Principles of Physical Mertallurgy

Prof. R. N. Ghosh

Department of Metallurgical and Materials Engineering

Indian Institute of Technology, Kharagpur

Lecture No. # 02

Atomic Bond and Crystal Structure

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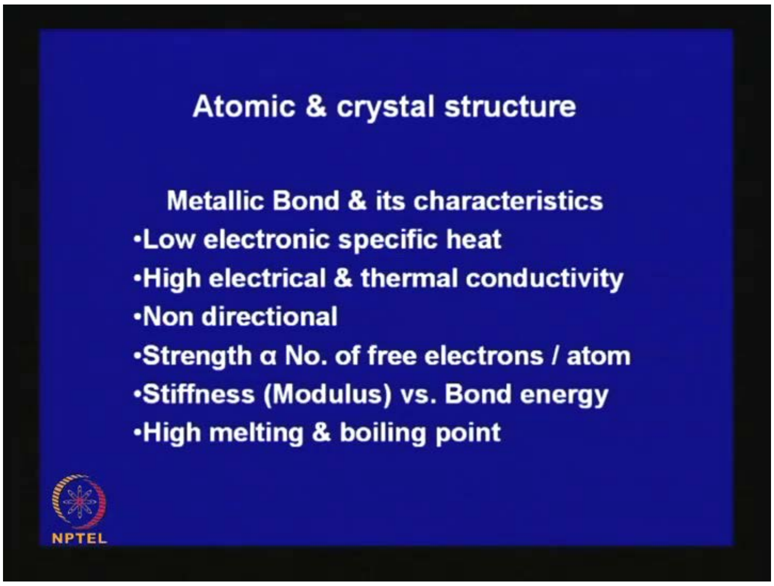

Atomic & crystal structure

Metallic Bond & its characteristics

- Low electronic specific heat
- High electrical & thermal conductivity
- Non directional
- Strength α No. of free electrons / atom
- Stiffness (Modulus) vs. Bond energy
- High melting & boiling point

Good morning, we start with the second lecture of this course. In the last class, we started talking about atomic bonding; and primarily looked at some of the important characteristics of metallic bond, which are listed here. Just to recapitulate, it has low electronic specific heat, it has high electrical conductivity, it is non-directional, strength of this bond is proportional to the number of free electrons per atom, it has high stiffness, and there is a relationship between stiffness and bond energy, and it has high melting and boiling point.

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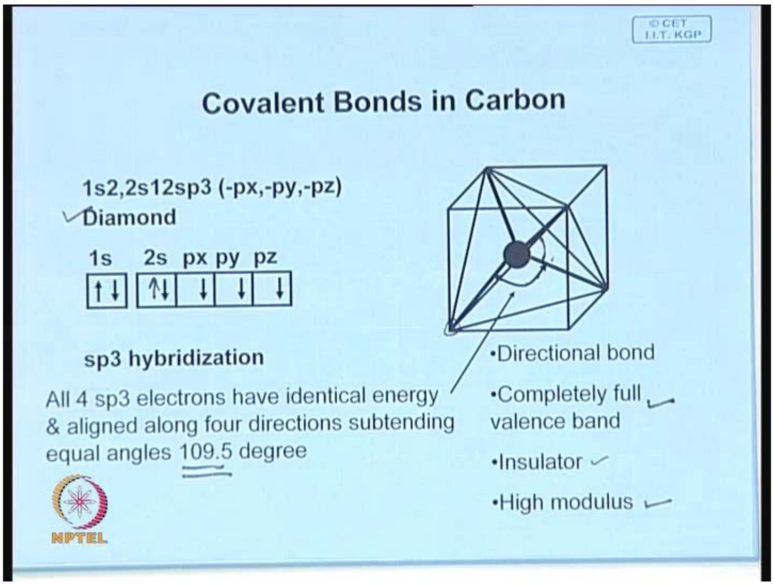

Covalent Bonds in Carbon

1s2,2s12sp3 (-px,-py,-pz)

Diamond

sp3 hybridization

All 4 sp3 electrons have identical energy & aligned along four directions subtending equal angles 109.5 degree

- Directional bond
- Completely full valence band
- Insulator
- High modulus

To recapitulate some of this, we talked about the bond in carbon; and carbon has half field outer orbit. As it was said, you know if the orbit is half full, so that means, there are four electrons in the outer orbit, all have parallel spin. In this case, we call this orbit as a hybridized orbit; and all 4 electron in this orbit have identical energy. So, therefore, if you arrange, try to arrange this in solid, these bonds will be subtending equal angle; so, four equal angle. The only way you can have this is like substitute at the centre of a cube; in that case, the other nearest atom will be located either here, here, here, here. So, of that, with that atom you know, it will form a bond with one having just opposite this beam. So, this atom will have this beam here; rest they are similar.

And I ask you to find out this angle, and I hope you have done; if not, I think, when we do little more detail the crystal structure, it will be evident. You can solve this by trigonometric, simple trigonometry plus an atom point at this centre of a tetrahedron, regular tetrahedron, and join the centre to the corner; this corner, this corner, and then try to find out this angle. Now, this type of bond you know, is highly directional, it has a completely filled up valence band; so, therefore, there is no electron to carry charge; therefore, it is insulator, it has insulating property, and this bonding is extremely strong; the distance between carbon to carbon atom is very less; so, therefore, it has high modulus. So, this is the structure, you get in diamond.

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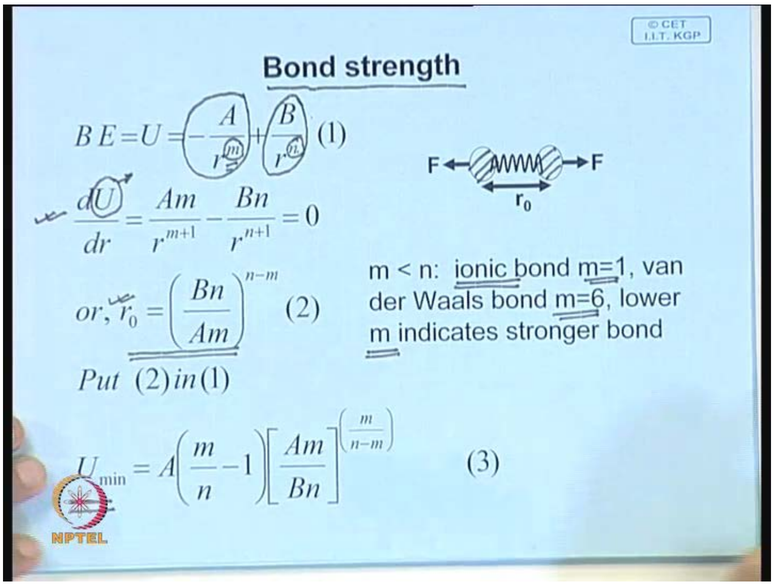

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Bond strength

$$BE = U = -\frac{A}{r^m} + \frac{B}{r^n} \quad (1)$$

$$\frac{dU}{dr} = \frac{Am}{r^{m+1}} - \frac{Bn}{r^{n+1}} = 0$$

$$or, r_0 = \left(\frac{Bn}{Am}\right)^{n-m} \quad (2)$$

Put (2) in (1)

$$U_{\min} = A\left(\frac{m}{n} - 1\right)\left[\frac{Am}{Bn}\right]^{\left(\frac{m}{n-m}\right)} \quad (3)$$

m < n: ionic bond m=1, van der Waals bond m=6, lower m indicates stronger bond

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Next, we looked at the nature of that bond strength, the origin of the bond strength. So, when you have two atom, you can visualize that this atom, and this atom; as if they are held by a spring, if you try to displays it a little, it will try to come back; but this spring is also strip, if you straight to push it too close, it will try to repair. And this is, so that is why you know, you have two kind of force; one is the force of attraction and other is a force of repulsion. I wanted you to show by differentiating the position or distances are at which this energy is bonding, this energy U is minimum. And I hope you have done; if not, the steps are shown; if you differentiate, you will find... and equate it to 0, you find. So, this is the equilibrium distance; this expression gives you the equilibrium distance.

And usually, look at this exponent m and n; now this is the attraction force; now in case of electro static bond or ionic bond, this m is 1; and m is usually m is always less than n. So, that is, so that means, when the atoms are nearby by this is much more denominate than the repulsion - repulsive force. Now in case of a vanderwaal bond, which is weaker, they are the index m is equal to 6. Now lower the value of m indicates that the bond is stronger. Now once you have found out this, if you substitute this r naught in this expression, you will get the expression for the minimum bond energy. And the reference was made that this bond energy will have a direct relationship with the strength of the material.

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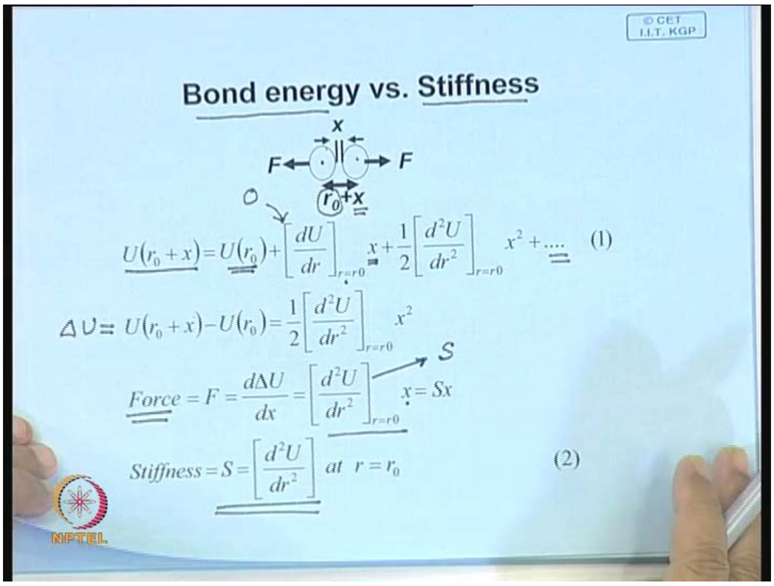

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Bond energy vs. Stiffness

$$U(r_0+x) = U(r_0) + \overset{0}{\left[\frac{dU}{dr}\right]_{r=r0}} x + \frac{1}{2}\left[\frac{d^2U}{dr^2}\right]_{r=r0} x^2 + \ldots \quad (1)$$

$$\Delta U = U(r_0+x) - U(r_0) = \frac{1}{2}\left[\frac{d^2U}{dr^2}\right]_{r=r0} x^2$$

$$Force = F = \frac{d\Delta U}{dx} = \overset{S}{\left[\frac{d^2U}{dr^2}\right]_{r=r0}} x = Sx$$

$$Stiffness = S = \left[\frac{d^2U}{dr^2}\right] \text{ at } r = r_0 \quad (2)$$

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Now, and to find out the relationship between bond energy and stiffness, you imagine that you have two atoms which are nearby its equilibrium distance between this and this is r naught; you try to displace it by a small distance x. And then the value of that energy U near r naught, that means at r naught plus x can be given by a Taylor series. So, this is the value of U at r naught; then the first differential at r naught, the times, distance x, then second differential, then x square times x square, there is a constant coefficient 1 over 2, and we can neglect that higher order term, which is smaller.

Now, from this, you can say the change in energy, you can rewrite this; and this form, and this we know that when U is minimum that is at r naught, this is equal to 0. So, therefore, this does not remain in this. And now, if you differentiate this with distance, then you get force. Then obviously, you get this term - the second differential d 2 U d r square at r equal to r naught times x; and this is known as second differential can be defined as stiffness. So, therefore, stiffness, relationship between stiffness and U is given by this.

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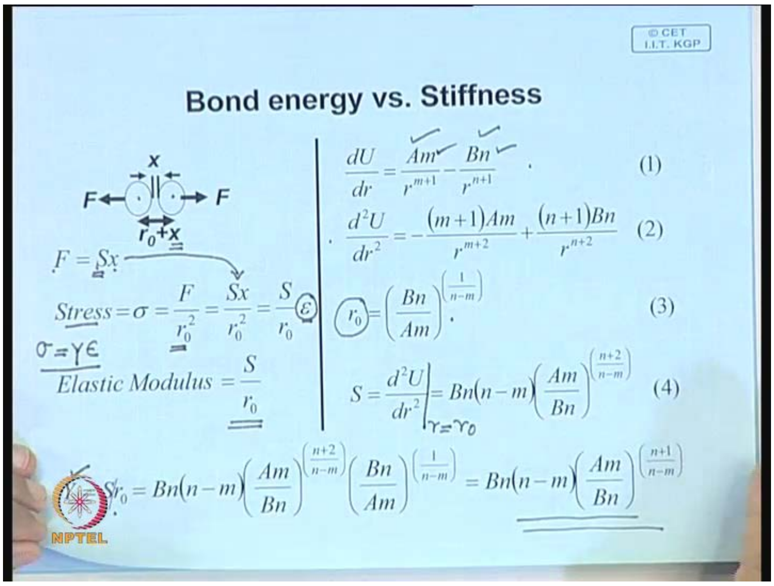
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Bond energy vs. Stiffness

$F = Sx$

$Stress = \sigma = \frac{F}{r_0^2} = \frac{Sx}{r_0^2} = \frac{S}{r_0}\varepsilon$

$\sigma = Y\epsilon$

$Elastic\ Modulus = \frac{S}{r_0}$

$$\frac{dU}{dr} = \frac{Am}{r^{m+1}} - \frac{Bn}{r^{n+1}} \quad (1)$$

$$\frac{d^2U}{dr^2} = -\frac{(m+1)Am}{r^{m+2}} + \frac{(n+1)Bn}{r^{n+2}} \quad (2)$$

$$r_0 = \left(\frac{Bn}{Am}\right)^{\left(\frac{1}{n-m}\right)} \quad (3)$$

$$S = \left.\frac{d^2U}{dr^2}\right|_{r=r_0} = Bn(n-m)\left(\frac{Am}{Bn}\right)^{\left(\frac{n+2}{n-m}\right)} \quad (4)$$

$$Y = S/r_0 = Bn(n-m)\left(\frac{Am}{Bn}\right)^{\left(\frac{n+2}{n-m}\right)}\left(\frac{Bn}{Am}\right)^{\left(\frac{1}{n-m}\right)} = Bn(n-m)\left(\frac{Am}{Bn}\right)^{\left(\frac{n+1}{n-m}\right)}$$

And I wanted you to go through and this, and derive an expression or relationship between, derive the relationship between bond strength and bond strength or bond energy and stiffness. Now we are very familiar with young’s modulus; now how do you, is there a relationship between young’s modulus and stiffness? So, visualize two atoms, and the same way separated by a distance r naught, you try to displace it by a distance small distance x. Then the force that is acting between the two the restoring force or that pull that which you are apply, this is stiffness time x. So, and this, and stress we know is defined as force over area; assume that this area of the cross section area of this atom is proportional to r naught square. So, F over r naught square is this stress; and therefore, you substitute here, and now we know that X, which is the displacement, X is the displacement, and r naught is the original distance between the two atom. So, this is equal to strain.

So, now we have a relationship between stress and strain; now we know the stress and strain, the relation that there is a proportionality constant, and which is known as young’s modulus. So, therefore, what we can say that young’s modulus is S over r naught. Now if you differentiate this bond energy, this is the first differential; differentiate it in second time, you get this. And substitute that r naught, the value of r naught over here; in that case, what you get is d 2 U d r square at r equal to r naught; in that case, this is the value, and then you try and find out that young’s modulus; young’s modulus will be S over r naught. So, again you substitute this over here, you get this. So, there is a direct relationship between young’s modulus and the bond energy or the co-efficient, which is defined by these four constants A, B and two index m and n.

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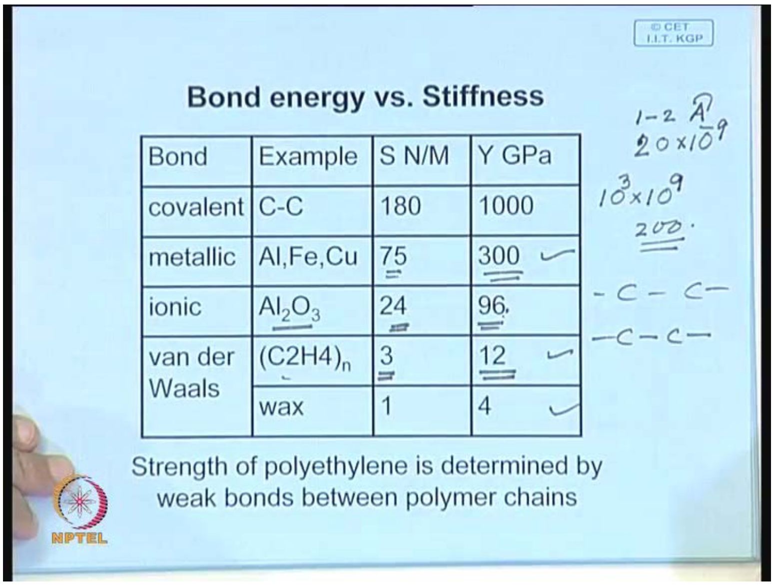

Bond energy vs. Stiffness

Bond	Example	S N/M	Y GPa
covalent	C-C	180	1000
metallic	Al,Fe,Cu	75	300 ✓
ionic	Al_2O_3	24	96.
van der Waals	$(C2H4)_n$	3	12 ✓
	wax	1	4 ✓

Strength of polyethylene is determined by weak bonds between polymer chains

1-2 Å

20×10^{-9}

$10^3 \times 10^9$

200.

-C-C-

-C-C-

If you look at this bond energy versus stiffness, here are some examples, which we have listed; it is a covalent bond, the carbon-carbon, in fact, the diamond is the strongest material, for this the young’s modulus is of the order of 1000 GPa. And from this, if you know this atomic distance, you will just multiply this by the atomic distance, you get the stiffness. So, basically this atomic distance roughly that is of the order of 1 to 2 angstrom, between 1 to 2 angstrom that is could be 1.5 or let us say that it is 2 angstrom or 20 nanometre, so 10 to the power minus 9. So, if you multiply, this is GPa so that means, this is 10 to the power 3 gigapascal that is 10 to the power 9.

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So, you will get that this may come around 200. So, same is true in all other cases also. So, here are the young’s modulus for few metallic bonds, which is of the order of 300 GPa; whereas, the young’s are this is, young’s modulus is of this order, and bond strength is this. Now, in ionic crystal like alumina, the values are this. So, simply you multiply this by the inter atomic spacing, the nearest inter atomic spacing, you get this stiffness. Now, if you look at the bond between these polymers, this is the young’s modulus, and this is the stiffness. Now here it is stiffness is very low, and it is primarily, if you look at the carbon - carbon bond, which is very strong; the carbon - carbon bond, but in polymer you know, along the chain it has high strength, but it strength is primarily determine by Vander Waal bonds, which are between chains; certainly, several chains. So between chain, there is a Vander Waal bond, so strength here, here and here, is primarily determined by Vander Waal bond.

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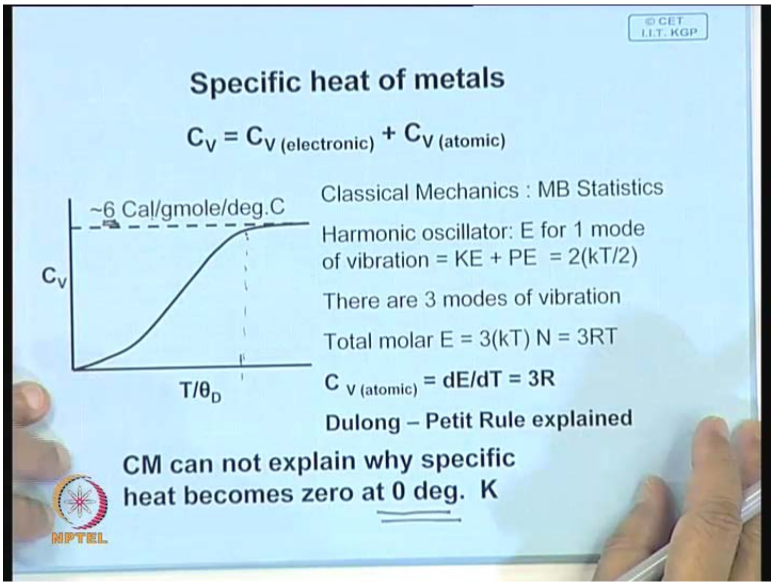

Specific heat of metals

$C_V = C_{V\,(electronic)} + C_{V\,(atomic)}$

Classical Mechanics : MB Statistics

Harmonic oscillator: E for 1 mode of vibration = KE + PE = 2(kT/2)

There are 3 modes of vibration

Total molar E = 3(kT) N = 3RT

$C_{V\,(atomic)} = dE/dT = 3R$

Dulong – Petit Rule explained

CM can not explain why specific heat becomes zero at 0 deg. K

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Now, we also looked at specific heat, we also looked at specific heat of metal, and where we came to know that classical mechanics cannot explain why specific heat becomes 0 at 0 degree kelvin? It can the classical mechanics can explain Dulong-Petit law, so that means, over here at a higher temperature or room temperature are normally metals, a room temperature is considered to be quiet high for most metallic materials. So, here most metallic material have a specific heat, molar specific heat around 6 calorie per gram mole per degree Kelvin So, it can explain that, but when you go to a lower temperature, it gradually a goes down to 0.

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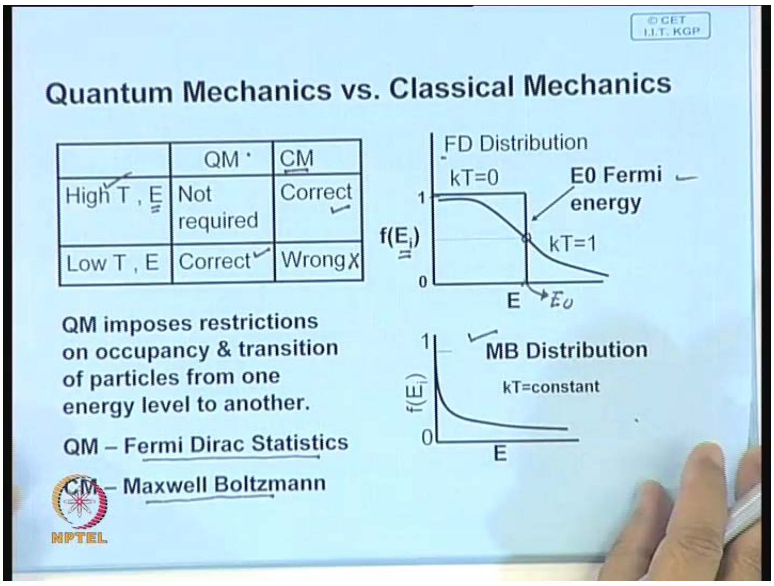

Quantum Mechanics vs. Classical Mechanics

	QM	CM
High T , E	Not required	Correct ✓
Low T , E	Correct ✓	Wrong X

QM imposes restrictions on occupancy & transition of particles from one energy level to another.

QM – Fermi Dirac Statistics

CM – Maxwell Boltzmann

And we talked about that to explain this, one has to refer to quantum mechanics; and quantum mechanics basically here is a table, short table which gives you when you apply quantum mechanics and then classical mechanics. Usually when we were looking at high temperature and high energy that when particles have higher energy, it is classical mechanics gives correct prediction. However, when the temperature goes becomes very low or energy or particles are also very low, in that case classical mechanics gives wrong prediction. And this is where one need to apply the principle of quantum mechanics, and usually the calculations using quantum mechanics a little difficult to understand and little complex.

So, therefore in normal cases, we do not at the temperature is high, and energy of the particles they are all so high, it is use of quantum… it is not required. Now, quantum mechanics imposes certain restrictions on occupancy and transition occupancy and transition of particles from one energy level to another. And this is given by this statistics - the probability of occupation, probability of a particular orbit being occupied or filled up is given by a statistics called Fermi Dirac statistics, in contrast to Maxwell Boltzmann statistics, which is applicable in case of classical mechanics. And the difference between the two is shown in this diagram, this is the probability that in energy level E i is occupied, 1 means it is fully occupied, 0 means it is break end; and at absolute 0, the Fermi Dirac distribution, look like this.

So, beyond an energy level say E naught, which is called Fermi energy, there is no electron in the band; whereas at high temperature, distribution will be something like this. So at Fermi level, you can say half the number of electrons, occupy energy less than the Fermi level, and half beyond the Fermi level. So, this part of the diagram, probability distribution is very similar to that of the Maxwell Boltzmann distribution; so, that is why at higher temperature, both predictions are similar.

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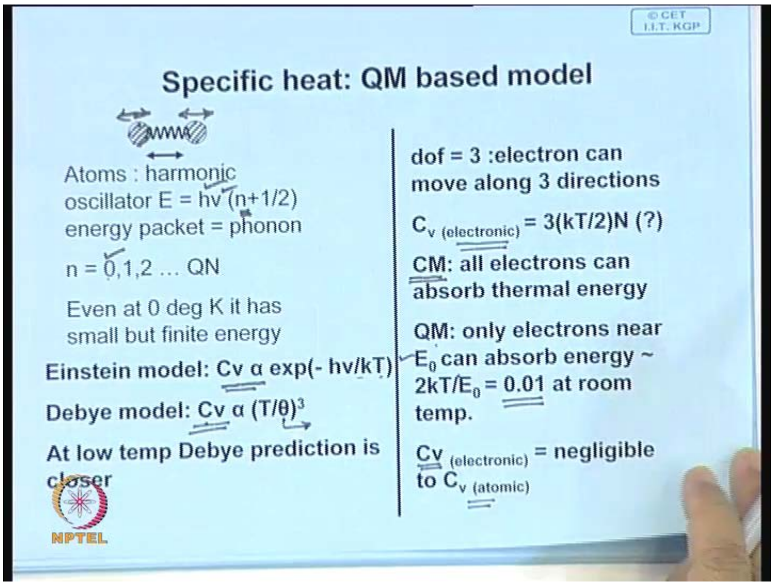

Specific heat: QM based model

Atoms : harmonic oscillator $E = h\nu(n+1/2)$
energy packet = phonon

$n = 0,1,2 \ldots$ QN

Even at 0 deg K it has small but finite energy

Einstein model: $C_v \alpha \exp(-h\nu/kT)$

Debye model: $C_v \alpha (T/\theta)^3$

At low temp Debye prediction is closer

dof = 3 :electron can move along 3 directions

$C_{v\ (electronic)} = 3(kT/2)N$ (?)

CM: all electrons can absorb thermal energy

QM: only electrons near E_0 can absorb energy ~ $2kT/E_0 = 0.01$ at room temp.

$C_{v\ (electronic)}$ = negligible to $C_{v\ (atomic)}$

Now, to calculate specific heat using quantum mechanics based model, one things of atoms, which are arranged in a periodic fashion in a crystal you know, as if they are connected by spring, and these atoms they keep on oscillating about its mean position of rest; and this oscillation, that frequency is a function of temperature. Now, in terms of in quantum mechanical model, it is assumed that this oscillator can have certain specified level of energy, which is given by this, this is plunk’s constant, this is the frequency, this is the quantum number n plus half. So, one point which obviously comes up that n is an integer, it can have 0, 1, 2. So, therefore, even when n is 0, so that is at 0 degree Kelvin, it can have, electrons will have small that some finite energy.

So, there is a basic difference between this and classical mechanics. Using this, Einstein worked out this was the first quantum mechanics based approach to explain molar specific heat, and he came out with an expression, which says that molar specific heat will decrease exponentially. Around the same time, a little later the Debye came up with another model, which predicted that molar specific heat is proportional to T to the power 3, and he introduced, but time stand here also you know, this theta is called Debye characteristic temperature; and above this characteristic temperature that molar specific heat obtained from classical mechanics and quantum mechanics, they are seen.

And at low temperature, the Debye prediction is closer to the experimentally determined values. And this I think we went through if you apply this to free electron, that means to apply this to find out what is the contribution of electrons that free electrons in an atom to this specific heat. If you go through this calculation, which was explained on the last class, you will find out that if you follow classical mechanics that means all electrons can observe thermal energy, then that electronic contribution it comes out to be very large.

But if you apply quantum mechanics, only the electron near the Fermi energy can absorb energy. So, therefore, the number of electrons, which can absorb thermal energy, is 2 k T over Fermi energy; and if you calculate this, it will come out to be very small, may be about 1 percent at room temperature. So, therefore, electronic contribution to specific heat is very negligible in compared to the atomic contribution, contribution of atomic vibration to specific heat.

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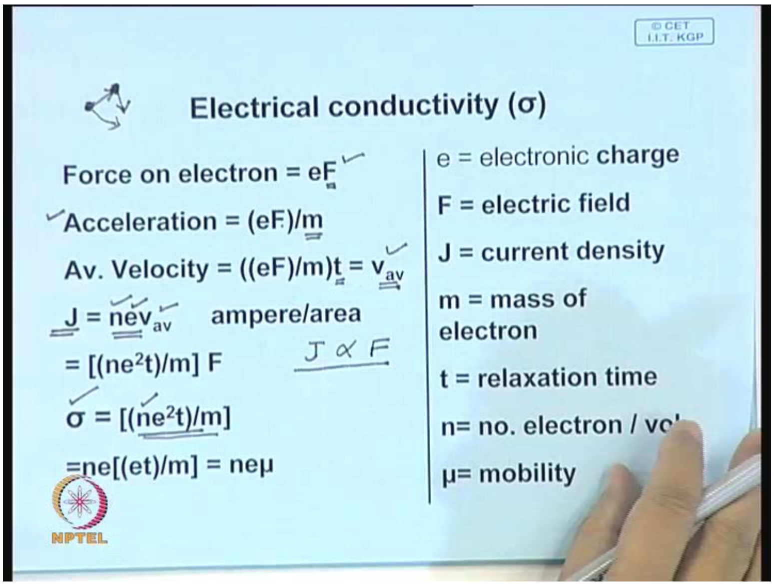

Electrical conductivity (σ)

Force on electron = eF

Acceleration = $(eF)/m$

Av. Velocity = $((eF)/m)t = v_{av}$

$J = nev_{av}$ ampere/area

$= [(ne^2t)/m]\ F$

$J \propto F$

$\sigma = [(ne^2t)/m]$

$= ne[(et)/m] = ne\mu$

e = electronic charge

F = electric field

J = current density

m = mass of electron

t = relaxation time

n= no. electron / vo

μ= mobility

So, with this briefly recollection of, what was covered in the last class, let us look at how do we explain that electrical conductivity of metallic material and what are the factors that determine electrical conductivity? The electrons are the charge carrier in metal, and when you apply an electric field, if there will be a force acting on the electron, which is given by this expression. Now we know the mass of electron is same, so if you divide this force by mass, you get acceleration. Now to calculate this average velocity, so imagine these electrons, which are moving in all directions, it can move in different directions, until it come mix an obstacle and its direction changes.

So, basically what we can say that what is the relaxation time or the time between this an electron heating and abstraction; if we say that that this time is T, then we multiply acceleration by time we get average velocity. Then the current flux, it is possible to calculate, that is current flux J will be proportional to the number of electrons n, electronic charge, and then average velocity. And here if you substitute that average velocity over here, you get this term. Now J is proportional to this expression say, the J is proportional to the electrical field; this is one way of specifying ohms law; and that constant of proportionality is sigma, which is known as conductivity. So, this is the expression for conductivity. So, it depends primarily on the number of charge carrier, E is constant, and the relaxation time T.

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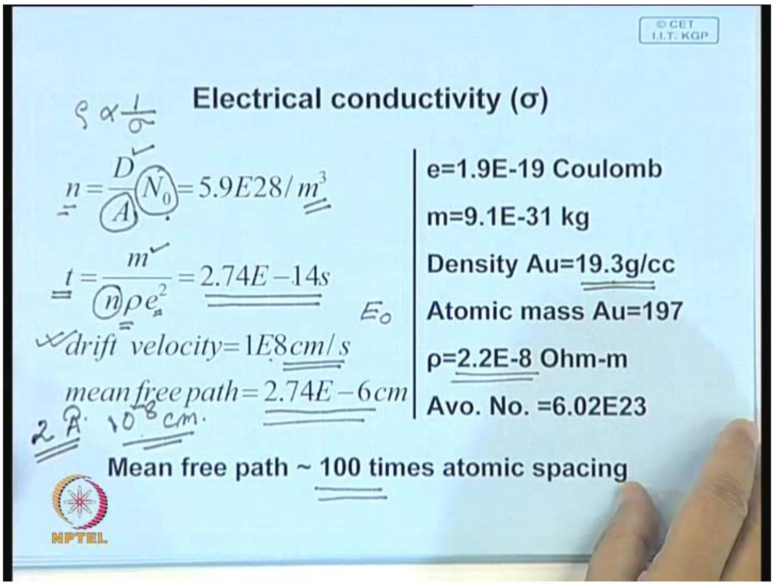

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$\rho \propto \frac{1}{\sigma}$

Electrical conductivity (σ)

$n = \frac{D}{\boxed{A}} \boxed{N_0} = 5.9E28/\underline{\underline{m^3}}$

$t = \frac{m}{\boxed{n}\rho e^2} = \underline{\underline{2.74E-14s}}$

E_0

$drift\ velocity = 1E8\underline{\underline{cm/s}}$

$mean\ free\ path = \underline{\underline{2.74E-6cm}}$

$\underline{\underline{2\,Å}} \cdot \underline{\underline{10^{-8}\,cm}}.$

e=1.9E-19 Coulomb

m=9.1E-31 kg

Density Au=19.3g/cc

Atomic mass Au=197

ρ=2.2E-8 Ohm-m

Avo. No. =6.02E23

Mean free path ~ 100 times atomic spacing

NPTEL

Now, with this back ground let us try an estimate, what is the lightly time or an idea about the time scale for this relaxation time T. Now, this is the expression for relaxation time, see one over this rho is the resistivity. So, rho is basically resistivity, which is one over conductivity. So, for metals, this is known, take a case of so, let us say gold; for which this resistivity is given by 2.2 into 10 to the power minus 8 ohm metre. Now this is a constant charge of an electron, which is known; what you need to calculate here is n, because m is also constant, this is known. And how do you calculate that number of electrons, which take part n conductivity or in conducting electricity.

Now one way could be if you, can you find it out from density? Density of a metal is known, say suppose this density of gold is D, which is given as around 19 gram per cc; if you divide this by its atomic weight, so you get the mass of 1 atomic mass of 1 cc of gold, and then you multiply it by Avogadro number. So, then you get n in number per cc, and you need to convert it into metre cube to substitute in this expression. So, one need to be careful about the units, you should put substitute all these constants or the values in consistent unit; once you do this, you get a value of around 2.74 into 10 to the power minus 14 second.

Now let us try and find out what is the drift velocity? It is possible to calculate drift velocity from it is related to Fermi energy E naught; in fact, if you look at that Fermi energy, here the entire energy is due to the kinetic energy of electron, and this is equal to half mass of electron into velocity square. So, from here it is possible to estimate the drift velocity, this is of the order of 10 to the power 8 centimetre per second. So, therefore, mean free path of this electron is, if you multiply this and this, you get this is of the order of 10 to the power minus 6 centimetre.

So, therefore, you can say that atomic distance for most crystalline structure is of the order of 2 Armstrong; so Armstrong means that is 10 to the power minus 8 centimetre. So, therefore, this mean free path is around, this is 2 order of magnitude higher than this, so you can see that mean free path of this electron is around 100 times atomic spacing. So therefore, in metals of good conductor, whereas covalent bonds you do not have free electron, so therefore, they are insulator.

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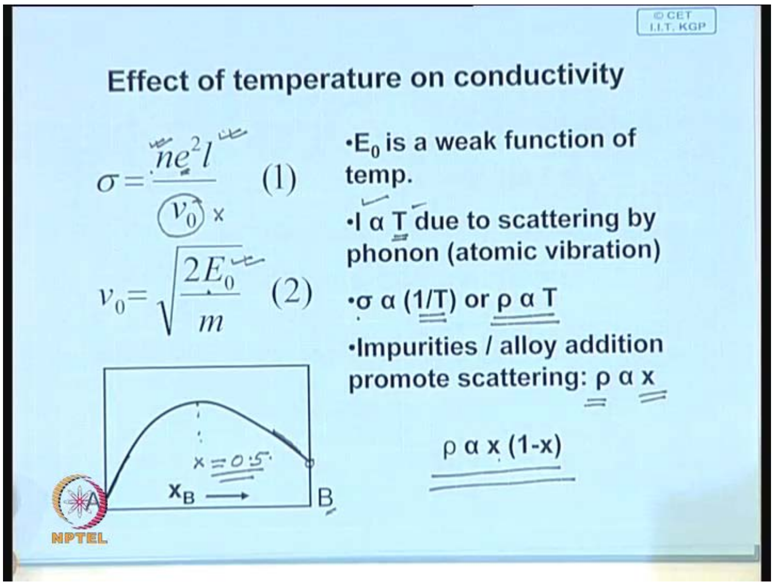

Effect of temperature on conductivity

$$\sigma = \frac{ne^2 l}{v_0} \quad (1)$$

$$v_0 = \sqrt{\frac{2E_0}{m}} \quad (2)$$

- E_0 is a weak function of temp.
- l α T due to scattering by phonon (atomic vibration)
- σ α (1/T) or ρ α T
- Impurities / alloy addition promote scattering: ρ α x

ρ α x (1-x)

Now, let us look at the conductivity in little more detail, so effect of temperature on conductivity. Now, this conductivity expression is written like this; so now there are, which are the terms, which are affected by temperature? This is the drift velocity, now the drift velocity, it is determined by Fermi energy; at this Fermi energy is a very weak function of temperature, so therefore, you cannot change much. So, this is ruled out. So, and here also, this number of electron, it is determined by the crystal structure or atomic structure, this is constant. So, the only term, which can change primarily, is l, so this is the mean free path can change.

Now, this mean free path is proportional to temperature due to scattering, these electrons are scattered by, because we can assume that crystal is made up of a periodic arrangement of atoms, atoms are placed at certain mean position of rest, they are not stationary, they keep vibrating; and this extend of vibration increases with temperature. So that means, there is a little loss in periodicity, and this vibrating atoms, they will emit particles called phonon, that vibration energy you can say it is emitted by the oscillating atoms as phonons; and this phonon and electron that there will be interactions, and this electron get scattered.

If they are too many phonons emitted, this extend of scattering will be high. So, therefore, at high temperature, higher the temperature, there will be more atomic vibration, there will be more scattering. So, therefore, you can say that, that mean free path is proportional to temperature, and resistivity is inversely proportional to temperature. So therefore, as resistivity is proportional to temperature; so most metals the resistivity increases with temperature, and this linear dependence at except that very low temperature, it deviates from linearity; but by and large resistivity, it is a linear function of temperature; therefore, resistance of metallic wires are often used as a temperature measuring device.

Now, electrons can also get scattered by impurities; if there are different atoms present which disturbs the periodic nature and the crystal structure, they also will contribute to scattering. Like when you do align, you put in a second element in the lattice, and they can be treated as impurity, because it is characteristic is different from the atoms of which the main metal that structure is made up of. So, therefore, they also will be a source of or they also will scattered electrons. So, therefore, if you increase this impurity, there should be a direct relationship between resistivity and the concentration of these impurity elements, which is represented like this rho is proportional to the atom fraction of that impurity.

Now, you can say suppose we take a binary system say two element, A and B both are conductor, and they can be mixed in all proportion. So, both end, and this end also the resistivity will go up with concentration, this end also, this is the base resistivity of metal B, so this also will go up. And if you plot the total, you will get a mix maxima, somewhere in between, where X is 0. 5. So, logically in such cases, effect of a impurity or effect of align can be put by a factor like this, X is rho is proportional to X into 1 minus X.

So, any align we will have poorer conductivity; there is a lot of similarity between thermal conductivity and electrical conductivity; it may be interesting to look at this. So, now, electrons are the primary career of electricity in metals. Now if you look at the thermal conductivity, this thermal conductivity will depend primarily on two factors; one is its specific heat; now this specific heat is actually controlled, primarily controlled by the atomic vibrations.

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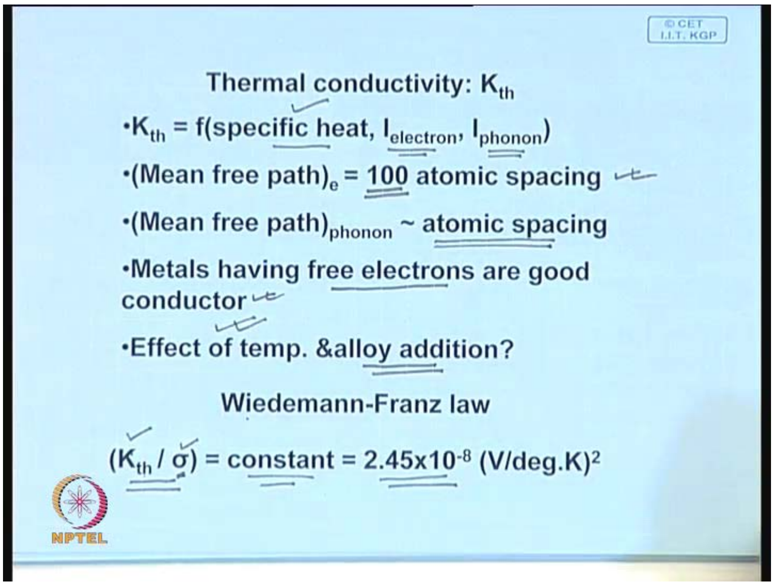

Thermal conductivity: K_{th}

- K_{th} = f(specific heat, $l_{electron}$, l_{phonon})
- (Mean free path)$_e$ = 100 atomic spacing
- (Mean free path)$_{phonon}$ ~ atomic spacing
- Metals having free electrons are good conductor
- Effect of temp. &alloy addition?

Wiedemann-Franz law

(K_{th} / σ) = constant = 2.45×10^{-8} (V/deg.K)^2

An apart from that, you have this atomic vibration you can say they are emitted as phonons; so and phonons, the displacement of this phonons, this wavelengths… So let us look at this specific heat will be a function of this thermal conductivity will be a function of specific heat, and the mean free path of electron, and mean free path of photon. Now mean free path of electron we have just seen is of the order of 100 atomic spacing; whereas, mean free path of phonon, so these wave lengths are much smaller, so they gets scattered very easily, and this is of the order of atomic spacing. So, therefore, any crystal structure or any structure solid, liquid, wherever you have basically the ionic or covalent bond, there is no free electron. So, they are bad conductor, in fact, even bad thermal conductor.

Metals have free electrons; they are good electrical conductors, so they are good thermal conductor as well. Now, here also you can discuss in the same way, what will be the effect of temperature. With increasing temperature with increasing temperature, resistivity goes up, so also thermal conductivity will go down. Similarly, alloy addition, also will bring down thermal conductivity. Now because it will be interesting to see what is the relationship between thermal conductivity and electrical conductivity, because both the cases, electron is the charge career; in fact, if you look at thermal conductivity and electrical conductivity for most metal, you will find that this is the constant, and this constant is known as Wiedemann-Franz constant, and this magnitude is given here

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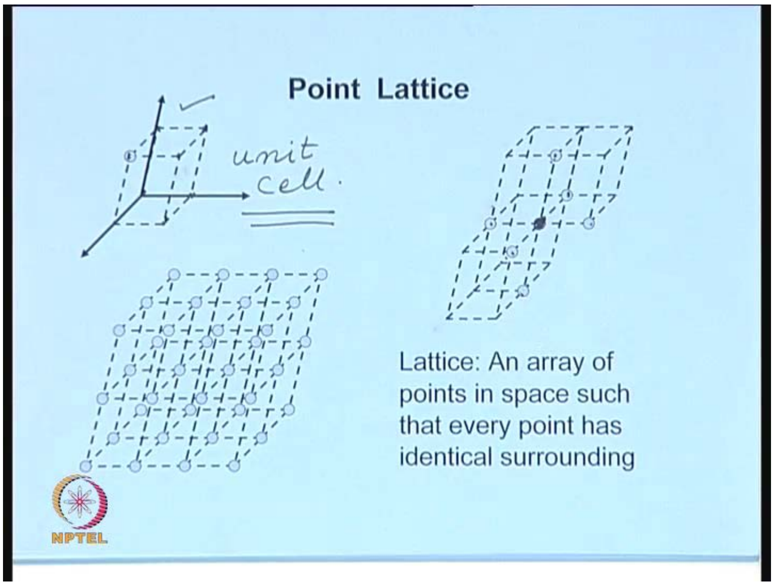

Point Lattice

Lattice: An array of points in space such that every point has identical surrounding

Now what this, we have covered the nature of a atomic bond; now let us look at the crystal structure. Metals, all metals they are crystalline; now crystalline material, the atoms are arranged in a periodic fashion. Now, how do we represent this periodicity or how do we visualize this periodic arrangement of atoms in a crystal? In order to do that, we make use of a framework and array of point in space. Now we visualize the array in such a way that each of this point have identical surrounding; and this array of point is in space is known as lattice.

Now let us try and look at let us try and look at, how does this point lattice look like? Now, suppose we consider 1 1 at this particular figure, consisting of 4 points here, 4 points here, and try to repeat case, and this direction as well as this direction, so something like this. So that means, one point has a surrounding, it has atoms one here, one here, one here, one here, one here, one here. So, this has a surrounding of 6 points; and if you repeat this, it is possible to generate the lattice of points like this; and this is called point lattice. And this smallest building block, this is known as unit cell. Now all crystal structures, we try to represent in terms of this lattice structure.

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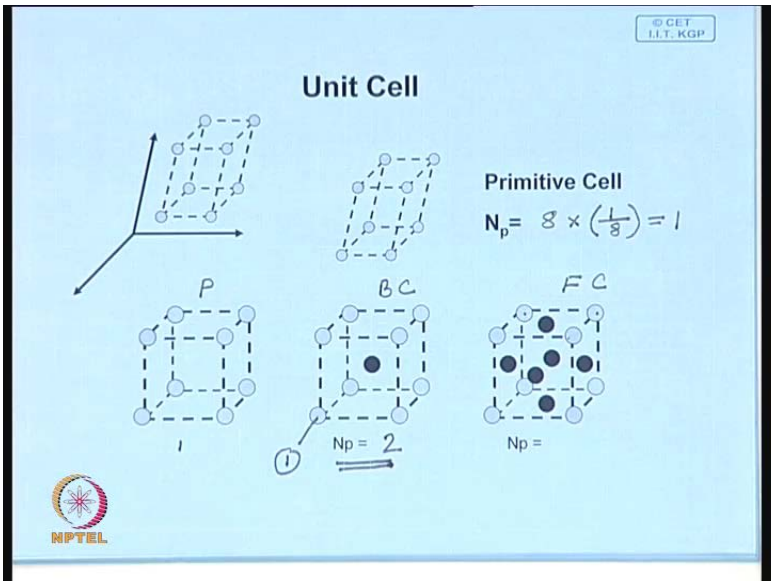

Unit Cell

Primitive Cell

$N_p = 8 \times \left(\frac{1}{8}\right) = 1$

P

BC

FC

1

Np = 2

Np =

Now, this is the lattice.

(No audio from 42:11 to 42:22)

This is the lattice structure. Now, when you have points… This is the smallest building block of that lattice called unit cell; and let us look at this particular unit cell. Recall here, we have points only at the corner of the cell. Now let us try to calculate, there are how many lattice point in a cell like this; this cell, where you have points only at the corner is called primitive cell. And let us try and calculate, what is the number of points in this primitive cell? Now here, if you go back to the previous is what you have this particular point does not (( )) belong to 1 unit cell, it is shared by all the adjacent unit cell. Now here, how many adjacent unit cells are there to this point? You have 1 here, 2 here, 3 similarly, another here 4, 4 this side, similarly 4 on this side as well. So, this point is shared by 8 unit cells nearby unit cell.

So, therefore, you can see that this primitive cell contains the number of points is it has 8 corners, but each corner point is shared by 8 such neighbouring unit cell. So, contribution of this, each is one-eighth, so this is 1. Now, you can also having unit cell it is not necessarily that not necessary that unit cell should have points only at the corner, they can have certain additional point as well, which is shown here. So, this is the primitive cell, here this number is 1; if you have 1 at this centre of the body, in that case that number of points per unit cell will be 2, because this corner, contribution of corner is 1;

and this central point exclusively belongs to this unit cell. So, it is not a part of any neighbouring cell.

So, therefore, here the number of points per unit cell is 2; similarly, this is called body centered unit cell, this is primitive cell, this called face centered. So, in addition to the corner points, you have points at the each of the face centred; by substituting this additional point, we do not violate the definition of point lattice, because point lattice we defined that a point lattice is an array of point in space, so that every point as identical surrounding; I think you can take this as an exercise, and try to find out or plot the array or arrangement of neighbouring points to a that a body centered unit cell and a face centered unit cell. And you also try to find out in a face centered unit cell, what is the number of points per unit cell?

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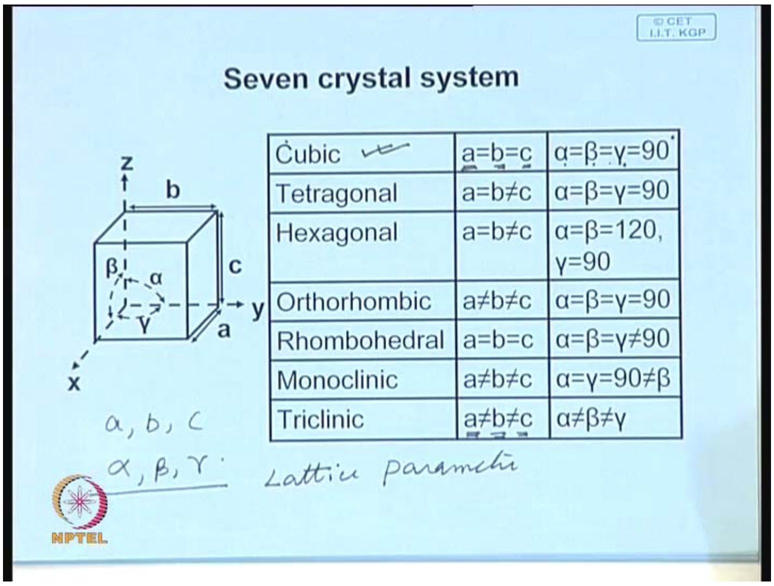

Seven crystal system

Cubic	$a=b=c$	$\alpha=\beta=\gamma=90$
Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90$
Hexagonal	$a=b\neq c$	$\alpha=\beta=120$, $\gamma=90$
Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90$
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq 90$
Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90\neq\beta$
Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma$

a, b, c

α, β, γ : Lattice parameter

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Now, let us look at the unit cell little more critically; how do you define this unit cell, which is shown in this slide. So, this is the unit cell, it is defined by its linear dimension, dimension of each of these edges. So, suppose this is an aspect of axis X, Y, Z, very often we normally represent in geometry, the axis as X, Y, Z. In crystallography, we try to represent then as a, b, c. So, for X, we put it X, so the distance between two points, along this direction is represented as a vector a similarly, the distance between two points along axis y is put as B, and the distance between two points along the z direction is c;

Similarly, apart from this linear dimension, we also need to defined angle between d’s axis; so this angle just opposite a, so this is x axis or in crystallography, we call it a, so opposite a, so this we call alpha. Similarly the angle opposite y, we call this beta; and the angle opposite z, we call gamma. Now, depending on the magnitudes of the relationship between this linear dimension a, b, c, and this angle alpha, beta, gamma, you can have different shapes for this unit cell, and which is listed here; and based on this, we can classify all crystals into 7 classes, which is listed here.

So in cubic, and for most metallic material, the crystal structure can be described by cubic or most of the cases as we will come to know, the crystal structure is cubic; here all the lattice a equal to b equal to c, and the three angles alpha, beta, gamma they are equal and equal to 90 degree. This is the most symmetric crystal that we can think of, and down this, as you go that element of symmetry goes on decreasing, and you have the other extreme triclinic, where none of these parameters a, b, c they are equal, and none of this angles are equal alpha, beta, gamma, they are different; and this is called triclinic. So, this is the this has the high symmetry, this has the least symmetry; and intermediate you have tetragonal, hexagonal, orthorhombic, rhombohedra and monoclinic; and the relationship between the a, b, c an alpha, beta, gamma are listed here; and these values they are called lattice parameter. So, a, b, c and alpha, beta, gamma they are called lattice parameter.

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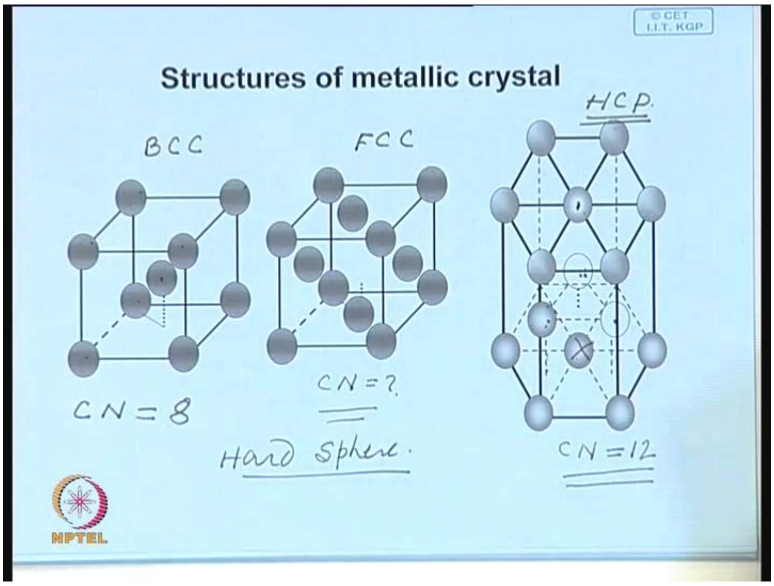

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Structures of metallic crystal

Now, most of the metallic crystals, they belong to one of these, not but there are no other crystal structure, but primarily this is body centered cubic, this is face centered cubic, and this structure although, it is primitive lattice is hexagonal, we call this hexagonal closed pair structure. Now it will be good to look at what is the number of nearest neighbour say like in case of a BCC lattice, so look at this, and the number of nearest neighbour is 1, 2, 3, 4 and the term 4 at the bottom. So, here we call this number of nearest neighbour as a coordination number, and this is 8. And from this it is little difficult to find out the coordination number, we will try and look at it little later. But here it is easy, relatively easy; you take this, and try to find out the number of nearest neighbour.

So, so let us say you take this, you have 6 in the plane, you have 3 neighbours here, this here, similarly you have 1 over here, 1, 2, 3 and similarly, 3 at the top. So, in this case, coordination number is 12. So, this is the maximum coordination number you can have in a crystal structure; and in this case, metals, so one of the simplest way, we can visualize this atom, we can assume then to be hard sphere, and go through if we calculation, hard sphere model and go through a few calculations.

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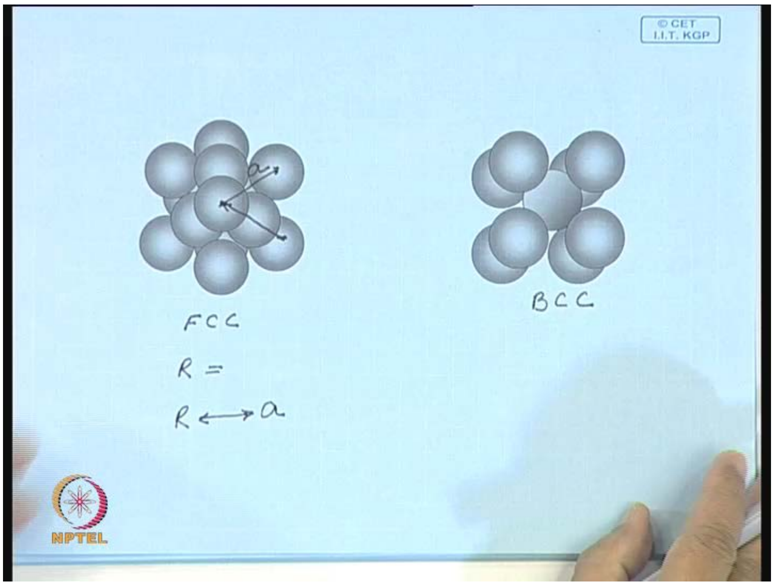

You try to find out this is a little elaborate view of the face centered cubic structure, assuming the hard sphere, along this directions, they touch each other. So, if we assume the radius of the atom to be R, then try and find out what is the relationship between R and the lattice parameter that is, this is the lattice parameter a. So, what is the relationship between the atom radius and a; so for FCC, and try to find this, for BCC.

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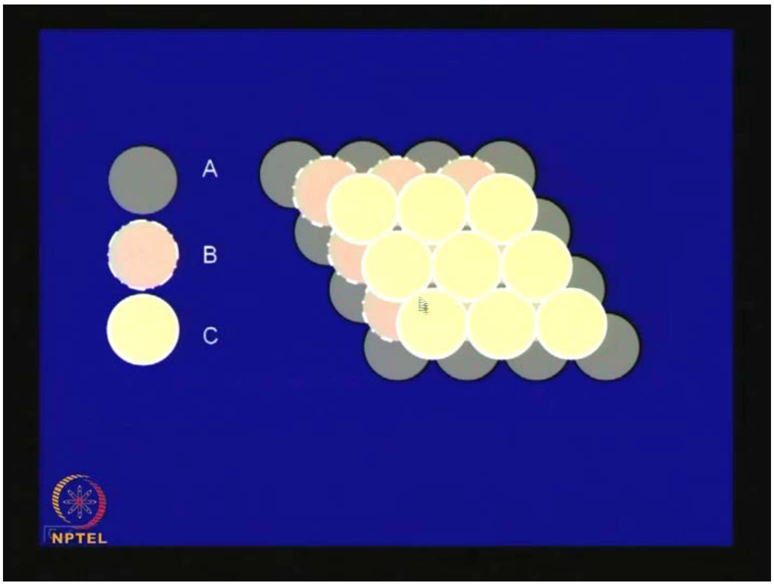

And another thing, it will be interesting to look at this the array little more carefully. If we look at that atomic array you know, they are arranged like this; you know, this is the hard sphere surrounding it you have 6 atoms. Suppose we call this layer, layer A. Now on that, if you try to bring another layer of hard sphere, so where does it go? There are two places here, say if I go to the previous here, there are two places next layer can occupy. So, one is here, another here. But if you put an atom here, part of this gets blocked. So, you can only have either here or here. So, here it comes, it occupies one of the position, we call this layer B. And then we bring in another to the other side, we call this as a layer C. So, look at this, this arrangement from this side, it has a similarity to face centered cubic structure.

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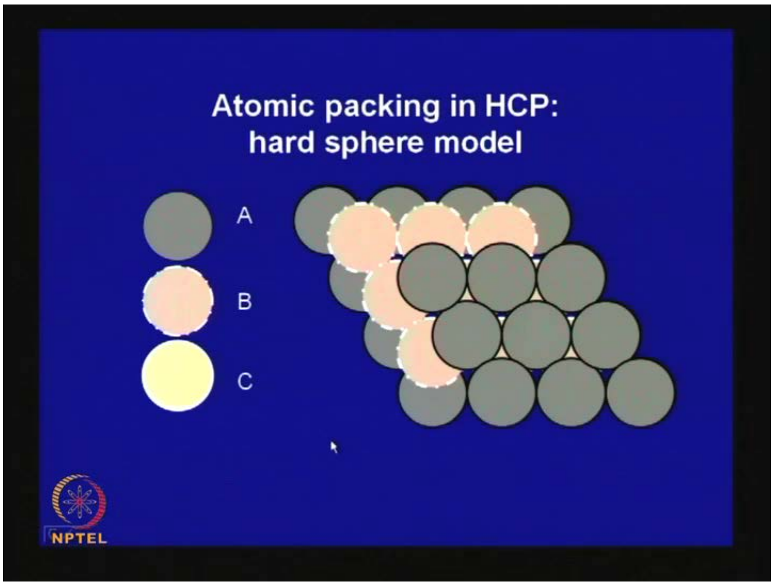

Atomic packing in HCP:
hard sphere model

So, you try and visualize the same thing in a hexagonal, which is shown over here; you have one layer, we call this A, second layer, and third layer, second layer is B; and the third layer it goes and occupy layer A, there is no C layer. And you try and visualize this, this resembles hexagonal closed pack structure. With this, we finish the second lecture on a atomic bond and crystal structure. You can go through this exercise particularly assuming atomic bond; and apart from calculating the relationship between the radius of the atom and lattice parameter, you try to find out lattice parameter from density of metal. And next class, we will talk about a little bit more detail, how do we represent the directions and planes in a crystal, introduce the concept of Miller indices, and we will talk a little about stereographic projection, thank you.