Physics of Functional Materials and Devices
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Lecture – 22, Week 6
Thermal Properties of Solids

Welcome back to the next set of lectures. So, today would be the first lecture of week 6. In the previous week we had stopped at a point where we were discussing about the mechanical properties of solids. So, today let us start with the topic that is thermal properties of solids. In today's and the next lecture what I will do will focus significant amount of time on thermal expansion in solids and how these properties can be tuned and why functional materials which have different orders and different types of thermal expansions have become extremely important in today's world. We also then move on and discuss about thermal stress and thermal conductivity.

So, if you look around you will find that if I talk about a material and if I talk about the physical, chemical or physiochemical properties of these materials. then we classify the properties of these materials under various subcategories. For examples, we have talked about mechanical properties, you can have properties which can be classifies under the heading of chemical properties. or you can have physical properties as you change the size of the particle or the body or the device you can have properties which would be size dependent or dimensional properties.

And let us start with an interesting topic that is the thermal properties in solids. As the name suggests what would these thermal properties mean? So, if you have thermal energy given to a material what will change? you have seen that if you put a heater very near to yourself when it is a cold winter day then you can sustain that heat for certain amount of time. And after that you start feeling agitated or you your body gets heated up and you want to switch off the heater or you want to move away from the heater. So, that you do not get the same magnitude of heat falling on your body which is increasing the temperature of your body or heating the skin at which these thermal radiations are falling. So, you have properties which would change as a function of temperature variation or we will say the variation in the thermal energy and those would appear as changes in heat capacity or expansion or stress or conductivity. What is heat capacity? Heat capacity is the amount of heat required to change the temperature of a body by a degree. that is what a heat capacity means and it is denoted by Joule per Kelvin that is the standard unit and mathematically it is expressed as:

$$C = \frac{\partial Q}{\partial T}$$

Now, why should heat capacity change and what is the origin of heat capacity? Some of the sources because of which you see the origin of heat capacity or variation in heat capacity are vibration or vibrations of an atom or vibrations in a set of atoms. How do you arrange these atoms? That means ordering of the atoms, it is long range ordering, short range ordering.

How do you arrange these atoms and finally, conduction of electrons that means you have a medium through which the carrier is moving from one place to the other and carrying certain information. It can be in the terms of charge or heat or energy, thermal energy or kinetic energy, but there is a medium in which the carrier is moving. Specific heat is related to the heat capacity of solids. it is defined as the heat required to enhance the temperature of a unit mass of a substance by a unit degree of temperature. So, rather than going from heat capacity sometimes you talk about specific heat because then you define unit mass and therefore, the comparison of performance of a material which is being characterized in different places in different labs or different research groups it becomes easier because specific heat means you will be talking about a unit mass of the substance.

Please note that when we talk about thermal energy there are certain factors which you should always have in your mind. thermal energy is a combination of kinetic energy of atoms which are undergoing motion. So, you do not have even at absolute 0, you do not have the condition where the atoms become static because you have 0 point energy. So, you always have kinetic energy associated with atomic motions. and along with that you have the potential energy due to the distortion of inter atomic bonds.

So, you have these atoms which are moving and so, you measure a length between two static atoms, but they are undergoing some motion and because of these continuous motions, there is some distortion of the inter atomic bonds and the associated potential energy. So, the thermal energy is a combination of kinetic energy and potential energy. the vibrations of the atoms which are arranged in a given order, the order can be short range or long range is the main source of thermal energy. Now, if I have two atoms which are placed near to each other and then I want to build a lattice around it. Then you put this building block two atoms then two atoms and two atoms and two atoms and two atoms.

So, you have an arrangement of these unit cells. Now, you will see each atom is linked to the nearest atom. So, this atom which is at let us say site A cannot go and sit at site B without displacing the atom. So, there is a limit up to which the atoms can vibrate. So, that you do not impinge or restrict the motion of the next atom and you also do not go to a state where you increase your Gibbs free energy.

A stable lattice means that you are in the minimal Gibbs energy state. So, you have a limit up to which the vibrations can take place. Therefore, vibrations of individual atoms are not independent from each other. And if they are not independent of each other that means, there is some kind of dependence and this is actually investigated in terms of the coupling of the atomic vibrations of the adjacent atoms which results in the waves of atomic displacement. So, there is a coupling between the atoms.

If you have this wave, then it is characterized by a wavelength and frequency. For a wave with given frequency υ, there is a smallest quantum of vibration energy that is hυ. and this is called as phonon where h is the Planck's constant. Thus the thermal energy is the energy of all phonons or all vibrational waves which are present in the crystal at a given temperature. This thing must be clear in your mind.

Now suppose you have a device it is operating in on a day where you have 0° that is a typical winter day then you want to use the same device in summer day where the temperatures may reach 45°. Will the performance of the device be same because most of the components of the device will have different thermal properties. So, there would be some variations in the response characteristics of each and every material which is being used to fabricate that device and hence the overall temperature dependence would be quite complicated. Hence, you must understand the thermal response of each and every material. before it goes into the device.

The heat capacity generally has weak temperature dependence at high temperature. So, if you go to very high temperatures, you see the change in slope is not as significant as it is at low temperatures. You see there is a significant change in the specific heat at lower temperatures. and at lower temperatures this specific heat obeys the Einstein's quantum theory and C_v therefore, varies as T^3. At room temperature C_v attains a constant value which is nearly $3R$ for one mole.

This law is the famous Dulong-Pettit's law. The law was invented in 1819 and it was based on the classical equipartition theory. Now if you look into the curve, if you look into the curve of C_v versus temperature in K, you will find that you clearly have two regions, but when the temperature is high then the value of specific heat approaches a certain constant value. And this is true for different types of alloys you will find that all these values for different alloys also are converging to a similar value at high temperatures, but at lower temperatures you can clearly see the materials behave differently from each other and the behavior can be quite different as you go in different regions. For example, if you see the change from let us say 100 to 200 K, you see the difference is much more in the specific heat variation in these materials when you are in the range of let us say 4 K to 75 K So, you can clearly see you have regions where the nature of specific heats are changing and hence you have to define the range of temperature where you want to use the specified material in a specified device.

You must characterize the material carefully as a function of varying temperature. Then comes the thermal expansions in matter. We all understand that when you heat a material it expands. This is what we always believe, but very soon Either in today's lecture or in the next lecture, I will introduce to you a class of materials which have become extremely important and those materials actually show negative thermal expansion that means, you heat those materials and they start to contract. What do we always believe that you heat a material it will expand, but there are a class of materials which contract when they are heated.

So, we will also talk about those materials in details, but in general if you see a material when it is heated it will expand you can have linear thermal expansion that means, in one dimension. You can have the aerial expansion that is you will have the area which is expanding. So, two dimension or you can have volume expansion where you believe that the material will expand in all the three dimensions that is x, y and z direction when it is heated. So, these are the three types of expansions which we see in materials. What is a linear thermal expansion? Let us take a case of a rod which is shown by the solid figure here.

You heat this material and take the temperature from T to $T + \Delta T$. The length changes from L to $L + \Delta L$. In this case what will you find $\frac{\Delta L}{L}$ would be proportional to certain number and the change in temperature. This proportionality constant is then known as coefficient of linear expansion and this is an intrinsic property of a given material. If you see the table, you will find that as you move from one material, let us say aluminum to lead to iron to copper to brass silver or pyrex, you can clearly see the expansion coefficients are very different.

You will say that it is let us say lead is 0.29 x 10 raise to the power of minus 5 per Kelvin and aluminum is just 2.5 x 10 raise to the power of minus 5 per Kelvin. We are already talking in terms of minus 5 order. So, how does it impact the overall properties, but if you look into the change in the behavior of these materials.

This is let us say 90 percent change. So, you have huge magnitude change. So, or you can say this is approximately 2.9 x 10 raise to the power of minus 6 and this is 25 x 10 raise to power of minus 6. So, it becomes a huge number you are seeing magnitude change.

So, you see an order different if you see the thermal expansion of lead compared to aluminum and that is where the choice of material comes in. Suppose, you want to have an application where you must see large change in the size of the material when there is small change in temperature. Then which material will you use? Will you use lead or will you use aluminum? For example, you want to have a thermal switch so that if there even if there is a change 20° you have significant change in the size of the material and if you are using it in certain alarm systems then if the two plates were separated from each other, but aluminum was in between then when there is a change in temperature the aluminum plate will then expand and it will connect the two conducting plates and you can have a current flowing and you have a alarm system in place. That is a typical fire alarm system which is made. So, which material will you use? Will you use aluminum or lead? Obviously, you will use a material which has much higher expansion coefficient.

Now you have seen you can have linear expansion or you can have areal expansion or you can have volume expansion. Is there a relationship which gives you a rough idea as to how these expansions are related? Let us start with the relationship derivation which will relate the linear expansion coefficient with the volume expansion coefficient. So, we have seen that ΔL is the change in length and ΔV is the change in volume temperature from T to $T + \Delta T$. $\Delta L = L \times \alpha_1 \times \Delta T$.

Now, this is a change in length in all the three dimensions.

So, you will see change of ΔL in x direction, ΔL in y direction, ΔL in z direction. So, what is going to happen if in terms of volume? volume would be:

$$(L + \Delta L)^3 - L^3$$

That would be equal to $3L^2\, \Delta L$. So, this is what you will get. In terms of ΔL^3 and ΔL^2, you will see that the cube and the squares of a small quantities are even smaller. Hence, you can neglect ΔL^3 and ΔL^2 values.

You can neglect, but you cannot say that they are not there. In some applications, you may have to use certain number of components, so that these factors are actually taken into consideration. but broadly to start we will believe that ΔL^3 and ΔL^2 can be recollected. Hence, what will you get? You will get ΔV by $V = 3 \times \frac{\Delta L}{L}$ that would be equal to thrice of $\alpha_1\, \Delta T$. Why? Because you are writing as $\frac{\Delta L}{L} = \alpha_1 \times \Delta T$. So, what you will get? $\frac{\Delta V}{V} = \alpha_{\mathrm{v}}\, \Delta T$ that is equal to $3\alpha_1\, \Delta T$.

So, using these two relations what do you get? You get $\alpha_{\mathrm{v}} = 3\alpha_1$ that is you are relating the volume expansion with linear expansion. I have written 1 or you can write l here because it is in one dimension. So, either α_l related to α_v or just to show that we are considering one of the dimensions we have taken it as α_1 Similarly, you can derive a relationship between the linear expansion coefficient and areal expansion coefficient. So, what are you going to do? You are going to consider B and A as the breadth and length respectively of the body. Now, when you heat there would be some change in length and breadth and you would then get the change as $a + \Delta a$ and $b + \Delta b$ and the overall increase would become $\Delta a \times \Delta b$.

This is what we are going to do. So, $\varDelta A$ would become equal to $a\varDelta b + b\varDelta a + \varDelta a\, \varDelta b$ because there is an increase in the area itself along with the increase in the length and breadth individually. So, what you will get? $\varDelta a$ would become $a \times b \times \alpha_1\, \varDelta T$. then you will get $b \times a \times \alpha_1\, \varDelta T$ because you are having expansion in a and b directions both. And finally, the third term which is coming from the area denoted by the grayish area you have $a \times b \times (\alpha_1\, \varDelta T)^2$. So, you have the relationship. Now, you see that the last term is coming as a square quantity and both α_1 and $\varDelta T$ can be small and so you have a square of that and therefore, this quantity itself becomes quite small and then it can be neglected. Hence, what will you obtain? You will obtain $\frac{\varDelta A}{A} = 2\alpha_1\, \varDelta T$ and from there you will see that $\alpha_a = 2 \times \alpha_1$ or α_l if you want to write in terms of linear expansion or we are considering one dimension.

So, we have written as α_1. So, that is equivalent. So, the relationship between linear, areal and volume expansion coefficient would become $\alpha_1 = \frac{\alpha A}{2}$ that is equal to $\frac{\alpha_v}{3}$. So, you can get $3\alpha A = 2\alpha_v$. Then comes the stress quantity. Now, if you let us say heat a material, but do not allow the material to increase or decrease in size because either you are giving temperature. thermal energy or you are taking away thermal energy, then there is a stress building inside the system and this could be both heat or cold stress.

What is stress? Stress is the force acting per unit area. This is what we know. Now, the force can be of any form when you have the applied force. in the form of temperature the resultant stress is simply called as thermal stress. Now, if you once again draw a similar figure which we had drawn couple of slides back then what do you see let us say that the temperature is raised by $\varDelta T$ and the rod increases by $\varDelta L$.

Now, if the expansion is stopped forcefully, you do not allow the expansion to take place that is where you force the material to undergo a stress. You want to expand, but you are not being allowed to expand. So, internally you have a stress building and if you do not allow the system to expand even if you are increasing the temperature continuously then after a certain point you know the material would just undergo a failure that is induced by excessive heating of the system. And for this case the thermal stress would be $\varDelta T$ is equal to $L\, \alpha\, \varDelta T$ and thermostat is a very good example of application of thermal stress.

Similarly, you have thermal conductivity that how the heat transfers from one side of the medium or a body to the other if you have temperature difference in two regions of the body or the medium. Fourier's law for thermal conduction is quite routinely used to understand the transfer of heat through a material. And this law tells us that it is proportional to the negative of the temperature gradient along with the area. through which the heat flows and hence you can write this equation as $Q = K\varDelta T$ where $\varDelta T$ refers to the temperature gradient Q denotes the thermal flux and K refers to the thermal conductivity of the materials. Metals are rich conductors of heat whereas, you see insulators which are pad thermal conductors as well.

Now, if you have two bodies let us say Tc is one and Td is the other region where a body is going to get connected to. So, you have a body a rod which has two ends which are dipped in a surrounding or a medium where the temperatures are different. Now, if you do that what will happen? Assuming the ideal condition that the sides of the bar are fully insulated. So, you do not have any losses taking place from the middle. So, that there is no exchange between the sides and the surrounding.

So, you have two regions which are immersed into two heat zones. the intermediate region is not losing any heat this is what we mean. After sometime a steady state would be obtained that means, the whole body will have the same temperature. What is happening? The temperature of the bar decreases uniformly with the distance from Tc to Td if Tc is greater than Td. you can calculate these values and these values of flow of heat or heat current h is proportional to the difference $Tc - Td$ because we are considering $Tc > Td$.

And the area of cross section A would be considered because if the body has very small area in contact or a very large area in contact it would play a significant role as to how much heat you can take from one side to the other. Along with that the heat transfer would be inversely proportional to the length. So, let us say you have a body at this point and the other edge at this point and you have to take the heat from this point to this point. Now, if they are very near to each other the two ends then that heat transfer will be easier, then you have a case which is intermediate and then you have a case where the two ends are far apart.

So, the flow of heat would be difficult. This whole concept of heat current hence could be written as $H = \frac{KA(Tc - Td)}{L}$ where K is called the thermal conductivity. And you can write thermal conductivity in terms of watt per meter per Kelvin or any other ways which are mentioned in the standard So, you can clearly see that different materials have different thermal conductivity and their range of applications vary. So, I hope you have seen that by the choice of material you can get different expansion in these materials, different stresses in these materials, conductivity which is thermal conductivity in these materials would vary. and their range of application would be different and you will be able to make different devices by choosing different materials that have different thermal properties. These are the references from which the lecture notes were prepared today.

You can read more about the topics which were discussed today from these references and in the next lecture, we will spend some more time on thermal expansions in solids and more so in negative thermal expansion ceramics. Thank you very much.