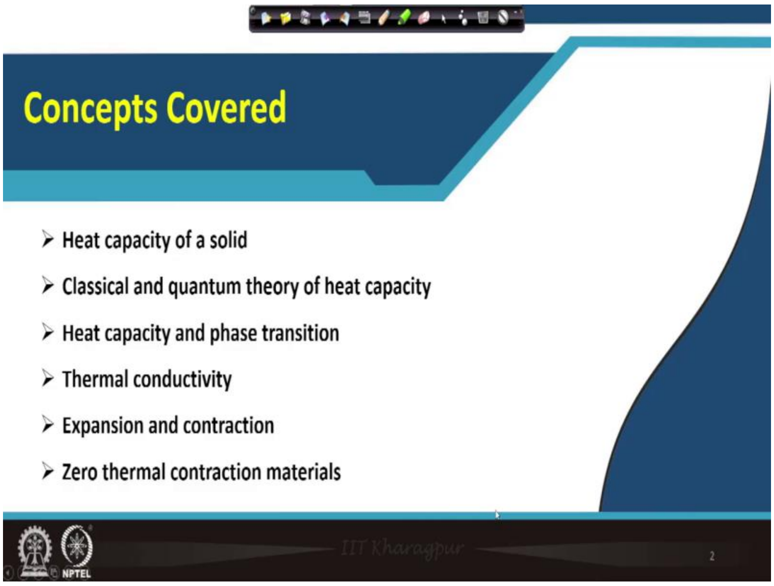
Non - Metallic Materials

Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module - 05
Electrical, magnetic and thermal properties of non - metallic materials
Lecture - 27
Thermal Properties: Specific heat, heat conduction, thermal diffusivity, thermal expansion

Welcome to my course Non - Metallic Materials and today, we are in module number 5 Electrical, magnetic and thermal properties of non-metallic materials and this is lecture number 27, where Thermal properties Specific heat, heat conduction, thermal diffusivity and concepts of thermal expansion will be described.

(Refer Slide Time: 00:55)



Concepts Covered

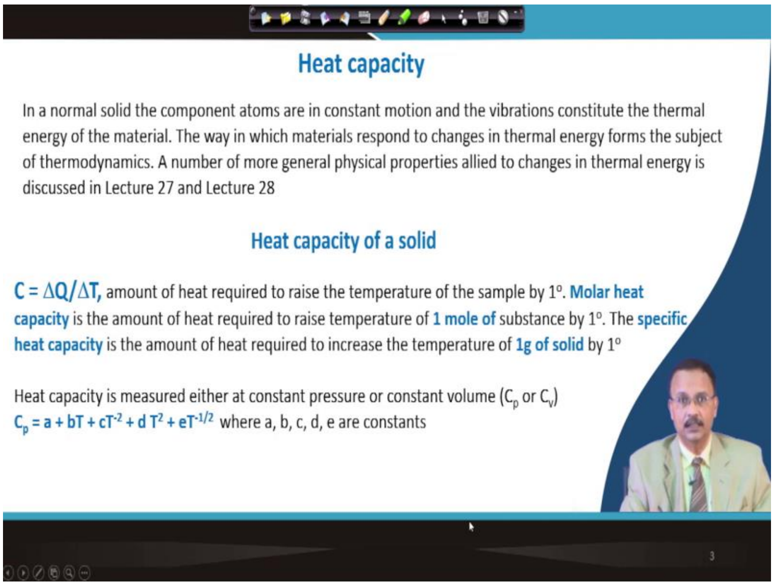
- Heat capacity of a solid
- Classical and quantum theory of heat capacity
- Heat capacity and phase transition
- Thermal conductivity
- Expansion and contraction
- Zero thermal contraction materials

So, this is a well-known material, right from your school age, you are studying the thermal properties of material in various form.

So, in this lecture, I will introduce the heat capacity of a solid. Already while I was discussing about the thermodynamic property, we in we just introduced this concept of heat capacity, then the classical and quantum theory of heat capacity will be explained, then how heat capacity is related to the phase transition. Also, this I have described earlier, but it will be elaborated a bit.

Then, we will talk about the thermal conductivity and then, the concept of expansion and in some materials concept of contraction with the increase of temperature will be described. And finally, we will talk about zero thermal contraction materials and as you will see that not everything is related to non-metallic materials, sometimes metallic alloys play a major role. So, in order to maintain the continuity, I will talk about the metal alloys also, wherever it is relevant.

(Refer Slide Time: 02:17)



Heat capacity

In a normal solid the component atoms are in constant motion and the vibrations constitute the thermal energy of the material. The way in which materials respond to changes in thermal energy forms the subject of thermodynamics. A number of more general physical properties allied to changes in thermal energy is discussed in Lecture 27 and Lecture 28

Heat capacity of a solid

$C = \Delta Q/\Delta T$, amount of heat required to raise the temperature of the sample by 1°. **Molar heat capacity** is the amount of heat required to raise temperature of **1 mole of** substance by 1°. The **specific heat capacity** is the amount of heat required to increase the temperature of **1g of solid** by 1°

Heat capacity is measured either at constant pressure or constant volume (C_p or C_v)

$C_p = a + bT + cT^{-2} + d\,T^2 + eT^{-1/2}$ where a, b, c, d, e are constants

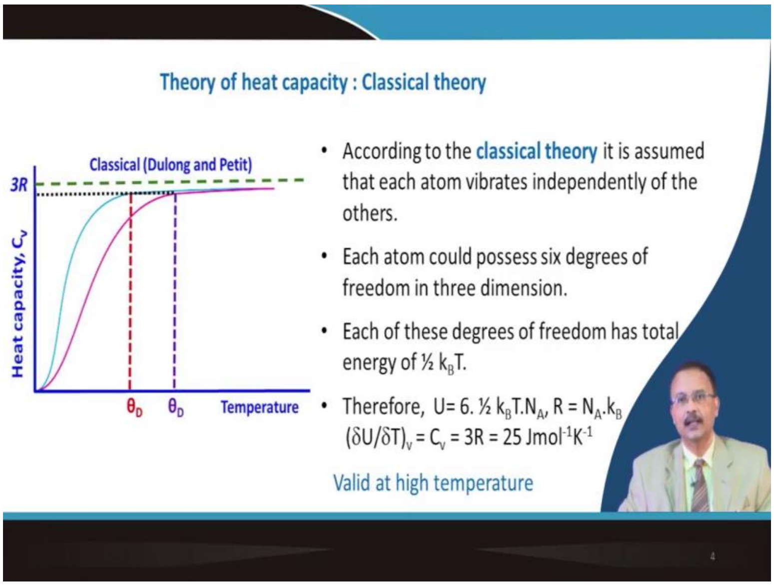
Now, the heat capacity in a normal solid as you know that a component of atoms are in constant motion and the vibration constitutes the thermal energy of that particular material. So, the way in which the materials respond to the change in thermal energy that forms the basis of a thermodynamics which I have already described which is relevant to material science.

So, I will not go into more details; but a number of more general physical properties which are allied with the change in thermal energy that is discussed in this lecture, lecture number 27 as well as in the subsequent lecture.

So, the heat capacity that you know that is the amount of the heat that is required to raise the temperature of a sample by 1 degree. So, we call it say molar heat capacity. It is the amount of heat required to raise the temperature of 1 mole of substance by 1 degree and we call its a specific heat capacity, when amount of heat required to increase the temperature of 1 gram of solid by 1 degree.

So, usually this is a common term to determine the specific heat at constant pressure. This is given by the polynomial equation as I have described here is of course, a function of temperature and there are several constant terms which is involved a, b, c, d, e etcetera. And note the power of the T also is a bit different in each case allied with the constant that we have described.

(Refer Slide Time: 04:13)



Theory of heat capacity : Classical theory

- According to the classical theory it is assumed that each atom vibrates independently of the others.
- Each atom could possess six degrees of freedom in three dimension.
- Each of these degrees of freedom has total energy of ½ k_BT.
- Therefore, $U = 6. \frac{1}{2} k_B T.N_A$, $R = N_A.k_B$ $(\delta U/\delta T)_v = C_v = 3R = 25\ Jmol^{-1}K^{-1}$

Valid at high temperature

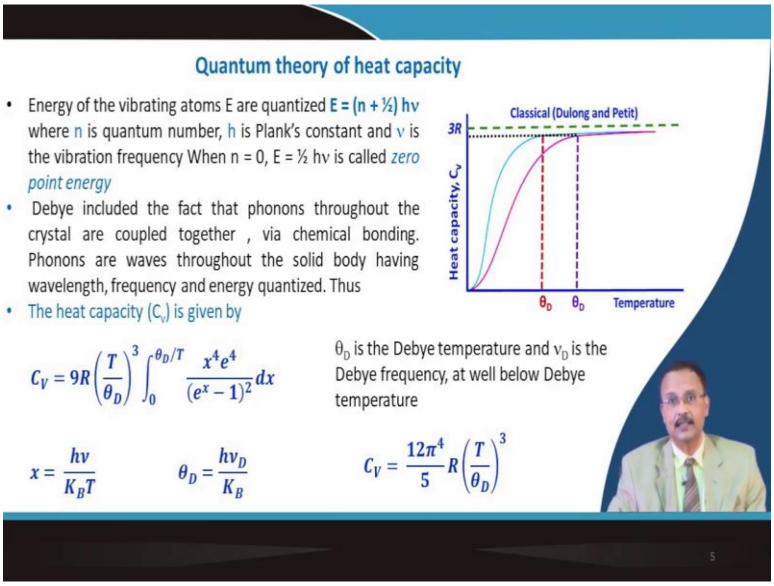
Now, according to the classical theory, it is assumed that each of the atom vibrates independently in a crystal structure and which is independently of the others. So, this is the vibration is not really coupled. So, as you can understand in a three Cartesian system, each atom could possess total 6 degree of freedom; x y, x minus y, y minus y, z minus y and each of this degree of freedom has a total energy of half k B; k is the base Boltzmann constant.

So, therefore, the energy total energy can be approximated as 6 into this half of k B into T that is the energy term and the Avogadro number is multiplied with that. So, it is multiplied with any for a molar energy and as you know that the universal gas constant is related with Avogadro number and Boltzmann constant.

Now, if you differentiate this equation, so that is del U by del T at constant v, we get the term which is a specific heat at constant volume and this can be approximated as 3 R and if you put the value of R, you will get typically 25 Joule per mole per degree Kelvin. So, actually this is valid. This value is valid at pretty high temperature. As you can see that for two different types of material, if you plot the molar heat capacity with temperature.

At very high temperature, it is indeed the value is equal to 3 into R; but at lower temperature, it is dramatically different. So, why this is dramatically different that is a separate story.

(Refer Slide Time: 06:19)



Quantum theory of heat capacity

- Energy of the vibrating atoms E are quantized **E = (n + ½) hν** where n is quantum number, h is Plank's constant and ν is the vibration frequency When n = 0, E = ½ hν is called *zero point energy*
- Debye included the fact that phonons throughout the crystal are coupled together , via chemical bonding. Phonons are waves throughout the solid body having wavelength, frequency and energy quantized. Thus
- The heat capacity (C_v) is given by

$$C_V = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^4}{(e^x-1)^2} dx$$

θ_D is the Debye temperature and ν_D is the Debye frequency, at well below Debye temperature

$$x = \frac{h\nu}{K_B T} \qquad \theta_D = \frac{h\nu_D}{K_B} \qquad C_V = \frac{12\pi^4}{5} R\left(\frac{T}{\theta_D}\right)^3$$

And it is related to the quantum theory of heat capacity. So, we assumed that the vibration of the atoms are actually independent to each other. But in reality, they are quantized and this energy is given by n plus half into h into nu; n as you know is the quantum number and h is the Planck's constant and nu is the vibration frequency. So, as you can see when n is equal to 0, then still some energy left. So, this is called zero-point energy.

Now, Debye included the fact that the phonon throughout the crystal is coupled together. Because in a crystal structure, each of these atoms or molecules are bonded by bonds and throughout the crystal structure, if you consider this phonon vibration, they are in fact, coupled together.

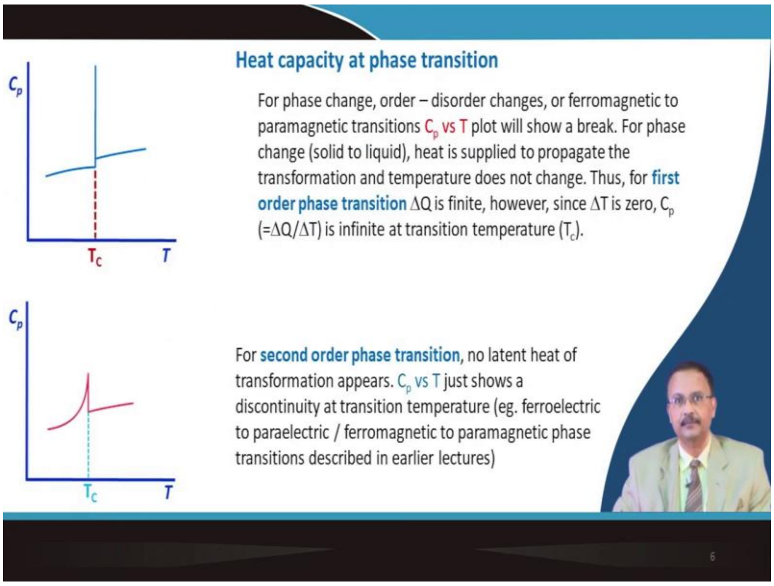
So, phonons are actually waves through the solid body and its having its own wavelength and frequency and the energies are quantized. So, the heat capacity that can be given approximate it by this complicated relation. I am not going into the details of this Debye amendment.

So, here you can see the value R is included; T is the temperature and we can define a Debye temperature. So, this is a particular temperature for a respective solid, where subsequently, it goes to the high temperature case.

So, it approaches the 3 R values. So, this theta D is the Debye temperature and you will have to integrate it from 0 to theta D by T, this parameter where x is given by h nu by K B T. So, nu is the frequency term and this Debye temperature is given by h nu D by K B and actually, ah it follows this relation in this region, where actually it is not only not follow the 3 R value.

So, at very low temperature well below the Debye temperature this equation is valid. So, it can be derived from this larger equation and here, you can see that C V that actually varies with a cubic power of the temperature.

(Refer Slide Time: 08:59)



Heat capacity at phase transition

For phase change, order – disorder changes, or ferromagnetic to paramagnetic transitions C_p vs T plot will show a break. For phase change (solid to liquid), heat is supplied to propagate the transformation and temperature does not change. Thus, for **first order phase transition** ΔQ is finite, however, since ΔT is zero, C_p ($=\Delta Q/\Delta T$) is infinite at transition temperature (T_c).

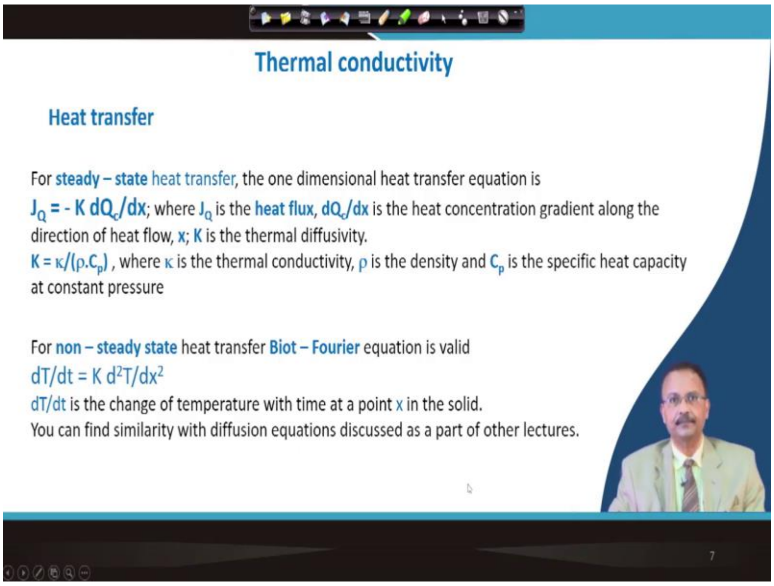
For **second order phase transition**, no latent heat of transformation appears. C_p vs T just shows a discontinuity at transition temperature (eg. ferroelectric to paraelectric / ferromagnetic to paramagnetic phase transitions described in earlier lectures)

So, heat capacity that is very closely related to the phase transition and partially, I have already described it. So, when the phase change is involved. So, it is a order to disorder change, ferromagnetic to paramagnetic transition temperatures can be considered and here in this case, C p is involved. C p as a function of temperature is involved. So, it actually both for first order and second order transition, there is a break in this C p versus T curve and corresponding to this break, that temperature is your transition temperature.

So, when phase change takes place as you can understand that for the first order phase transition, when phase changes involved say solid to liquid kind of phase transition taking place. So, there heat is being taken, but temperature is not changing. So, del T is essentially zero. So, the value of your constant I mean C p at that particular temperature, this is in finite. So, it is expected because delta T is zero. So, it is almost undefined.

For second order phase transition, no latent heat transformation case appears. So, C p and T is just so show some kind of discontinuity at the transition temperature. Typical example is ferroelectric to paraelectric or ferromagnetic to paramagnetic kind of phase transition that already I have described in my earlier lectures.

(Refer Slide Time: 10:41)



Thermal conductivity

Heat transfer

For **steady – state** heat transfer, the one dimensional heat transfer equation is

$J_Q = - K\, dQ_c/dx$; where J_Q is the **heat flux**, dQ_c/dx is the heat concentration gradient along the direction of heat flow, x; K is the thermal diffusivity.

$K = \kappa/(\rho.C_p)$, where κ is the thermal conductivity, ρ is the density and C_p is the specific heat capacity at constant pressure

For **non – steady state** heat transfer **Biot – Fourier** equation is valid

$dT/dt = K\, d^2T/dx^2$

dT/dt is the change of temperature with time at a point x in the solid.

You can find similarity with diffusion equations discussed as a part of other lectures.

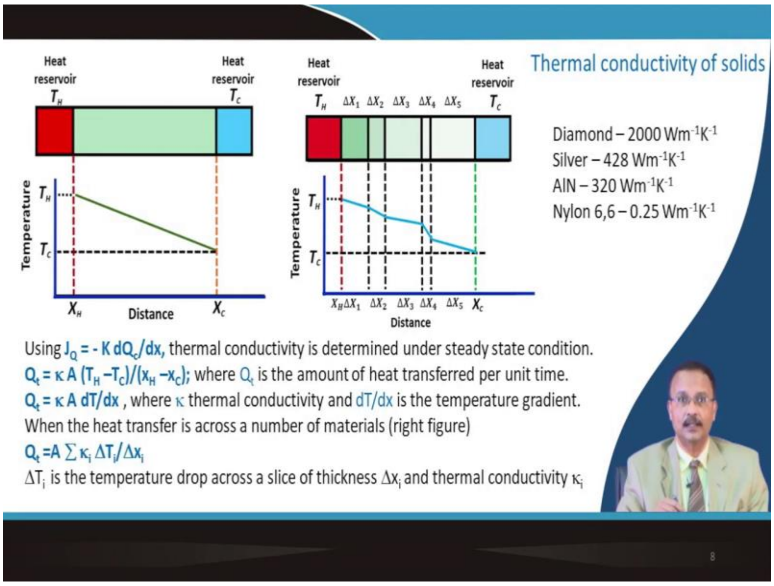
Now, in order to explain the thermal conductivity, we will have to understand the basics of heat transfer. So, for the steady state heat transferred in one-dimensional case, this equation is valid. So, J Q is K into dQ dQ c by dx. So, that is the gradient.

So, J Q is your heat flux and dQ c by dx that is heat concentration gradient along with the direction of the heat flow and this K is called the thermal diffusivity. Now, thermal diffusivity is related to thermal conductivity and in this relation, as you can see the density of the material as well as C p is also involved at constant pressure.

So, thermal diffusivity and thermal conductivity, they are related. If you go for a non-steady kind of heat transfer which is actually known as Biot-Fourier equation. So, that is the temperature gradient not sorry the rate of temperature change dT by dt that is equal to diffusivity and d squared T by dx squared.

So, dT by dx is the change of temperature with time at a point particular point x in the solid and you can find the similarities with this equation as we have described with the diffusion equation, I described earlier.

(Refer Slide Time: 12:25)



Thermal conductivity of solids

Diamond – 2000 $Wm^{-1}K^{-1}$
Silver – 428 $Wm^{-1}K^{-1}$
AlN – 320 $Wm^{-1}K^{-1}$
Nylon 6,6 – 0.25 $Wm^{-1}K^{-1}$

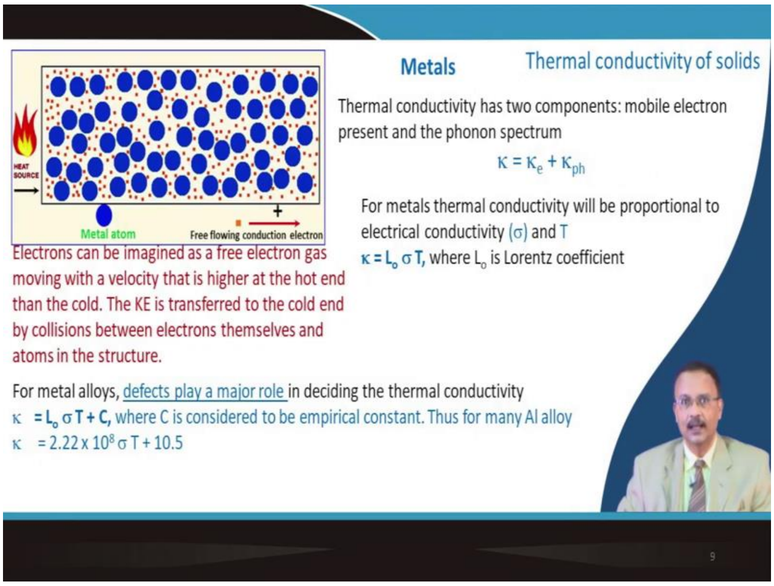
Using $J_Q = - K\, dQ_c/dx$, thermal conductivity is determined under steady state condition.
$Q_t = \kappa A (T_H - T_C)/(x_H - x_C)$; where Q_t is the amount of heat transferred per unit time.
$Q_t = \kappa A\, dT/dx$, where κ thermal conductivity and dT/dx is the temperature gradient.
When the heat transfer is across a number of materials (right figure)
$Q_t = A \sum \kappa_i \Delta T_i/\Delta x_i$
ΔT_i is the temperature drop across a slice of thickness Δx_i and thermal conductivity κ_i

Now, using this relation of J Q the thermal conductivity is determined under steady state condition. So, I can define the amount of heat transferred per unit time by this Q t term that is equal to thermal conductivity and area, cross sectional area of the solid in consideration and the change in temperature hot and cold and the gradient of x.

So, the equation is you can approximate like this that this Q t is thermal conductivity into area and this is the temperature gradient. So, that is the steady state equation.

And when you have multiple material connected in series, then across this number of materials which is shown in the right diagram, you can see, it is also a linear drop and this can be approximated as Q t is equal to area and then, summation of individual thermal conductivity and the surface temperature change del T i by del x i. So, this del T i is the temperature drop across a small slice whose thicknesses is xi and thermal conductivity is k i.

(Refer Slide Time: 13:55)



Metals Thermal conductivity of solids

Thermal conductivity has two components: mobile electron present and the phonon spectrum

$$\kappa = \kappa_e + \kappa_{ph}$$

For metals thermal conductivity will be proportional to electrical conductivity (σ) and T

$\kappa = L_o \sigma T$, where L_o is Lorentz coefficient

Electrons can be imagined as a free electron gas moving with a velocity that is higher at the hot end than the cold. The KE is transferred to the cold end by collisions between electrons themselves and atoms in the structure.

For metal alloys, defects play a major role in deciding the thermal conductivity

$\kappa = L_o \sigma T + C$, where C is considered to be empirical constant. Thus for many Al alloy

$\kappa = 2.22 \times 10^8 \sigma T + 10.5$

So, in case of metal, you know that the thermal conductivity has of course two component; one is of course, the mobile electron and you know that in case of metal, it is in a pool of electron and also, the phonon spectrum. So, your total thermal conductivity that will be a contribution from electronic as well as phonon contribution both will be there.

So, the metal thermal conductivity that will be proportional to electrical conductivity because they are also the charge carrier is involved.

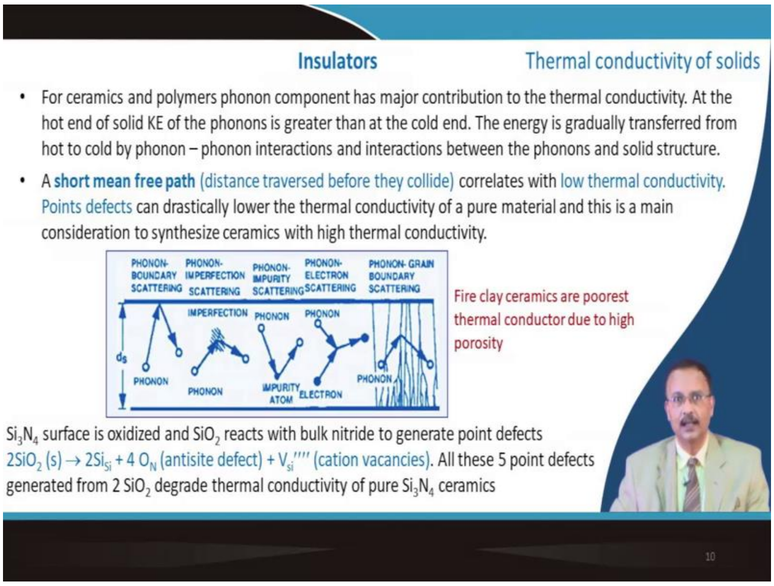
So, the electrical conductivity and temperature with thermal conductivity that is related by this relation which is L 0 into the electrical conductivity and the temperature and this constant is term as Lorentz coefficient. So, in case of alloy, you have also defect because it is not in pure form. So, it has also defects.

So, in defect is introduced, then you have an additional term here C and it indeed plays a major role towards the thermal conductivity. So, this empirical relation is valid for material with defect.

So, as for example, in case of aluminum alloy, this relation is valid. So, as you can see this is 2.22 into 10 to the power 8 and multiplied by the electronic conductivity and temperature plus a constant term which is exclusively for the defects.

So, as this view graph shows that electron can be imagined as I said in a pool of electron and the velocity of it is higher at the hot end than the cold and so, the kinetic energy is in fact transferred to the cold end by collusion collision between electron itself or collision with the atoms in the structure and thus, the heat is transferred.

(Refer Slide Time: 16:07)



Insulators Thermal conductivity of solids

- For ceramics and polymers phonon component has major contribution to the thermal conductivity. At the hot end of solid KE of the phonons is greater than at the cold end. The energy is gradually transferred from hot to cold by phonon – phonon interactions and interactions between the phonons and solid structure.
- A **short mean free path** (distance traversed before they collide) correlates with low thermal conductivity. Points defects can drastically lower the thermal conductivity of a pure material and this is a main consideration to synthesize ceramics with high thermal conductivity.

Fire clay ceramics are poorest thermal conductor due to high porosity

Si_3N_4 surface is oxidized and SiO_2 reacts with bulk nitride to generate point defects $2SiO_2\,(s) \rightarrow 2Si_{Si} + 4\,O_N$ (antisite defect) + V_{Si}'''' (cation vacancies). All these 5 point defects generated from 2 SiO_2 degrade thermal conductivity of pure Si_3N_4 ceramics

In case of insulator like polymers or ceramics, phonon component is of course having the major contribution to the thermal conductivity. So, at the hot end, the solid kinetic energy of the phonon is of course the greater than the cold end and energy is gradually transferred from hot end to cold end by phonon-phonon interaction and interaction between the phonon and the solid structure, similar to the electrons.

So, a mean path is important. So, that is the distance travel before it is actually collide. So, short mean path correlates with low thermal conductivity.

So, if you have point defects that can drastically lower the thermal conductivity because that will reduce the collision of the phonon. So, as compared to the pure material, it will have lower thermal conductivity and this is the main consideration to synthesize ceramics with high thermal conductivity. So, introduce defects.

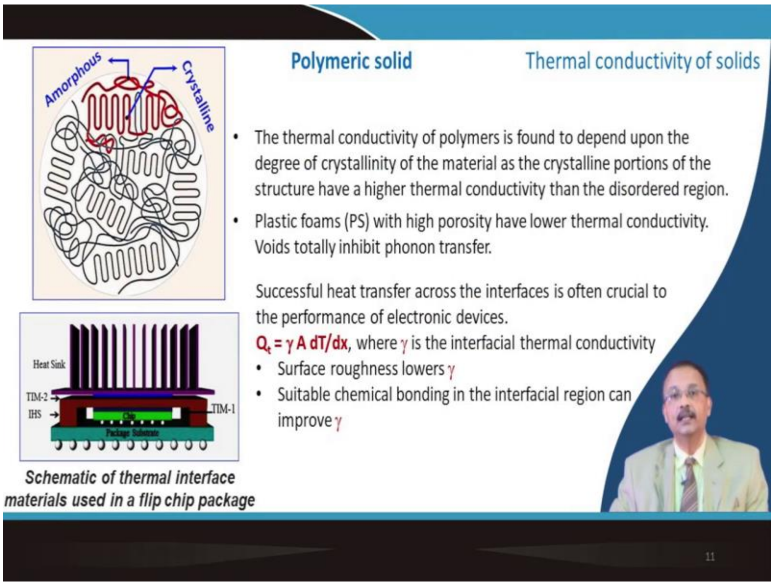
So, here I have shown different types of phonon interaction. So, phonon with boundary scattering, phonon scattering with the imperfection, with impurity atom and decide atom, then phonon electron interaction, phonon interaction with the grain boundaries. So, various mechanisms are possible.

So, if you consider a ceramic which is reasonably good thermal conductor. So, that surface of say silicon nitride and this kind of material is oxidized when it reacts with oxygen ambient oxygen and it forms a layer of Si O 2 and it generates point defect. As you can see that it generates the point defect and you know that how point defects exactly is denoted.

So, you can have silicon in regular silicon site and then some of the oxygen is going to the nitrogen site, which we call antisite defects and also, cation vacancies will be created.

So, totally if you do the balance, you can see that of course oxygen is plus 2 valent and nitrogen is having different balanced it. So, all these five point defects generated for the creation of a Si O 2 that eventually degrades the thermal conductivity of pure Si 3 and 4 ceramic. So, this oxidation will have to be taken care off.

(Refer Slide Time: 18:49)



Polymeric solid

Thermal conductivity of solids

- The thermal conductivity of polymers is found to depend upon the degree of crystallinity of the material as the crystalline portions of the structure have a higher thermal conductivity than the disordered region.
- Plastic foams (PS) with high porosity have lower thermal conductivity. Voids totally inhibit phonon transfer.

Successful heat transfer across the interfaces is often crucial to the performance of electronic devices.

$Q_t = \gamma A\, dT/dx$, where γ is the interfacial thermal conductivity

- Surface roughness lowers γ
- Suitable chemical bonding in the interfacial region can improve γ

Schematic of thermal interface materials used in a flip chip package

In case of polymeric solid, the thermal conductivity of the polymer is usually depend on the degree of crystallinity and material with a crystalline portion if it is high, then the structure will have higher thermal conductivity than the disordered region as we have shown it here, most of the amorphous region and some places, they are crystalline, so that will conduct it.

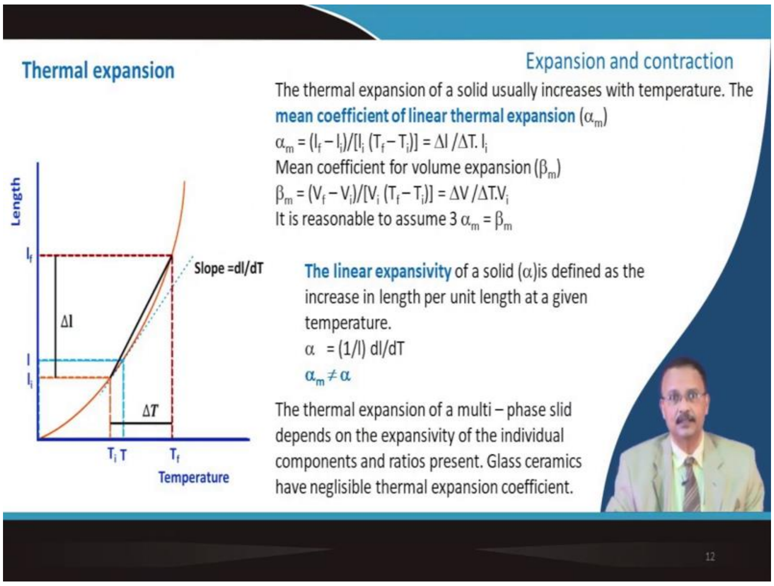
So, the foams are developed plastic foams that will have high porosity in inside the structure and they have relatively lower thermal conductivity and voids actually inhibit this phonon transfer which I just mentioned.

So, successful heat transfer across the interface is often important. So, this is not within a single material; but a interface in electronic circuitry. Many of the cases, you know that in the computer also you have the chip which is having a heat sink, here as you can see this metal fins are fitted on the top and actually, there are certain material that is involved in a flip chip package.

So, that actually gives the good interfacial conductivity. So, now the equation is slightly changed instead of thermal conductivity, I will introduce a term of interfacial conductivity which depends on the surface roughness. So, if it is surface roughness is more, then this your gamma will be deteriorated and suitable chemical bonding in the interface region can improve gamma.

So, there are a lot of pastes etcetera is available. So, once you put it, then you put that paste on top of it this is we call it say TIM kind of material; so, Thermal Interface Material that is given there. So, that the heat transfer is perfect. So, the thing is not heated up.

(Refer Slide Time: 21:01)



Thermal expansion

Expansion and contraction

The thermal expansion of a solid usually increases with temperature. The **mean coefficient of linear thermal expansion** (α_m)

$\alpha_m = (l_f - l_i)/[l_i (T_f - T_i)] = \Delta l / \Delta T. l_i$

Mean coefficient for volume expansion (β_m)

$\beta_m = (V_f - V_i)/[V_i (T_f - T_i)] = \Delta V / \Delta T. V_i$

It is reasonable to assume $3 \alpha_m = \beta_m$

The linear expansivity of a solid (α)is defined as the increase in length per unit length at a given temperature.

$\alpha = (1/l) dl/dT$

$\alpha_m \neq \alpha$

The thermal expansion of a multi – phase slid depends on the expansivity of the individual components and ratios present. Glass ceramics have neglisible thermal expansion coefficient.

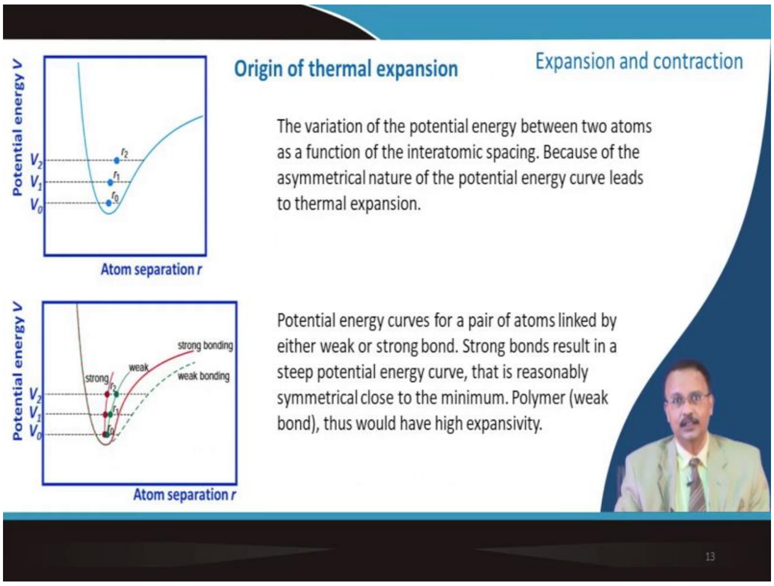
So, it dissipates, then let us talk about the thermal expansion. So, thermal expansion of the solid usually increases with the temperature and we can define a mean thermal coefficient of linear thermal expansion. So, that is given by this relation final length minus initial length divided by initial length into change in the temperature.

So, this is del l by li divided by delta T. So, mean coefficient of the volume that also can be estimated and tentatively, this linear coefficient is one-third; sorry, three times of the volume coefficient. So, 3 alpha m is your volume coefficient which is given by beta m.

The term the linear expansivity of a solid which I have defined as alpha here is the increase of length per unit increase in the length per unit length is given by this relation. So, it is dl by dT by l. So, that define the linear expansivity and clearly, if you then compare the two, alpha m is certainly not equal to alpha.

So, the thermal expansion of a multi-phase solid depends on the expansivity of the individual component and also, the ratio of the component that is present in the material. Glass ceramics for example, they have negligible thermal expansion coefficient and that is why it is used for the cook top etcetera.

(Refer Slide Time: 22:39)



Origin of thermal expansion

Expansion and contraction

The variation of the potential energy between two atoms as a function of the interatomic spacing. Because of the asymmetrical nature of the potential energy curve leads to thermal expansion.

Potential energy curves for a pair of atoms linked by either weak or strong bond. Strong bonds result in a steep potential energy curve, that is reasonably symmetrical close to the minimum. Polymer (weak bond), thus would have high expansivity.

So, the origin of the thermal expansion, you can derive it from first principle calculation. Although, explicitly have not taken as a part of this course, but you can calculate the attractive potential between two atoms as well as repulsive potential.

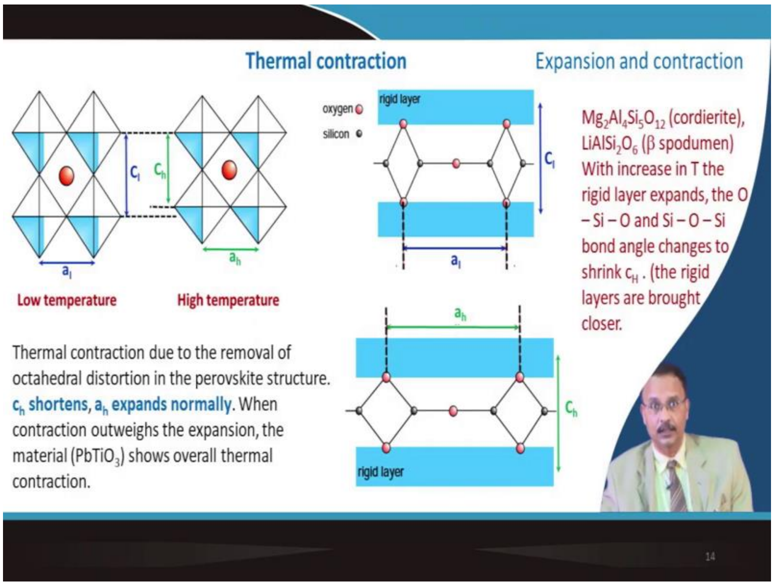
And I think partly, I have described it in one of my earlier lectures and you can calculate the variation of potential energy as a function of the separation between these two atom. So, that curve is shown here. So, the minimum inter atomic position is somewhere here. Now, if you increase the temperature, then it will be average position will be maintained between these two extreme position.

So, as you can see that if this one is totally asymmetric, something like this; it is asymmetric the dotted line, then this mean position with the increasing temperature that will be expanded.

So, this material will show large thermal expansion coefficient. As compared to the material with stronger bond, where it is more or less symmetric, this potential well is symmetric. So, the mean position will be maintained even if you increase the temperature and those kind of material will not exhibit appreciable thermal expansion coefficient.

You can work it out; say for example, you can compare between magnesium oxide and sodium chloride and calculate the attractive and repulsive potential and then, sum it up to get the total potential and then, you can see exactly how it varies assuming some arbitrarily the value of r, so that you can generate this whole curve and accordingly, you can see that whether it will be thermal expansion will take place or not in this type of material.

(Refer Slide Time: 24:39)



Thermal contraction

Expansion and contraction

Low temperature

High temperature

Thermal contraction due to the removal of octahedral distortion in the perovskite structure. c_h shortens, a_h expands normally. When contraction outweighs the expansion, the material ($PbTiO_3$) shows overall thermal contraction.

$Mg_2Al_4Si_5O_{12}$ (cordierite), $LiAlSi_2O_6$ (β spodumen) With increase in T the rigid layer expands, the O – Si – O and Si – O – Si bond angle changes to shrink c_H . (the rigid layers are brought closer.

Now, for certain material thermal contraction is also applicable and one example already I had sited, when I was talking about the ferroelectric phase transition. As you can see that once you have a low temperature case, then the tetragonal phase for this hypothetical octahedra and your cation is sitting exactly at the central position.

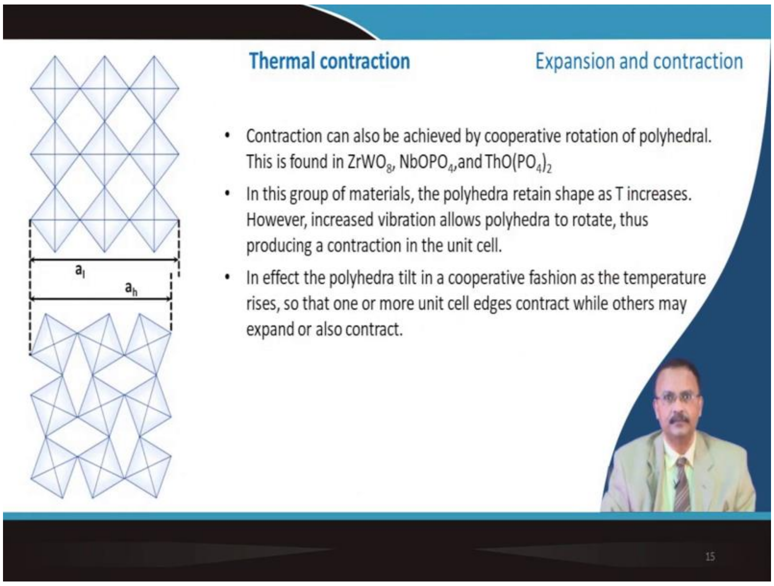
So, it is having a tetragonal structure. So, the value of this one at low temperature is C l and then, once you cross the phase transition temperature; then of course, this diagonal this is a bit increased, but mostly this one is reduced.

So, you will have to see that when the contraction outweighs the expansion of a material like perovskite lead titanate, then overall thermal contraction takes place. Another example is for this types of ceramic which is cordierite or which is spodumene type ceramics, it has two rigid structure.

As you can see two rigid structure and it is bounded by either silicon-oxygen, oxygen-oxygen, silicon-oxygen or silicon-oxygen-oxygen kind of bond. So, what happens when you increase the temperature, then this rigid bond, they are actually this is expanded.

So, this part is expanded the rigid layer and this oxygen-silicon-oxygen and silicon-oxygen-silicon bond angle changes, so that basically shrink and once it shrink, that brings this rigid layer close to each other. So, then the thermal contraction takes place in this type of material.

(Refer Slide Time: 26:37)



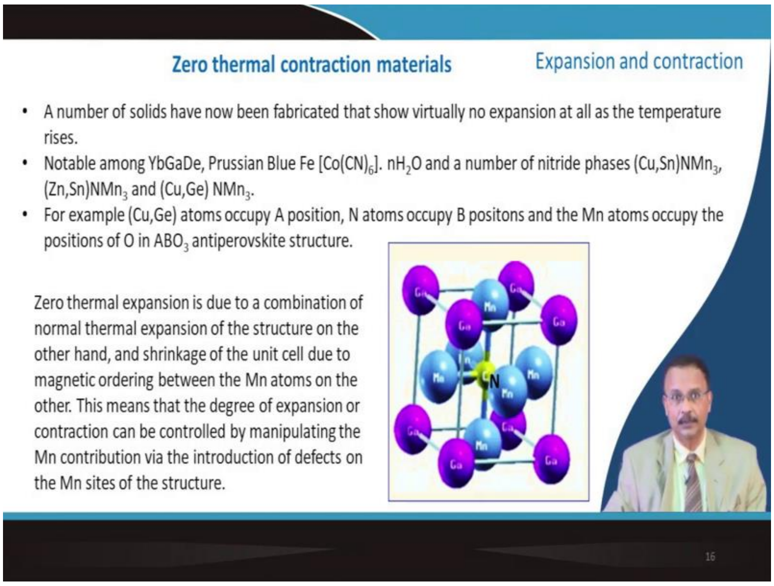
Thermal contraction

Expansion and contraction

- Contraction can also be achieved by cooperative rotation of polyhedral. This is found in $ZrWO_8$, $NbOPO_4$, and $ThO(PO_4)_2$
- In this group of materials, the polyhedra retain shape as T increases. However, increased vibration allows polyhedra to rotate, thus producing a contraction in the unit cell.
- In effect the polyhedra tilt in a cooperative fashion as the temperature rises, so that one or more unit cell edges contract while others may expand or also contract.

There are other types of material typically this tungsten oxide base or a phosphate base material, where this polyhedral, it changes its shapes. So, it is not actually changing the dimension; but it just rotates, it distorts and effectively, due to this cooperative distortion there is a thermal contraction.

(Refer Slide Time: 27:07)



Zero thermal contraction materials

Expansion and contraction

- A number of solids have now been fabricated that show virtually no expansion at all as the temperature rises.
- Notable among YbGaDe, Prussian Blue Fe [Co(CN)$_6$]. nH$_2$O and a number of nitride phases (Cu,Sn)NMn$_3$, (Zn,Sn)NMn$_3$ and (Cu,Ge) NMn$_3$.
- For example (Cu,Ge) atoms occupy A position, N atoms occupy B positons and the Mn atoms occupy the positions of O in ABO$_3$ antiperovskite structure.

Zero thermal expansion is due to a combination of normal thermal expansion of the structure on the other hand, and shrinkage of the unit cell due to magnetic ordering between the Mn atoms on the other. This means that the degree of expansion or contraction can be controlled by manipulating the Mn contribution via the introduction of defects on the Mn sites of the structure.

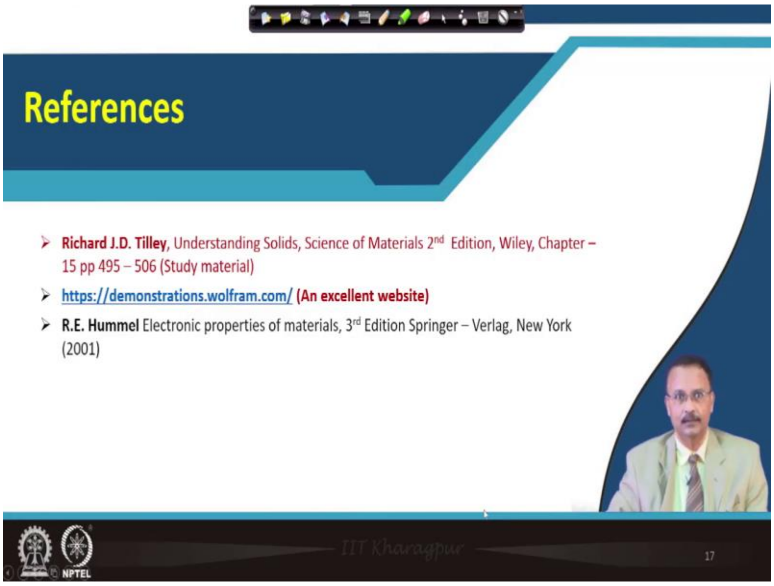
So, then people start working on a material. If it is possible which is does not have any thermal expansion or thermal contraction at all. So, number of solids now it is known. So, what are notable? This is your Prussian Blue is one of them, ytterbium, gallium and De that is another material. This exhibits actually no thermal contraction. So, this is actually the material, it exhibits this kind of non-thermal expansion, this is called the anti-perovskite material.

So, this is a combination of normal thermal expansion of course it will take place, but in addition a shrinkage of the unit cell will occur, mainly due to the magnetic ordering between the manganese atoms.

So, in this case, I have cited an example of copper germanium which actually takes this A site in the near three lattice and N atom is occupy in the octahedral site and actually, the oxygen in regular perovskite that is taken by manganese. So, this manganese atoms, they have this magnetic ordering.

So, eventually, the degree of expansion or contraction can be controlled by manipulating this manganese contribution via the introduction maybe of defects or by dopant cation. So, this type of material actually they are zero thermal expansion, sorry zero thermal contraction or you can see thermal expansion material that has been worked out.

(Refer Slide Time: 29:03)

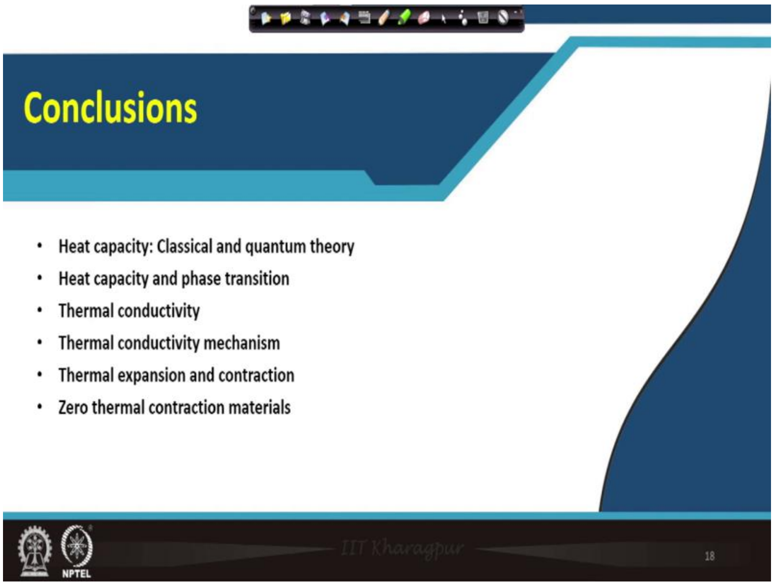


References

- **Richard J.D. Tilley**, Understanding Solids, Science of Materials 2nd Edition, Wiley, Chapter – 15 pp 495 – 506 (Study material)
- https://demonstrations.wolfram.com/ (An excellent website)
- **R.E. Hummel** Electronic properties of materials, 3rd Edition Springer – Verlag, New York (2001)

So, these are the references. Mostly, in the book by the J. D. Tilley. There are certain very good sites available in the internet, where interactively, you can understand the crystal structure and other phenomena.

(Refer Slide Time: 29:33)



Conclusions

- Heat capacity: Classical and quantum theory
- Heat capacity and phase transition
- Thermal conductivity
- Thermal conductivity mechanism
- Thermal expansion and contraction
- Zero thermal contraction materials

So, here we have described the heat capacity concept, both classical and quantum theory for the specific heat. Then, heat capacity and phase transition, this interrelation was explained in order of first order and second order phase transition. Then, introduced thermal conductivity concept, thermal conductivity mechanism also was outlined and thermal expansion and contraction, why it happens in a nonmetallic material that we talked about and finally, we talked about zero thermal contraction material.

Thank you for your attention.