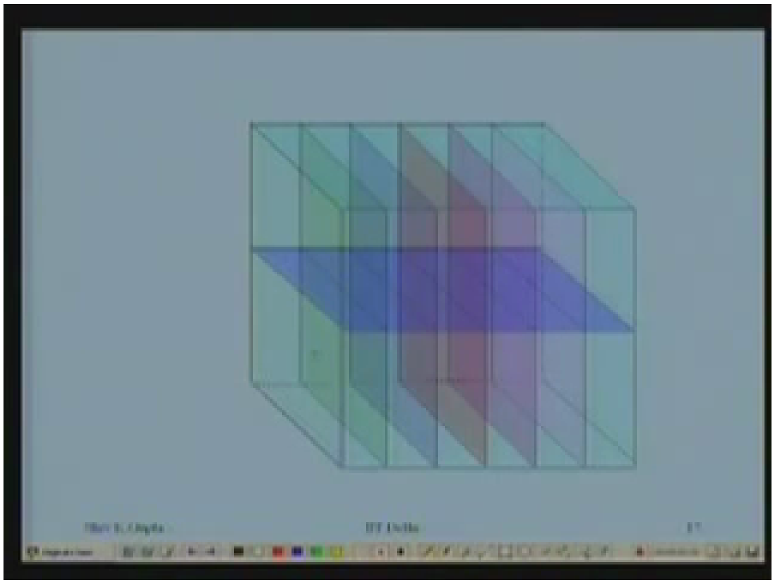

In here, I show a simple cubic crystal, not very complex situation. I demonstrate this with the help of a very simple crystal, is a simple cubic crystal. In here I have shown the vertical planes arranged parallel to each other at the regular spacing. And these are the vertical planes you see.

These are the vertical planes, one, two, three, four, five, six, seven. This is 6 unit cells you can say in between. But of course I am showing these.

And these are all full planes, complete planes from top of the crystal to the bottom of the crystal, each one of them. In the middle I have shown one more plane which is perpendicular plane, somewhere in the middle. And these are the lines which I show here, they are the intersection of these vertical planes with this horizontal plane, is a crystalline arrangement. The planes are going from top to the bottom of the crystal, they are complete planes. These are called complete planes. Such a crystal is perfect, as of base it does not have any line imperfection.

All planes are going from top to bottom. No problems. Problem arises when one of these planes let us say in the middle this one, below this plane, horizontal plane here does not have this part. No atoms are placed here. Then no atoms are placed here, that is in this area. In this area no atoms are placed. What would happen? The atoms which are placed in this plane, they become too far, they will try to come closer because they will like to form bonds. And they come together because this is, these atoms in this plane are missing. Other word, this plane I call an incomplete plane. Let us see what happens when I have an incomplete plane.

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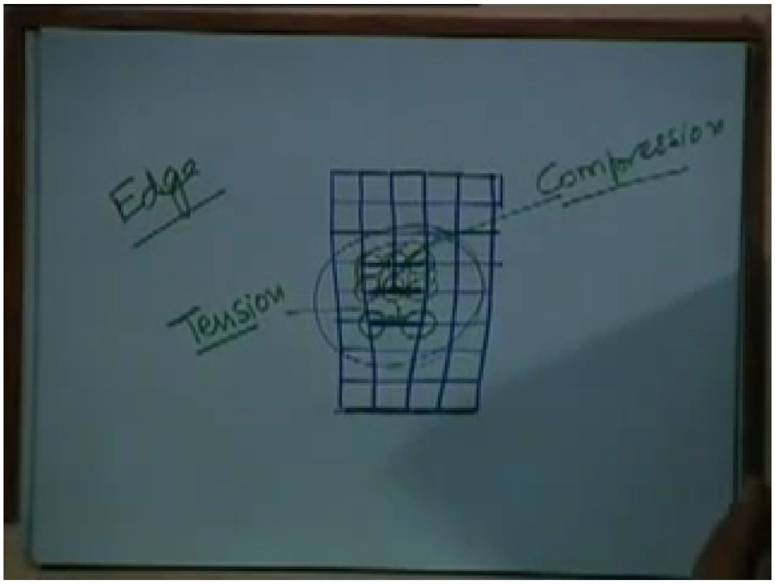

Let us show it here. One of the planes in the middle is incomplete. So what happens to the neighboring planes? And if I make all the unit cells, see the region here, these bonds here are much shorter than the bond which is here. Other words, this place, atoms which are placed here they are in tension. And these atoms which are placed here, these are in compression. But as I go away from this region, I go here, I do not find that problem here.

“Professor-student conversation starts.”

Professor: I do not find this problem here. They are the usual lengths as I go away from there. But these strains or the strains in the bonds, they are present only in this region which is around this place. What is this place?

Student: Which is terminating all those planes.

Professor: So I call it the edge of the part plane. And this edge of the part plane is what I refer to as edge dislocation. Please make this configuration by hand to understand this better.

“Professor-student conversation ends.”

We shall start from here the next class.