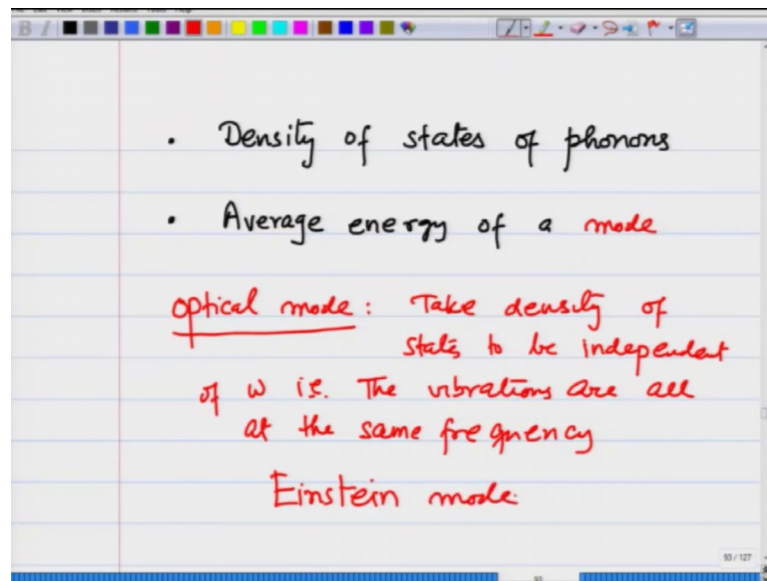**Introduction to Solid State Physics**
Prof. Manoj K. Harbola
Prof. Satyajit Banerjee
Department of Physics
Indian Institute of Technology, Kanpur

Lecture – 53
Debey model of specific heat of crystals

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We have calculated and discussed the Density of states of phonons and we have also discussed the average energy of a mode and we are now ready to combine the two to get the specific heat through the root of calculating total energy of a system, where these phonons are there or a crystal with vibration both are equivalent. So, let us see what we did. We said if I have an optical mode in this take density of states to be independent of omega and that means, the vibrations are all at the same frequency and this we call this the Einstein model.

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And we also had Debye model, in which case we assumed that omega as a function of k is always k equal to v sound times k that is a linear dispersion and in that case the density of states d omega came out to be v over 2 pi square omega squared over v s cubed.

So, this changes with the frequency and then we had also calculated energy of a mode with frequency omega, this I will call average energy of a mode with frequency omega at temperature T and this came out to be let us call it E averaged came out to be h cross omega over e raised to h cross omega over k Boltzmann T minus 1. And on the side it also meant that the number of phonons is equal to 1 over e raised to h cross omega over k BT minus 1. Number of phonons times the energy of each phonon h cross omega gives you the average energy.

So, we now combine all this and get the specific heat. So, let us first do Einstein's model and this is applicable to optical phonons in a good way, because optical phonons have a very flat omega k versus k curve. So, in this case the density of states is equal to N delta omega minus omega 0 where omega 0 is the frequency of oscillation and where N is the number of atoms or number of cells over which the boundary condition is applied. This is for one particular mode and this is an optical mode we are talking about.

So, this is about one particular mode it could be a transverse mode or a longitudinal mode total number of modes is going to be 3 N. So, in this case when I calculate the total energy is going to be E equal to integration over all omegas average energy of this mode times D omega the 0 to infinity and this comes out to be.

So, let us write this again E omega will come out to be 0 to infinity d omega h cross omega over e raised to h cross omega over k BT minus 1 d omega now is N times delta omega minus omega 0.

So, this comes out to be h cross omega 0 over e raised to h cross omega 0 over k BT minus 1 times N. Now for counting all modes because remember this is 1 mode over which I applied the periodic boundary condition there are 2 other modes. So, there are going to be 2 transverse and 1 longitudinal mode I have to multiply this number by 3. You can think of it another way these N cells if there are N atoms or N units all of them together are going to have 3 N degrees of freedom and we have calculated this energy only for 1 degree of freedom. So, actual energy is going to be E equal to 3 N h cross omega 0 over e raised to h cross omega 0 over k BT minus 1.

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So, if all atoms vibrate with the same frequency, the total energy E comes out to be N times 3 h cross omega 0 where omega 0 is the frequency of vibration e raised 2 h cross omega 0 over k BT minus 1. Now this is a little complicated expression let us learn about it more by taking different limits. So, if I take T going to infinity very large, then e raised to h cross omega 0 over k BT minus 1 is approximately equal to h cross omega 3N over k BT.

And therefore, total energy e is going to be 3 n h cross omega 0 over h cross omega 0 over kBT and this term cancels and I get total energy to be 3 N k Bt and therefore, C v which is de dt at constant volume; constant volume because then the frequency would remain the same is 3 N kB which is 3 r per unit mole which is the Dulong Petit law experimentally you observe that at high temperatures the specific heat is 3 r or 24 Joules per mole.

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So, I have e equals 3 N h cross omega 0 over e raised to h cross omega 0 over k BT minus 1. As T goes to 0 e raised to h cross omega 0 over k BT goes to infinity it becomes very large. So, I can neglect that 1 and write the total energy E as 3 N h cross omega 0 e raised to minus h cross omega 0 over k BT. And therefore, C v which is dE dT at constant volume is going to be equal to 3N h cross omega 0 times h cross omega 0 over k BT square e raised to minus h cross omega 0 over kBT.

So, this is nothing but 3 N h cross omega 0 square over k BT square e raised to minus h cross omega 0 over k BT. As T tends to 0 this exponential factor goes down to 0 very fast much faster than any polynomial and therefore, this 1 over T square in front does not really matter and the heat capacity C v we tend to 0 as T tends to 0.
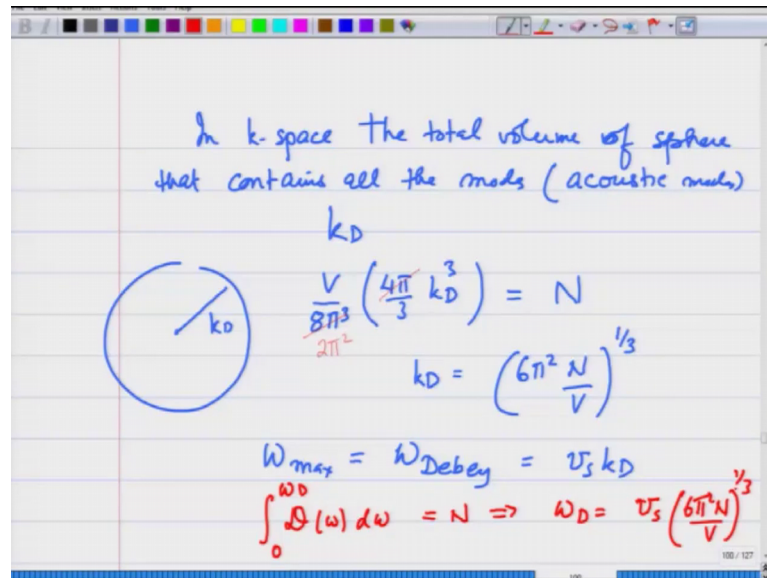
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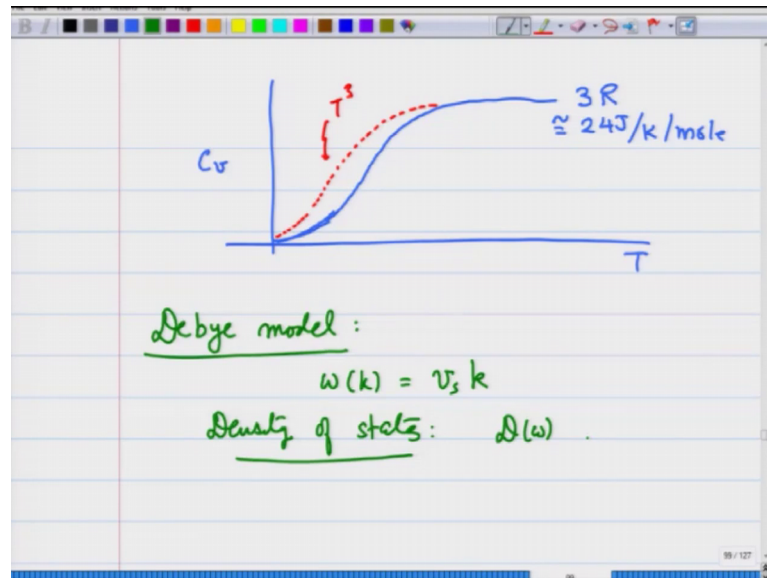
If I plot it therefore, T versus C v, I am going to get a curve this fellow goes to 0 exponentially and as T goes to large value it goes to 3 R roughly 24 Joules per Kelvin per mole and it goes to 0.

So, this was the first calculation that was done by Einstein, to show that quantum mechanically if I treat the vibrations of a crystal quantum mechanically; that means, the energy excitation is going to be with h cross omega the C v indeed goes to 0 as T goes to 0. And this was a very very nice discovery by him and proposed that these vibrations should be treated quantum mechanically. Although the actual experimental test it was found that the behavior is not quite as fast going to 0 as proposed by Einstein it goes more as T cubed. So, we have to explain that and that comes through Debye model.

So, next we are going to discuss now is Debye model. So, remember in Debye model what we have is omega k is equal to velocity of sound times k. Density of states I am going to calculate now again it does not hurt if I just repeat myself is D omega which is calculated through counting the number of states in k space. So, let me just do it quickly.

In k space the total volume of sphere that contains all the modes and these are going to be acoustic modes let us say is k D then the sphere of radius k D has volume 4 pi by 3 k D cubed. And the total number of modes is therefore, going to be V over 8 pi cubed times this volume and this is equal to the total number of modes let us do some translations this gives me 2 pi square and therefore, k D comes out to be 6 pi square N over v raised to one third that is for one of the modes.

And correspondingly I would also have omega maximum which I will call omega Debye, that is what this d stands for which will be equal to vs k D up to which all the modes will be exhausted. If you look at it slightly differently what I am going to have is integral D omega integrated over from 0 to omega D should be equal to total number of modes, which will again gave me I leave this calculation to you is going to give me that omega D by is going to be v s times 6 pi square N over v raised to one third.

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So, let us just estimate this omega D corresponds to what temperature which I will call Debye temperature. So, Debye temperature let me call it theta Debye which is going to be equal to h cross omega D over kB. omega D is equal to vs times 6 pi square N over V raised to one third. N over V is the density of atoms. So, if I substitute the numbers v s is of the order of 1000. So, this is of the order of 1000 6 pi square times N over V and is Avogadro's number, but I want to write in the units per meter cubed. So, its going to be 6 times 10 raised to 29 raised to one third roughly equal to 1000 times pi square is roughly 10. So, 10 times 10 raised to 20 gives me 10 raised to 30.

So, that is going to be 10 raised to 10 and 6 times 6 is 36. So, I can write it as 36 one third of 36 is roughly 3. So, this is equal to 3 times 10 raised to 13 radians per second and therefore, theta Debay will be equal to h cross which is 10 raised to minus 34 times 3 times 10 raised to 13 divided by kB which is 10 raised to minus 23. So, this comes out to be roughly 300 K.

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So, let me collect all this and tell you that in Debye model, I have omega D which is the omega max up to which all the modes are exhausted; that means, by this frequency all the modes are exhausted. So, this is the uppermost frequency that I excite that is omega D. Correspondingly there is a Debye wave vector right and there is a temperature theta D. Omega D is of the order of 10 raised to 13 k D would be correspondingly whatever you calculate this I will maybe give it as an assignment and theta D is of the order of 300K.

So, let us say 300 to 500 K let us calculate the total energy therefore. The total energy of the system is going to be integral 0 to omega Debye v over 2 pi square omega square over v s cubed that is the density of states times h cross omega over e raised to h cross omega over k BT minus 1 d omega.

So, which I can collect different terms write as v h cross over 2 pi square v s cubed integral 0 to omega D, omega cubed d omega over e raised to h cross omega over k BT minus 1 that is the expression.

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So, the total energy is v h cross over 2 pi square v s cubed integral 0 to omega d omega cubed over e raised to h cross omega over k BT minus 1 the omega. To facilitate the integral, I am going to change variables to x equals h cross omega over k BT.

So, that I have omega equals k BT over h cross x d omega equals kBT over h cross dx for a given temperature and the upper limit of the integral is x D which is theta Debye over V v h cross over 2 pi square v s cubed 0 to theta Debye over T; omega cubed is going to be kB cubed T cubed over h cross cubed times d omega which is going to be kB T over h cross dx there is going to be an x cubed here and 1 over e raised to x minus 1.

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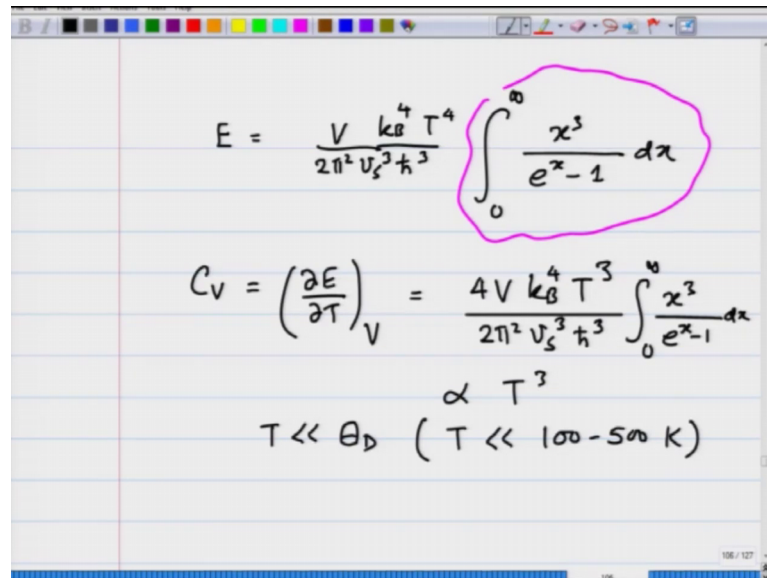
Collecting different terms I am going to get from here E equals V h cross over 2 pi square v s cubed kB raised to 4 T raised to 4 over h cross raised to 4 integral 0 to theta Debye divided by T x cubed over e raised to x minus 1 dx which is equal to V kB raised to 4 T raised to 4 divided by 2 pi square vs cube h cross cubed 0 to theta D over T x cubed over e raise to x minus 1 dx that is the total energy in this volume. We notice that there is a term here proportional to T raised to 4 if this theta D by T was not there this is reminiscent of Stefan's law for phonons where the energy comes out to be proportional to T raised to 4 there the uppermost limit because the number of modes is infinity.

So, the proportionality exactly T raised to 4; here there is slightly more complication, but in appropriate limits you will. See that limits the law becomes exactly like Stefan's law. So, if I take the limit of T becoming very small in that case E becomes V kB raised to 4 over 2 pi square vs cube h cube 0 to infinity and there is a T raised to 4 x cubed over y raised to x minus 1 dx and then the dependence on temperature for the total energy becomes exactly T raised to 4 which is like the photon energy and notice that this integral is a number it is does not depend on T anymore.

So, this is exactly like photon dependence; on the other hand if the temperature becomes very large then the upper limit becomes very small.

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So, in the limit of T going to 0 I have E which is v over 2 pi square vs cube h cross cube kB raised to 4 T raised to 4 integral 0 to infinity x cubed e raised to x minus 1 dx. This number is well known the value of the integral is pi raised to 4 over 15, but anyway this is a constant. So, if I take C v which is dE by dT at constant volume is going to be come out to be 4 v kB raised to 4 T cubed over 2 pi square v s cubed h cross cubed integral 0 to infinity x cubed over e raised to x minus 1 dx. So, its proportional to T cubed how the small this temperature? We are talking about temperature which is much much less than theta Debye.

So, we are really talking about temperature T which is much much less than say 100 to 500 K depending on the material. So, we are really talking about temperature in the range of maybe 1 degree 2 degree 10 degrees or so on in that case the specific heat is going as T cubed. Now let us look at the other limit.

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If I take T becoming very large; in that case I have E equals V over 2 pi square v s cubed h cross cubed kB raised to 4 T raised to 4, integral 0 to very small number theta D over T x cubed over e raised to x minus 1 dx. And now theta D over T is a very small number. In fact, much much less than 1 and therefore, I can write the integrand x cubed over e raised to x minus 1 as roughly equal to x square by expanding e raised to x minus 1 as x and we get therefore, e equals v over 2 pi square v s cubed kB raised to 4 T raised to 4 times theta D cubed over 3 T cubed.

Now, I can cancel certain terms, this T cubed goes with this T raised to 4 this becomes T and I get energy proportional to T and this implies C v is equal to a constant. Now notice that all this I have done taking only 1 mode into account.

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Now, I should be actually writing E taking all 3 modes or 3 dimensional feature or 3 n degrees of freedom into account as 3 v over 2 pi square vs cubed h cross cubed kB raised to 4 T raised to 4 0 to theta Debye over T x cubed over e raised to x minus 1 dx. So, I have to multiply by this factor 3.

So, as T goes to infinity, this E goes to 3 v over 2 pi square v s cubed kB raised to 4 T raised to 4 over h cross cubed 0 2 very small number x cubed over e raised to x minus 1 dx and e raised to x minus 1 the integrand now is only for small values can be approximated as 1 plus x minus 1, which is equal to x this is because I have the theta D over T to be much much less than 1.

And this immediately tells me that the integrand now is nothing, but this integral is 0 to theta D over T x square dx and therefore, I can write the total energy E as 3 v over 2 pi square vs cubed kB raised to 4 T raised to 4 over h cross cubed the times theta D cubed over T cubed cancelling this T cubed with T raised to 4 and getting T here I get e is proportional to T. So, energy in the limit of large temperature comes out to be proportional to T let us see exactly what the expression is.

So, I get E equals 3 v over 2 pi square vs cubed h cross cubed times kB raised to 4 T theta D cubed over 3. Again cancelling this 3, we get total energy equals V kB raised to 4 theta Debye cubed over 2 pi square vs cubed h cross cubed times T.

And therefore, C v which is dE dT at constant volume is going to be V kB raised to 4 theta Debye cubed over 2 pi square vs cube h cross cubed. I leave it as an exercise for you to show that by substituting theta D by and all those things together this actually is 3 N kB and therefore, per mole it comes out to be 3 R per mole. So, let me summarize this lecture by pointing out that we have calculated total heat energy if you like.

So, which I mean because of the temperature in a crystal by doing this integral 0 to infinity, D omega, h cross omega over e raised to h cross omega over k BT minus 1 d omega. And in the limit of large and small temperatures we have calculated this an Einstein model, where the heat capacity goes to 0 as T goes to 0, but exponentially and we have calculated this in Debye model where we had an approximation for omega k.

So, here omega is a constant, here omega k depends on the material on k as omega k equals v sk and we have found that C v.
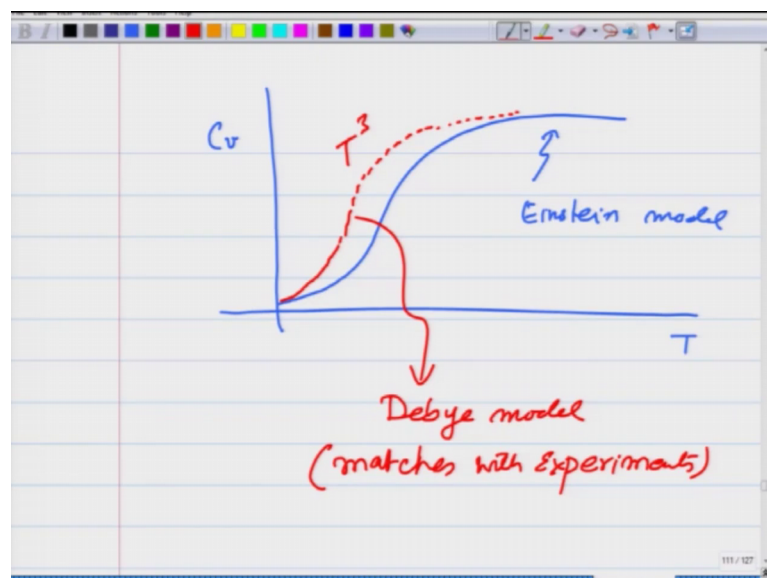
As a function of temperature goes as exponentially down in Einstein model and as T cubed in the large limit both goes to 3 r as T cubed in Debye model and this matches with experiments as a supplement to this lecture I will send you some experimental figures, they will show you the real graphs for real systems where you see this T cube behavior.

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In this lecture, I have derived the formula for specific heat of insulators (that arises only due to vibrations of the lattice) using Einstein and Debye models. In particular, it was shown that using the Debye model, one obtains T^3 dependence of specific heat at low temperatures. In this supplement some additional points are made about the specific heat and some experimental results are shown.

Points:

(1) In solids, one measures the specific heat at constant pressure, i.e. Cp is measured. Theoretically however, it is the Cv which is calculated because during the calculation all modes are calculated at fixed lengths of a crystal.

(2) In a solid, there is not much difference between Cp and Cv since the compressibility of a solid is very small. This is unlike in gases where the difference is of the order of gas constant. This is a point that you should check by explicit calculations yourself. We therefore refer to specific heat as simply C in the following discussion.

(3) Debye model is a model and uses the approximation of frequency of vibrations being linearly proportional to the wavevector with constant of proportionality being the speed of sound. Although it is a very good model, there will be deviations from it because of the assumption above. Nonetheless, it is standard model with experimental comparisons are made because it gives a good zeroth level approximations. Deviations from it can then lead to important physical insights into the behaviour of the system under consideration. One of the problems relates to that. Now the results with those with deviations that will point to the discussion above.

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Some experimental results:

Shown in Figure 1 below is the specific heat of silicon with C/T plotted against T^2 [Keesom and Seidel, Phys. Rev. **113**, 33 (1959)]. You see that the plot is a straight line for both pure silicon as well as a degenerate (doped) one. The plot shows the T3 nature of the lattice (phonon) specific heat [Question: What does the non-zero intercept in the degenerate sample correspond to?]
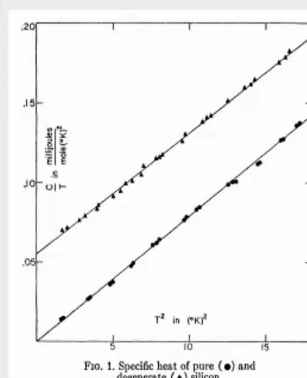

FIG. 1. Specific heat of pure (●) and degenerate (▲) silicon.

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In figure 2 below the results for C/T plotted against T^2 [Keesom and Seidel, Phys. Rev. **113**, 33 (1959)] are shown for degenerate germanium.
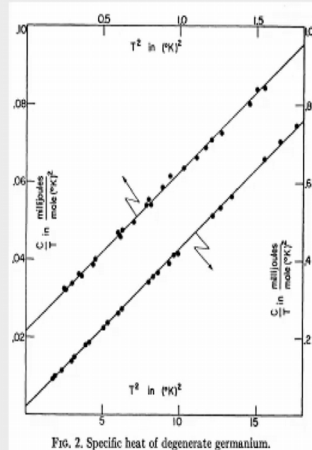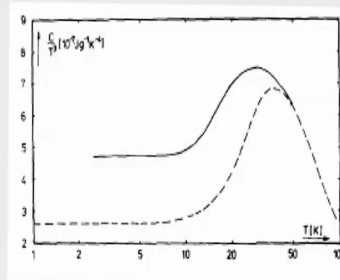

FIG. 2. Specific heat of degenerate germanium.

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Figure 3: C/T vs. T^2 for amorphous-silicon. Open circles are the data points that are best fitted with the Debye temperature of 497 ± 5 K

Now to show the deviation from the Debye behaviour, we show in Figure 4 below C/T^3 versus T for amorphous silicon [Mertig et al. Solid State Commun. **49**, 369 (1984)] One sees that it is a constant up to about 10K but deviates from it as one goes beyond this temperature.

Thank you.