Introduction to Solid State Physics

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Lecture – 54
Anharmonic effects in crystals: Thermal expansion and Umkclapp processes

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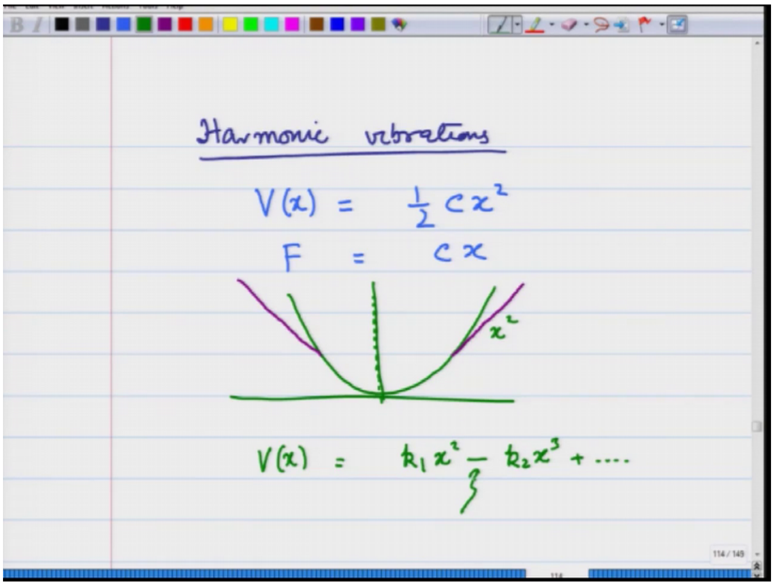

Harmonic vibrations

$$V(x) = \frac{1}{2} c x^2$$

$$F = c x$$

$$V(x) = k_1 x^2 - k_2 x^3 + \dots$$

So, far what we have considered are what is called harmonic vibrations or harmonic effects in that we have considered at the force or the potential between two atoms to be varying as x square and the force between two atoms to be proportional to the displacement between them. If I were to plot them the harmonic potential looks like this it is going as x square as the atoms distance changes; however, in real life it is not always x square it changes in particular it may become slightly softer as you go further out.

So, that I can write V x taking only the next correction into account as some constant let us so call it k 1 x square minus another constant k 2 x cubed and there could be higher order terms, but I am I will stop at x cube and when I put this minus sign; that means, the potential is becoming softer and that has interesting effects.

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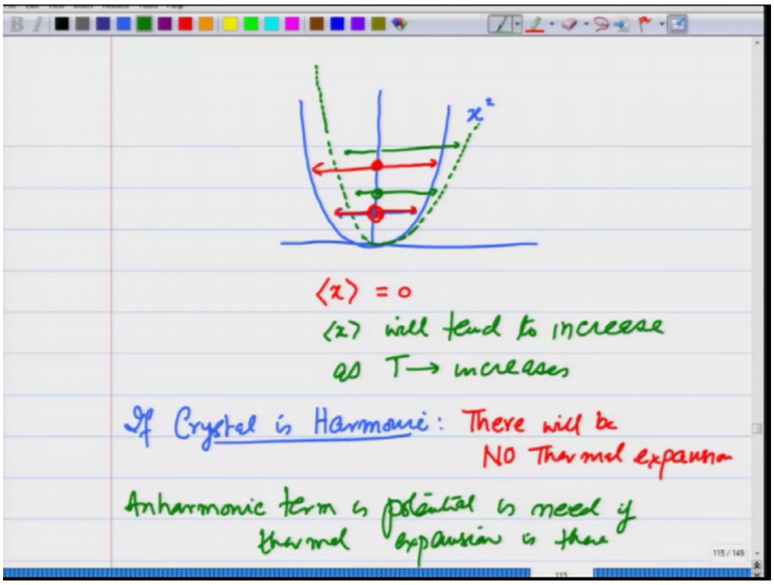

$\langle x \rangle = 0$

$\langle x \rangle$ will tend to increase
as T → increases

If Crystal is Harmonic: There will be
NO Thermal expansion

Anharmonic term is potential is need if
thermal expansion is there

Consider this suppose, an atom is in the harmonic potential x square, if I include the x cubed term on one side as x increases the potential will on one side as x increases the potential will become smaller because minus gx cubed and on the other side because x cube will be negative and minus will make the potential larger.

So, it will become asymmetric. Now imagine an atom here which is oscillating back and forth, let me make this atom by orange and it was oscillating back and forth as I increase the energy of the atom, it goes back and forth, but it is symmetric about x equals 0 and therefore, this average x remains 0. On the other hand if the potential was an harmonic that is shown by green then the atom would spend more time on the right hand side and less time on the left hand side as its energy increased and therefore, x will tend to increase as T increases.

Because as T increases the average energy of the atom goes up and it will shift towards softer side of the potential, notice what we have said what we have said is if crystal is harmonic; that means, the interaction between atoms is harmonic there will be no thermal expansion.

So, an harmonic term in potential is needed if thermal expansion is there. So, there are these and harmonic terms we need them to explain thermal expansion so, this is one effect of thermal expansion. The other effect which in particular I want to talk about is that it changes the thermal conductivity what is known as Umkclapp process and there is something new that you should know about.

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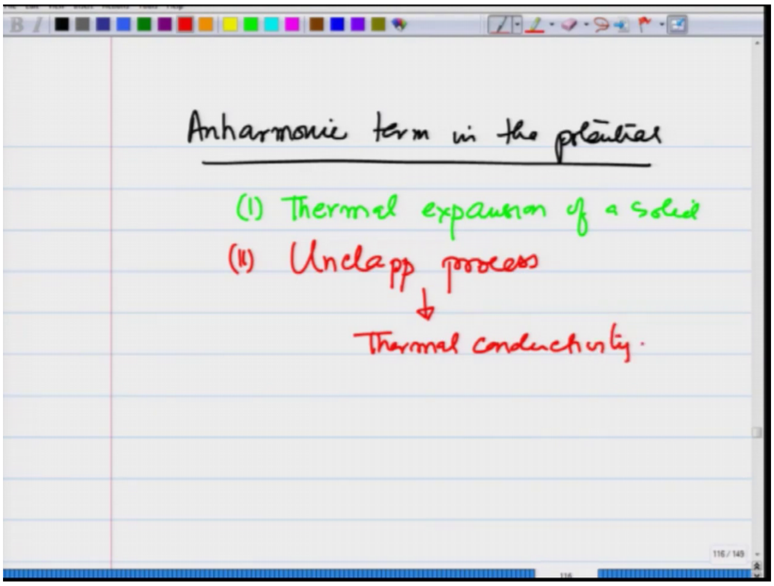

Anharmonic term in the potential

(I) Thermal expansion of a solid

(II) Unclapp process

$\downarrow$

Thermal conductivity.

So, I will talk about these two things in the context of an harmonic term, in the potential and two things that I am going to talk about is number 1 thermal expansion of a solid and the other thing that I am going to talk about is what is known as Umkclapp process? And this affects thermal conductivity.

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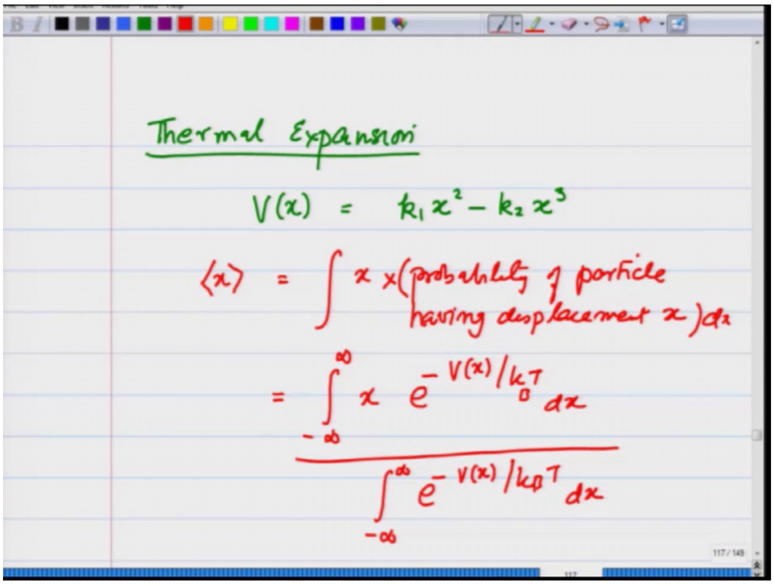

Thermal Expansion

$$V(x) = k_1 x^2 - k_2 x^3$$

$$\langle x \rangle = \int x \times (\text{probability of particle having displacement } x)\, dx$$

$$= \frac{\int_{-\infty}^{\infty} x\, e^{-V(x)/k_BT}\, dx}{\int_{-\infty}^{\infty} e^{-V(x)/k_BT}\, dx}$$

So, let us take a talk about thermal expansion first, the potential energy is given as let us say k 1 x square minus k 2 x cubed and if I want to calculate the average x this will be x times probability of particle having displacement x and then you integrate it over all the x and this taking the Boltzmann factor into account is going to be minus infinity to infinity x e raise to minus v x by k B T dx divided by the total probability which is 1. So, I have to normalize this whole thing e raise to minus v x over k B T dx.

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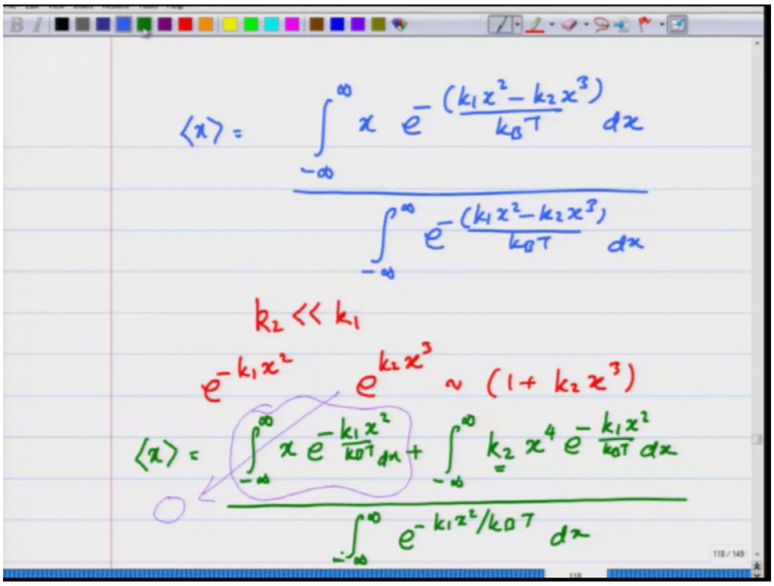

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} x\, e^{-\frac{(k_1x^2-k_2x^3)}{k_BT}}\,dx}{\int_{-\infty}^{\infty} e^{-\frac{(k_1x^2-k_2x^3)}{k_BT}}\,dx}$$

$k_2 << k_1$

$$e^{-k_1x^2} \qquad e^{k_2x^3} \sim (1+k_2x^3)$$

$$\langle x\rangle = \frac{\underbrace{\int_{-\infty}^{\infty} x\, e^{-\frac{k_1x^2}{k_BT}}dx}_{0} + \int_{-\infty}^{\infty} k_2\, x^4 e^{-\frac{k_1x^2}{k_BT}}dx}{\int_{-\infty}^{\infty} e^{-k_1x^2/k_BT}\,dx}$$

Lets now put in the expression for v x and then we get x equals integral minus infinity to infinity x e raised to minus k 1 x square minus k 2 x cubed dx divided by minus infinity to infinity e raised to minus k 1 x square minus k 2 x cubed divided by k B T divided by k B T dx and I want to this retain terms up to first order in k 2 now k 2 an harmonic effect we are taking to be much much smaller than k 1 and that is pretty ok.

Because experimentally what we find is that the first term itself explains a lot of things as we have been doing in the past few lectures. Now this thermal expansion comes about which is a very small number and that is affected by k 2 so k 2 is much smaller than k 1. So, therefore, what I am going to do is retain e raised to minus k 1 x square as is and take e raise to k 2 x cubed as 1 plus k 2 x cubed and keep terms only up to linear in k 2.

And therefore, I can have x is equal to integral minus infinity to infinity x e raised to minus k 1 x square plus minus infinity to infinity k 2 x raise to 4 e raise to minus k 1 x square dx divided by I have already taken care of this k 2 here up to linear term in the denominator, the lower term I will just neglect k 2 x cubed term even if I retain it will go upstairs as sum k 2 and then I can just ignore it.

So, I have expanded this up to k 2 and in the lower term I will just keep the quadratic term minus infinity to infinity e raised to minus k 1 x square over k B T dx I have forgotten k B T here dx divided by k B T dx. Now as we have argued earlier if you keep only the harmonic turns it does not give you any expansion and you can see it right here, that this term out here is odd in x and therefore, this integral is actually 0.

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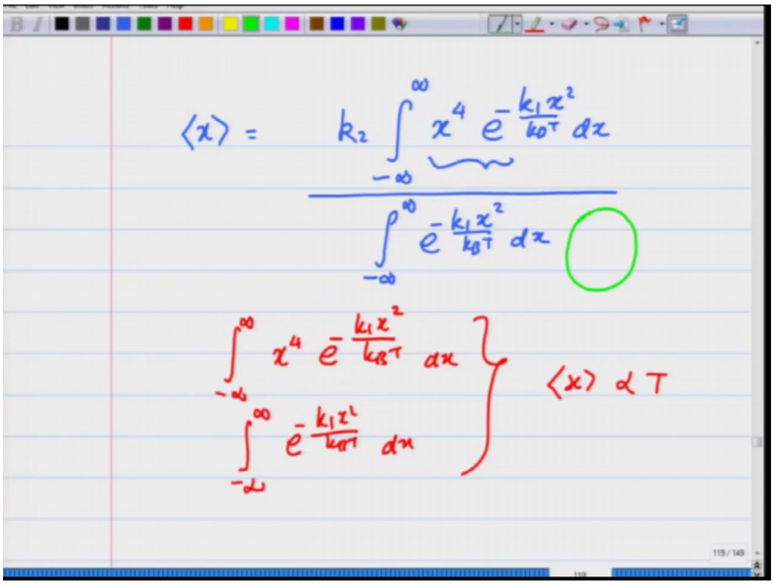

$$\langle x\rangle = \frac{k_2 \int_{-\infty}^{\infty} \underbrace{x^4 e^{-\frac{k_1 x^2}{k_B T}}} dx}{\int_{-\infty}^{\infty} e^{-\frac{k_1 x^2}{k_B T}} dx}$$

$$\left.\begin{array}{l} \int_{-\infty}^{\infty} x^4 e^{-\frac{k_1 x^2}{k_B T}} dx \\ \int_{-\infty}^{\infty} e^{-\frac{k_1 x^2}{k_B T}} dx \end{array}\right\} \langle x\rangle \propto T$$

And therefore, I have average x is equal to k 2 integral x raise to 4 e raise to minus k 0031 x square dx minus infinity to infinity divided by integral minus infinity to infinity e raised to minus k 1 x square dx there is a divided by k B T which I keep forgetting and you can see that x is now increasing this number is non 0.

So, if I include this x cubed term x is increasing as temperature goes up because as temperature goes up this term becomes smaller and smaller and therefore, this integral becomes larger and larger. In fact, this problem I will give you in the assignment is that you can integrate this very easily x raise to 4 e raised to minus k 1 x raise to x square over k B T dx and so you can the other integral e raise to minus k 1 x square over k B T dx and when you do this division you get x proportional to T.

So, the distance between these atoms increases, linearly with temperature and this is what you find in thermal expansion. If you include higher order terms there may be some corrections, but this is the first correction and so what you realize is that an harmonic terms are important, infact are responsible for thermal expansion.

You may be wondering why I dropped the an harmonic term here even if you include that it will be proportional to k 2 and if you take it through binomial expansion to the numerator since the first term is 0 this does not any have any effect on our answer. So, I could easily neglect that, I will I made these statements I like you to confirm those.

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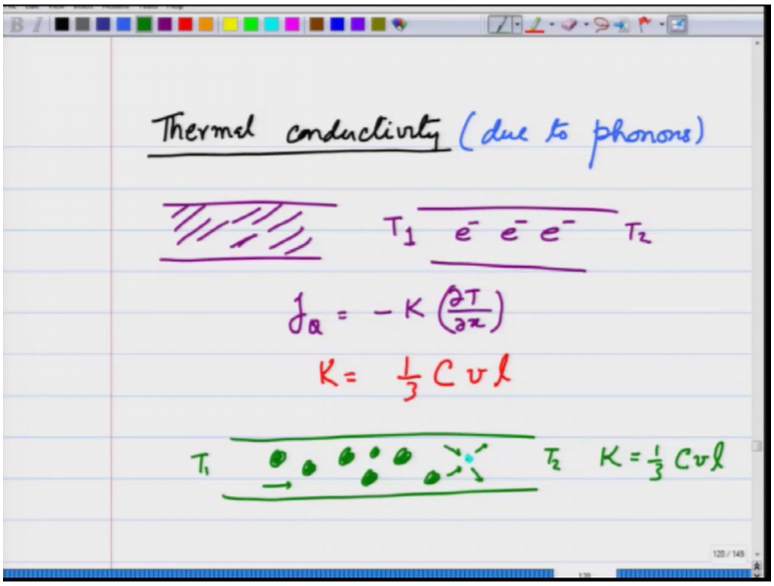

Thermal conductivity (due to phonons)

T_1 e^- e^- e^- T_2

$j_Q = -K\left(\frac{\partial T}{\partial x}\right)$

$K = \frac{1}{3} C v l$

T_1 T_2 $K = \frac{1}{3} C v l$

Second thing that I want to address now is, the thermal conductivity and this time thermal conductivity due to phonons; that means, due to atomic vibrations the first answer is exactly the same as in electrons. In electrons when you had a solid and professor Banerjee has already derived this.

If I had these electrons moving from one end to the other when there was a temperature gradient from T 1 to T 2 one saw that the current heat current was minus the thermal conductivity dT by dx and the thermal conductivity answer came out to be one third the heat capacity the average velocity of electrons times the mean free path.

Now change this picture to phonons and what you will find is that if I think of these phonons, like photons, like electrons particles carrying heat which vibrations certainly do from one way into the other, I will get exactly the same answer if I go from T 1 to T 2 the thermal conductivity due to phonons will be one third C v l, where C is the heat capacity due to phonons which we have already derived v is their average speed which you can take to be in a speed of sound for acoustic phonons and l is their mean free path why does mean free path arise?

Because these phonons are scattered by imperfections in the lattice, so there is a phonon which is coming in it may get scattered it may get scattered just like electrons were getting scattered due to imperfections in the Drude model, so this is the standard formula.

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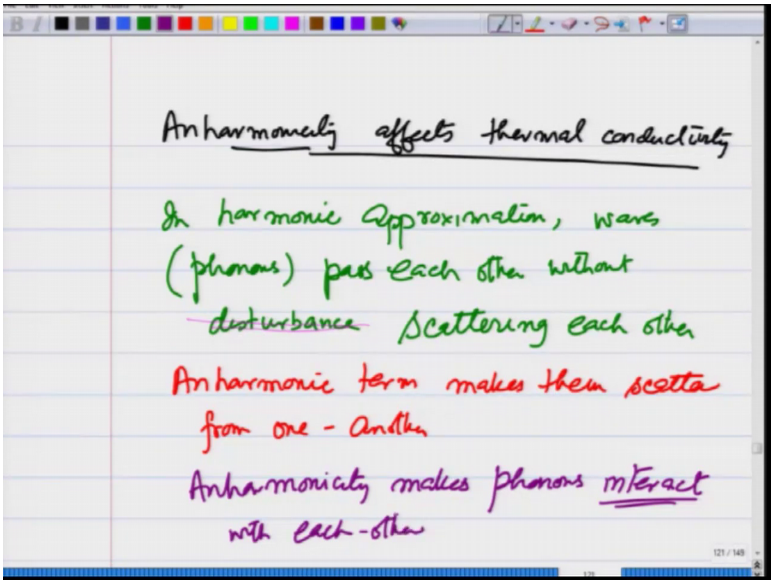

Anharmonicity affects thermal conductivity

In harmonic approximation, waves (phonons) pass each other without ~~disturbance~~ Scattering each other

Anharmonic term makes them scatter from one - another

Anharmonicity makes phonons interact with each-other

Now, how does an harmonicity affects it affects how so what I want to answer is how does it affect the thermal conductivity. Let us explore that, suppose there are an harmonic terms what will happen to phonons? Now you see if there are these only harmonic terms you have studied in your twelfth grade waves move around without interfering each other. So, in harmonic approximation when crystal is taken to be perfectly harmonic crystal waves and therefore, phonons pass each other without disturbance; without disturbance to each other and what we mean in technical language I will cut this disturbance and say without scattering each other.

So, a phonon comes in other one comes in and they go through they do not really scatter each other they may interfere because these are waves they interfere, but after that they pass through what an harmonicity does? An harmonic term and this I am not proving I am just saying it makes them scatter from one another why because you can think of an harmonicity makes phonons interact not just interfere, but interact with each other and when they interact they scatter each other.

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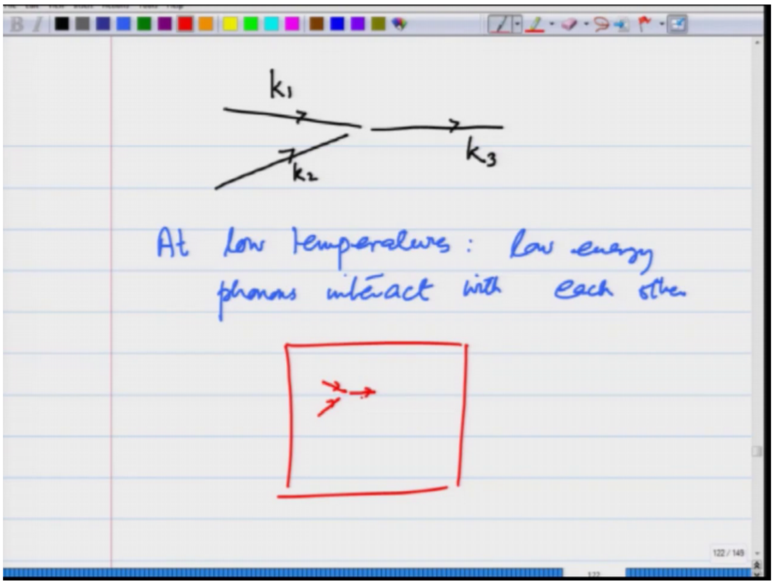

At low temperatures : low energy phonons interact with each other

Now, let us see what happens in the scattering? We have discussed earlier if there is a phonon off crystal momentum k 1 coming in and there is a phonon of crystal momentum k 2 coming in, they may combined due to this an harmonicity and you may finally, get a phonon of crystal momentum k 3. At low temperatures phonons of low energies are excited, if phonons of low energies are excited then k is also very small. So, what happens is low energy phonons interact with each other.

So, suppose I have a bridge one zone, one low energy phonon comes in another low energy phonon comes in and you get a final k which is very small, these are known as normal or in short N processes.

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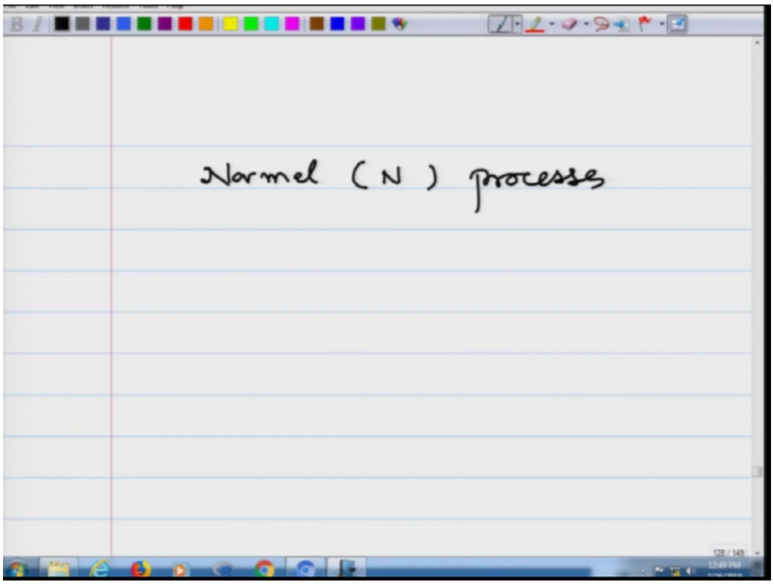

Normal (N) processes

So, even if the phonon scatter or combined together after this interaction they still continue to carry energy forward in this normal scattering or normal process.

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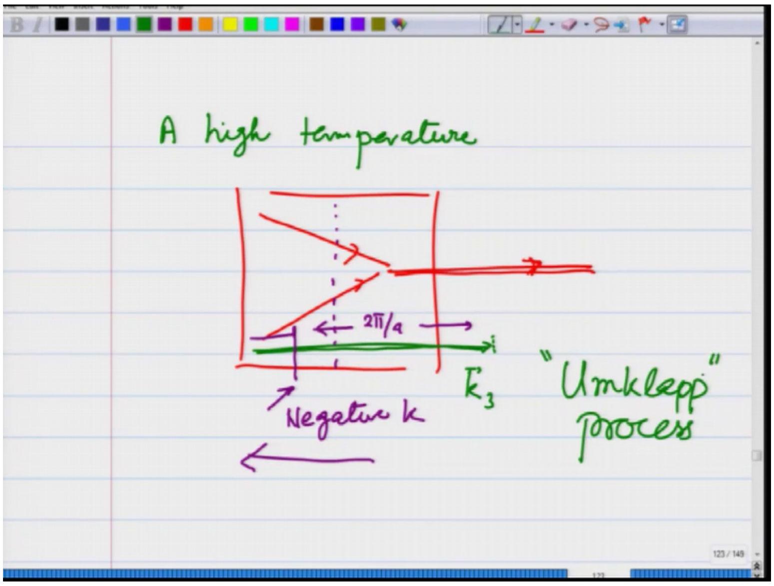

A high temperature

On the other hand let us look at what happens at high temperature? At high temperature now I have high k phonons also so, what could happen is I have a phonon coming in I have another phonon coming in and they combine into a k which is very very large. In fact, it may be so large and I will show it with green that it may be going outside the build one zone.

So, this is of k final k 3 this k; however, is equivalent to I can subtract 2 pi from here this k is; however, equivalent to k at this point where this is 2 pi by a because all case are equivalent to modulo 2 pi by a. Now notice this by this scattering I created a very large k 3 which is equivalent to a k out here is a negative k and what does that mean?

When these two phonons interacted they were carrying momentum in one direction or energy in one direction and after they interacted made a new phonon which could be going the other way, in effect you stopped the heat and not only you stopped it you made it through the other way and this reduces the conductivity. This is known as Umkclapp; Umkclapp is a German word which means flip over.

So, the two phonons which are going in one direction have flipped made a new phonon which is flipped over, it starts taking the heat the other way and it reduces conductivity. So, at high temperatures because of Umkclapp process the conductivity may go down and this is a purely an harmonic effect, if the phonons did not interact they would not have this process.

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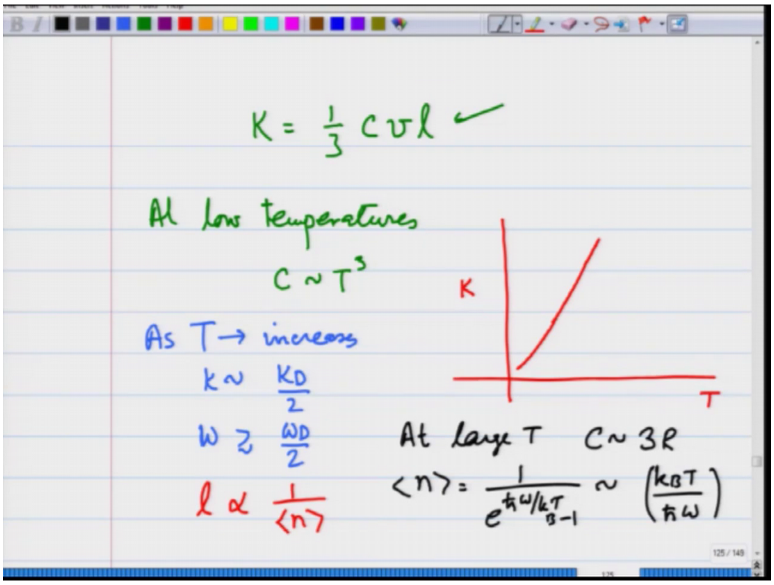

$$K = \frac{1}{3} C v l$$ ✓

At low temperatures

$$C \sim T^3$$

As T → increass

$$k \sim \frac{K_D}{2}$$

$$\omega \gtrsim \frac{\omega_D}{2}$$

$$l \propto \frac{1}{\langle n \rangle}$$

At large T $\quad C \sim 3R$

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_BT} - 1} \sim \left(\frac{k_BT}{\hbar\omega}\right)$$

So, let us see what should we expect on the basis of all this for the conductivity of an insulator, on the basis of the formula K equals one third C v l, where C refers to the specific heat due to phonons v their speed and l their mean free path. At low temperatures, where normal processes take place where the collisions take place, but the phonon wave vector resulted resulting phonon wave vector does not go to the Brillouin zone l would be determined by the imperfections and at low temperatures C goes as T cubed velocity of phonons is like velocity of sound.

So, I would expect that thermal conductivity with temperature should rise like T cubed; however, as the temperatures go up and we would expect increases we would expect, when K larger than half the Brillouin zone size increase start dominating or start coming into the picture; that means, K roughly equal to KD by 2 because by D by wave vector all the modes are exhausted. So, we will take that to be roughly the size of the Brillouin zone or omega greater than or equal to omega D by 2 we will start seeing Umkclapp processes and at this point the mean free path would be determined by Umkclapp processes mainly if they start dominating.

So, in this case the mean free path l would go as 1 over the average number of phonons and at large T C is roughly a constant, number of phonons is 1 over e raised to h cross omega by k T minus 1 which can roughly be written for large temperatures as k B T divided by h cross omega.

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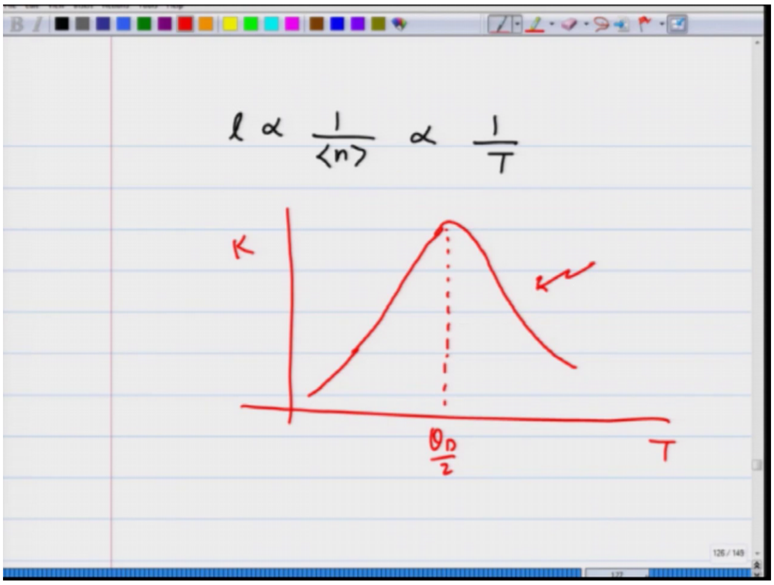

$$l \propto \frac{1}{\langle n \rangle} \propto \frac{1}{T}$$

Therefore if you collect it you will have l which is proportional to be a saying 1 over n will be proportional to 1 over T. So, mean free path will start going down so if you collect the picture what we will have is T, the conductivity as a function of temperature will go up as T cubed and add a certain temperature around theta D by 2 will start going down as 1 over T.

So, this is the behavior one should expect for the conductivity of an insulator when Umkclapp processes start dominating and this is again a result which is confirmed experimentally and I will send you the results in a supplement to this lecture.

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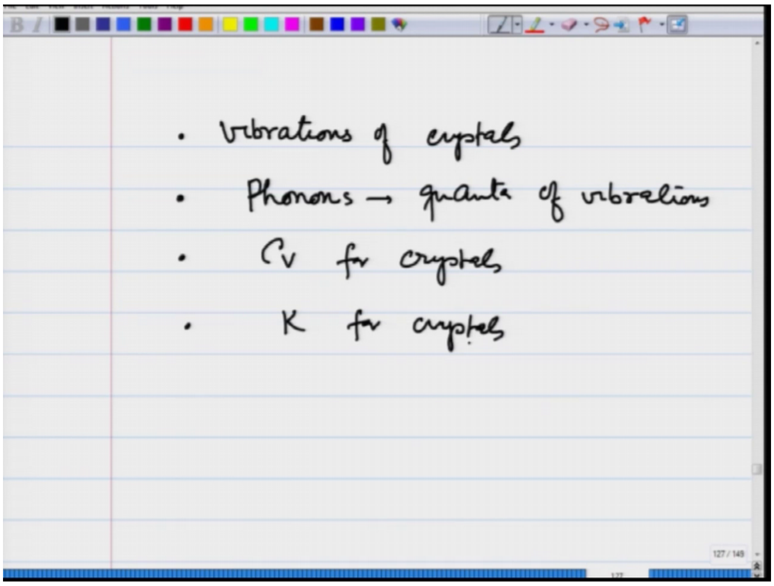

- Vibrations of crystals
- Phonons → quanta of vibrations
- C_v for crystals
- K for crystals

Finally, to conclude we have completed in these 2 weeks, the vibrations of crystals we have introduced the concept of phonons which are nothing, but quanta of vibrations and through these we have also studied the Cv for crystals as well as thermal conductivity for crystals.

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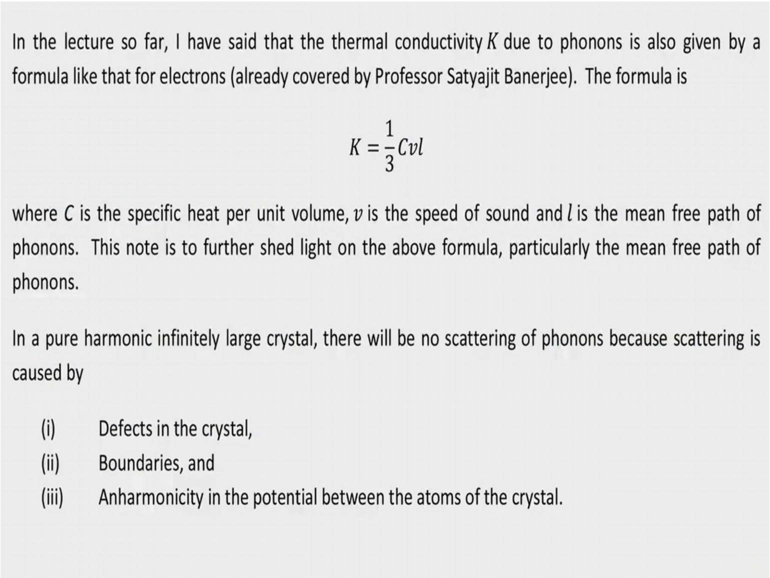

In the lecture so far, I have said that the thermal conductivity K due to phonons is also given by a formula like that for electrons (already covered by Professor Satyajit Banerjee). The formula is

$$K = \frac{1}{3}Cvl$$

where C is the specific heat per unit volume, v is the speed of sound and l is the mean free path of phonons. This note is to further shed light on the above formula, particularly the mean free path of phonons.

In a pure harmonic infinitely large crystal, there will be no scattering of phonons because scattering is caused by

(i) Defects in the crystal,
(ii) Boundaries, and
(iii) Anharmonicity in the potential between the atoms of the crystal.

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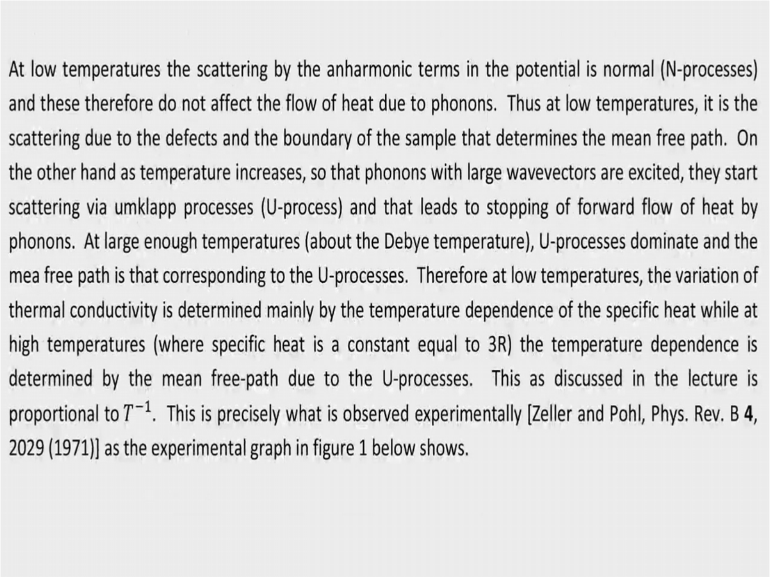

At low temperatures the scattering by the anharmonic terms in the potential is normal (N-processes) and these therefore do not affect the flow of heat due to phonons. Thus at low temperatures, it is the scattering due to the defects and the boundary of the sample that determines the mean free path. On the other hand as temperature increases, so that phonons with large wavevectors are excited, they start scattering via umklapp processes (U-process) and that leads to stopping of forward flow of heat by phonons. At large enough temperatures (about the Debye temperature), U-processes dominate and the mea free path is that corresponding to the U-processes. Therefore at low temperatures, the variation of thermal conductivity is determined mainly by the temperature dependence of the specific heat while at high temperatures (where specific heat is a constant equal to 3R) the temperature dependence is determined by the mean free-path due to the U-processes. This as discussed in the lecture is proportional to T^{-1}. This is precisely what is observed experimentally [Zeller and Pohl, Phys. Rev. B **4**, 2029 (1971)] as the experimental graph in figure 1 below shows.

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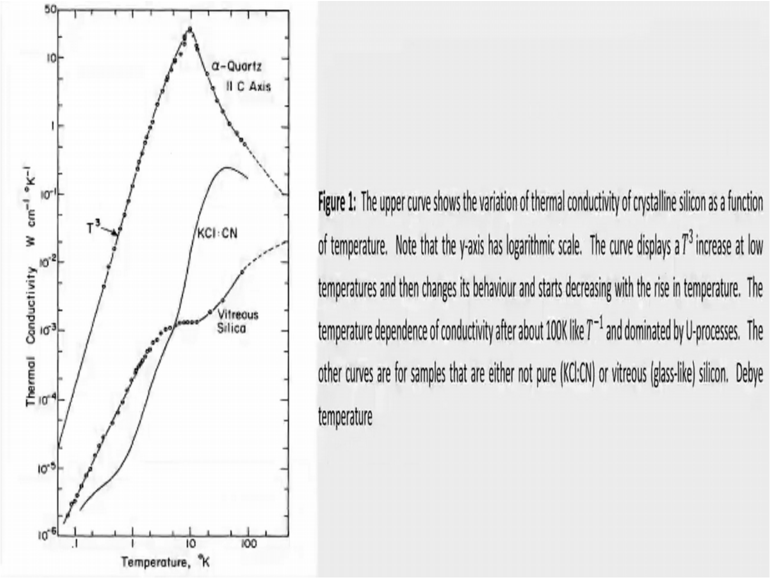

Figure 1: The upper curve shows the variation of thermal conductivity of crystalline silicon as a function of temperature. Note that the y-axis has logarithmic scale. The curve displays a T^3 increase at low temperatures and then changes its behaviour and starts decreasing with the rise in temperature. The temperature dependence of conductivity after about 100K like T^{-1} and dominated by U-processes. The other curves are for samples that are either not pure (KCl:CN) or vitreous (glass-like) silicon. Debye temperature

Now in the next week and following weeks we will be switching over to the electronic properties again and I will discuss blocks theorem and things like those.

Thank you.