

Introduction to Solid State Physics
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Lecture –23
Understanding Thermal conductivity of metals

In the last lectures, we saw that we could calculate the specific heat of the electron gas in a solid using the Sommerfeld's theory or the Sommerfeld's model. And, from that we found that the specific heat of the electron gas is proportional to temperature.

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$E_F = k_B T_F$

$$(C_V)_{e\text{-gas}} = \frac{\pi^2}{3} \left(\frac{3}{2} \frac{R}{V}\right) \left(\frac{k_B T}{k_B T_F}\right)$$

$\frac{T}{T_F} \approx 10^{-2}$ ← Kinetic Theory

$$(C_V)_{e\text{-gas}} \sim \left(\frac{3}{2} \frac{R}{V}\right) (0.01)$$

$C_V \propto T$; $C_V = \frac{\pi^2}{3} g(E_F) k_B^2 T$

Where, there are these constants of proportionality which is related to the density of states at the Fermi level. Because, those are the electrons which are really going to contribute to excitations when you apply a temperature and will contribute to the specific heat.

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$$C_v = \gamma T \quad ; \quad \gamma: \text{Sommerfeld's constant}$$

$$\gamma = \frac{\pi^2}{3} g(E_F) k_B^2 = \frac{\pi^2}{3} \frac{3}{2} \frac{n}{E_F} \frac{k_B^2}{2m} \rightarrow \frac{\pi^2}{2m} (3\pi^2 n)^{2/3}$$

$$\gamma = \left[\frac{\pi^2}{3} \frac{k_B^2 n^{1/3}}{\hbar^2 (3\pi^2)^{2/3}} \right] m$$

m mass of the e^- in the solid.

$\gamma = \text{function (density \& mass of electrons) in the solid.}$

So, the specific heat is some constant into temperature of the electron gas and gamma is called the Sommerfeld's constant. And, this constant is related to the density of states of the electrons at the Fermi level and, if you put in the value of these density of states and if you put in the Fermi energy which is related to the mass of the electron; you can show that this constant is actually related also directly proportional to the mass of the electron which is there inside the solid. So, if you measure the specific heat of the electron gas as a function of temperature from the slope of C_v versus T of the electron gas you can determine gamma.

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$\hbar \omega = \frac{1}{2} m v^2$
 $f = n, m, m: \text{mass of } e^-$
 $\text{or } \frac{dC_v}{dT} = \gamma$

	Calculated $\gamma \left(\frac{mJ}{\text{mole} \cdot K^2} \right)$	$\frac{\gamma_{\text{observed}}}{\gamma_{\text{theory}}} = \frac{m_{\text{actual}}}{m_e}$
Na	1.38 (1.034)	1.26
Cu	0.635 (0.505)	1.38
Au	0.729 (0.642)	1.14
Al	1.35 (0.912)	1.48
Li	1.63 (0.749)	2.18
Sr	3.6 (1.790)	2.0

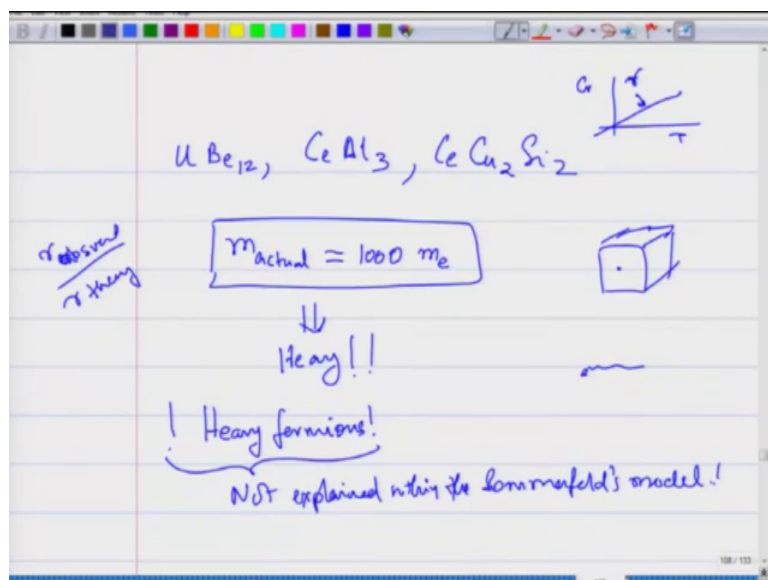
$\gamma = (\gamma_{\text{obs}})^{2/3} n^{1/3} m$
 $\frac{\gamma_{\text{observed}}}{\gamma_{\text{theory}}} = \frac{m}{m_e}$
 m free e^-

e^- inside the solid becomes heavy!!
 $m_{\text{actual}} = 2 m_e \leftarrow \text{free electron}$

And, that is what people did in experiments at very low temperatures the measured C_v , the measured the specific heat as a function of temperature at very low temperatures you can measure the specific heat of the electron gas. And, from there from the slope you can measure the gamma which is proportional to the mass. You can also use the expression which is already derived for the specific heat and you can calculate gamma, put in the mass of the electron and you can theoretically also calculate the value of the Sommerfeld's constant. And, you can take a ratio of what is experimentally observed versus theory; namely you put in the density of electrons the mass and all the other constants.

And, you will get a ratio which is the ratio of the gamma observed to gamma theory is nothing else, but the actual mass of the electron in the solid to the mass of the free electron. And, people wanted to know is the mass of the electron inside the solid really equal to the mass of the free electron. So, by taking the ratio of the theoretical value of gamma and the experimental value of gamma you will get this measure. And, what they found is that for most metals for a lot of simple metals it is actually of the order of 1 namely the mass of the electron is equal to the mass of the free electron. But there are materials as I said where the mass can start becoming larger.

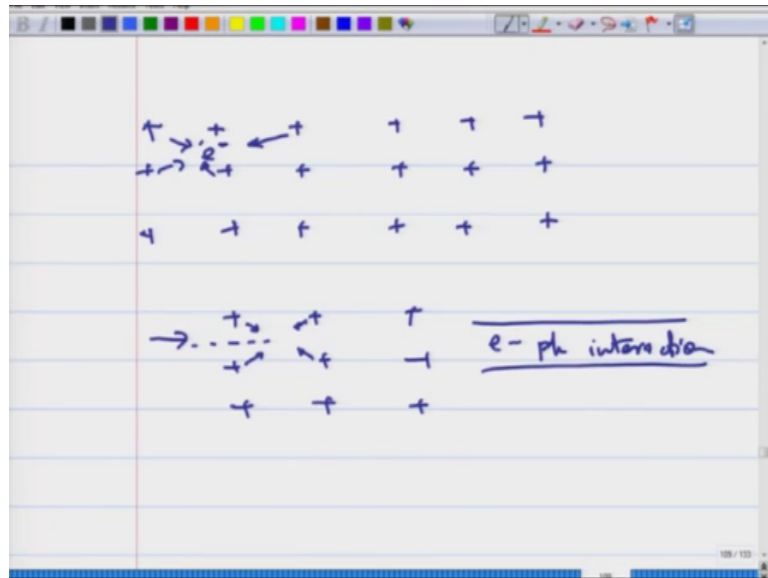
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In fact, there are solids which I have told you there are heavy fermion materials in which the actual mass of the electron can be 1000 times the mass of the electron. So, these were

some surprises which came up and said that there are the Sommerfeld's model. And, specifically the limitations of the Sommerfeld's model were, in the context of this when you have a substantial increase in the mass of the electron is that, we have not considered, that the electron is moving in a lattice of ions.

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And, as a result we have not considered that when the electron is moving it is interacting with the ions inside the solid. We have not considered the interaction of the ions of the electrons with the ions inside the solid because, the electron is moving through a periodic potential which is created by these ions, but we have neglected all of that. So, if you include all of that then the effect of these interactions actually acts like a drag on the electrons and it increases its effective mass.

And of course, you will come across it in the later half of the course; how is exactly is the effective mass of the electron defined. Similarly, electron-electron interactions have not been considered. And, when an electron moves through a ionic lattice then there is an effect that as the electron passes through this ionic lattice there is a tendency to polarize the lattice, it actually causes a slight distortion of the lattice. And so, when the electron moves through the lattice it actually causes a temporary distortion in the lattice and this is related to something called as an electron phonon interaction.

So, these effects have also been completely neglected we will not be discussing it all of this within the context of these lectures, but it is something for you to be aware that

many of the interactions of the electrons with the lattice have been completely eliminated or not being considered in the Sommerfeld's theory. And, that is why there are all these affects which cannot be explained within the Sommerfeld's theory. So, this is as far as some of the drawbacks are concerned. Now, if you recall in some of our earlier lectures we have looked at the thermal properties of electron in a metal namely we have calculated the specific heat of electrons in a metal.

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Thermal Conductivity due to e's in a metal (Recall this from Lecture's 9 & 10)

(3D metal) Drude's

$$k = \frac{1}{3} n v^2 \tau C_v ; C_v = \text{Specific heat per electron} = \frac{3}{2} k_B$$

$$k = \frac{1}{3} v^2 \tau C_v ; C_v = \text{Specific heat per unit volume of e's in the metal}$$

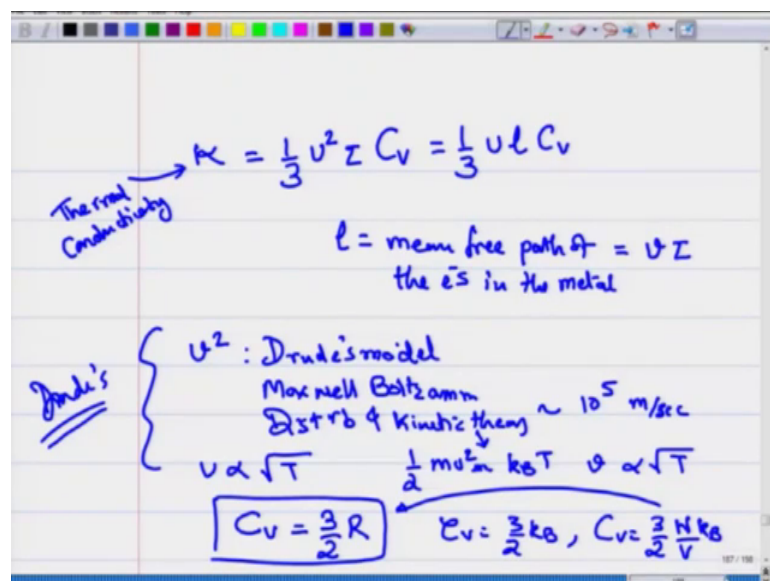
$$C_v = \frac{N E_c}{V} = n E_c \rightarrow \text{nos. density of e's in the metal} = \frac{N}{V}$$

And, let us recall another property which is the thermal conductivity due to electrons in a metal and you may recall this from lectures 9 and 10. So, here in lectures 9 and 10 and especially in lecture 10, we had derived that the thermal conductivity kappa for a 3D metal for a 3 D metal with electrons using Drude's assumptions; we had shown was $\frac{1}{3} n v^2 \tau C_v$. Where, n is the density of electrons, v is the mean average velocity, tau is the collision time and C_v is the specific heat per electron.

I would like to clarify that in this lecture 10 the C_v that was derived was C_v was the specific heat per electron which was $\frac{3}{2} k_B$ which I had done in lecture 10. You can also rewrite this expression in a slightly different way kappa can be written as $\frac{1}{3} v^2 \tau C_v$. Just for preventing any confusion let me write the above one which we had derived in lecture 10 as curly C_v . This curly C_v was specific heat of electron equal to $\frac{3}{2} k_B$ ok. And, now this capital C_v that I am writing, this capital C_v is the specific heat per unit volume of electrons in the metal.

So, here we are looking at the specific heat due to all the electrons inside the metal and it is per unit volume. And, what is the relationship between this capital C_v and curly C_v , capital C_v which is the specific heat of the electrons per unit volume of the metal is equal to the total number of electrons into the specific heat per electron which is this; the specific heat per electron divided by the volume. But, this will be nothing else, but n into curly C_v where, n is the number density of electrons in the metal which is equal to total number of electrons divided by the volume and this curly C_v is the specific heat of electron per electron.

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So, with this consideration your thermal conductivity of the metal due to electrons inside the metal the conductivity is $\frac{1}{3} v^2 \tau C_v$, where now C_v is the specific heat of the electrons inside the solid per unit volume which we can also write it as $\frac{1}{3} v$ into l into C_v where, l is the mean free path of the electrons in the metal and it is nothing else, but the velocity into τ . Now, if you recall from lecture 10 that the velocity of the electrons which we had used this v^2 was in Drude's model was related to Maxwell-Boltzmann distribution. And, from kinetic theory this was evaluated to be about 10^5 metres per second.

And, this velocity proportional to square root of temperature because, if you recall $\frac{1}{2} m v^2$ was of the order of $k_B T$ from kinetic theory of gases. So, v was proportional to square root of temperature. This was as far as Drude's model was concerned. So, the

velocity was 10^5 and the specific heat of the electron was $\frac{3}{2} R$; curly C_v was of course, $\frac{3}{2} k_B$. But, capital C_v is $\frac{3}{2} N$ into V divided by k_B which gives you this of course, per unit volume. So, I am suppressing the volume this is your even this is per unit volume. So, this is what you get $\frac{3}{2} R$.

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Handwritten notes on a whiteboard:

- $K_{\text{Drude}} \sim \frac{1}{3} v_{\text{Drude}}^2 \tau (C_v) \sim \frac{3}{2} R$ (with 10^5 m/sec written above v_{Drude})
- Sommerfeld $\rightarrow v^2 \rightarrow$ Drift velocity $\rightarrow v \rightarrow v_F \sim 10^6 \text{ m/sec}$ (with $e^2 s$ written below v^2)
- Pauli's exclusion principle
- $v_F \sim 10^6 \text{ m/sec}$ (Independent of Temp)
- $(C_v)_{\text{Sommerfeld}} = \gamma T = \left(\frac{3}{2} R\right) \left(\frac{T}{T_F}\right)^{\frac{1}{2}}$ (with T_F : Fermi Temp $\sim 10^4 \text{ K}$)
- Room $T \sim 300 \text{ K}$, $(T/T_F) \sim 10^{-2}$

So therefore, in the Drude's theory your thermal conductivity the kappa from Drude was $\frac{1}{3} v^2$ which is from Drude into τ into C_v which was $\frac{3}{2} R$. And, this was 10^5 metres per second ok. Now, when we come to Sommerfeld the v^2 was drift velocity of electrons and which was governed by the Pauli's exclusion principle. And, namely only those electrons are contributing to charge transport or thermal transport those which are at the Fermi level; only those electrons are contributing to the velocity. And so, this velocity turned out to be equal to the Fermi velocity which was 10^6 metres per second.

So, the Fermi velocity was almost 10 times the velocity from Drude's model which was basically from kinetic theory of gases. This is this velocity was of course, independent of temperature. The velocity the Fermi velocity is independent of temperature. Now, the specific heat of the electron per unit volume from Sommerfeld's model was equal to γT where, γ is the Sommerfeld's constant into temperature. And, if you recall this was of the order of $\frac{3}{2} R$ into T by T_F where, T_F is the Fermi temperature which is of the order of about 10^4 Kelvin ok.

And, there is a factor of about pi square by 3 out here ok. This I had shown in my earlier lecture that the Sommerfeld C_v is 3 by $2 R$ which is there in your Drude's model also, but it is multiplied by a factor which is T by $T F$ into pi square by 3. Now, at room temperature which is of the order of 300 k this term T by $T F$ becomes, of the order of 10 raise to minus 2. So, if you take pi square by 3 into T by $T F$; if you will get a number for C_v from Sommerfeld's model would be of the order of 10 raise to minus 2 into 3 by $2 R$.

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The whiteboard contains the following handwritten text and equations:

$$(C_v)_{\text{Sommerfeld}} \sim 10^{-2} \left(\frac{3}{2} R \right) \text{ at room } T$$

$$\text{at room } T, (\kappa)_{\text{Sommerfeld}} \sim \frac{1}{3} \left(\frac{v_F^2}{v_D^2} \right) (C_v)_{\text{Sommerfeld}}$$

Sommerfeld theory → 10 (v_Drude)

$$= \frac{1}{3} (v_{\text{Drude}})^2 (10^2) (C_v)_{\text{Drude}} \cdot 10^{-2}$$

(3/2 R)

$$\underline{\text{at room } T} (\kappa)_{\text{Sommerfeld}} = (\kappa)_{\text{Drude's model}}$$

At this is of course, at room temperatures. So, at room temperature if you calculate the kappa using Sommerfeld's theory this is of the order of 1 by $3 v_F$ square into tau into C_v which is from the Sommerfeld's model. And, this is about 1 by 3 , this velocity is about 10 times v_{Drude} the velocity that you get from Drude's model. So, this is v_{Drude} square into 10 raise to 2 because, v_F square is about square of the Drude's velocity into 10 raise to 2. Because, the v_F is about 10 times the velocity from Drude's model and the C_v for Sommerfeld's model is C_v from Drude's model which is 3 by $2 R$ into 10 raise to minus 2.

And, as a result these two factors come out cancel out and the kappa which you get at room temperature from Sommerfeld's model is approximately the same as the kappa you get from Drude's model. And so, with a strange combination of these quantities namely a combination of velocities and specific heats they actually cancel out, the velocity turns out to be higher. But, the specific heat due to electrons in the Sommerfeld model turns

out to be lower in such a way that they completely cancel out. And, the Sommerfeld and the Drude's model estimation of the thermal conductivity turn out to be identical at reasonably high temperatures where, we are looking at this at room temperature. So, this is one set of aspects which is associated with the Sommerfeld's model.

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Drude's model, $v \propto \sqrt{T}$, $(C_v)_{\text{Drude}} = \frac{3}{2} R$ (independent of T)

$(K)_{\text{Drude}} = \frac{1}{3} v^2 \tau C_v \propto T$

Sommerfeld theory: $v \rightarrow v_F \rightarrow$ Independent of T

$(C_v)_{\text{Sommerfeld}} = \gamma T \propto T$

$(K)_{\text{Sommerfeld}} \propto T$

And there are of course, some differences in Drude's model if you recall that the velocity is proportional to square root of temperature and C_v in Drude is just $\frac{3}{2} R$ which is independent of temperature. So, the κ in Drude's model which is $\frac{1}{3} v^2 \tau C_v$ is going to be proportional to T because, this and if you recall in Sommerfeld's theory the velocity is the Fermi velocity which is independent of temperature. But, the specific heat in Sommerfeld's model is γT ; it is proportional to temperature.

So, the κ in Sommerfeld's model also because the velocity is independent of temperature and Sommerfeld's model, but the specific heat is linearly dependent on temperature. So, this κ in Sommerfeld's model also turns out to be proportional to temperature. So, whether you look at Drude or whether you look at Sommerfeld at room temperature the values are typically similar. And, the temperature dependence of κ also turns out to be roughly similar, whether you look at Sommerfeld or Drude's model.

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$$\kappa = \frac{1}{3} v_F^2 \tau C_v = \frac{1}{3} v_F \ell C_v$$
 (Fermi vel. ℓ mean free path, C_v Specific heat of e's per unit volume of metal.)

$$\sigma = \frac{n e^2 \tau}{m}$$

$$\tau = \frac{m \sigma}{n e^2}$$

$$v_F^2 = \frac{2 E_F}{m}$$

$$\frac{1}{2} m v_F^2 = E_F$$

$$C_v = \frac{\pi^2}{3} g(E_F) k_B^2 T$$

$$g(E_F) = \frac{3}{2} \frac{n}{E_F}$$

$$C_v = \frac{\pi^2}{3} \left(\frac{3}{2} \frac{n}{E_F} \right) k_B^2 T$$

$$\kappa = \frac{\pi^2}{3} \left(\frac{k_B^2}{e} \right) \sigma T$$

$$\text{or } \left(\frac{\kappa}{\sigma T} \right) = \frac{\pi^2}{3} \left(\frac{k_B^2}{e} \right) = \text{Lorentz no.}$$

Now, if you look at the kappa it is $\frac{1}{3} v_F^2 \tau C_v$ or more accurate way to write kappa is of course, $\frac{1}{3} v_F \ell C_v$ where, this is the specific heat of the electrons per unit volume which is also equal to $v_F \ell C_v$. Where, this is the Fermi velocity, this is the mean free path of the electrons and this is the specific heat of electrons per unit volume of metal. This is your thermal conductivity expression. And, now if you recall the expression for sigma also turns out to be; you can use the expression for sigma to be the same as that given by the Drude's model.

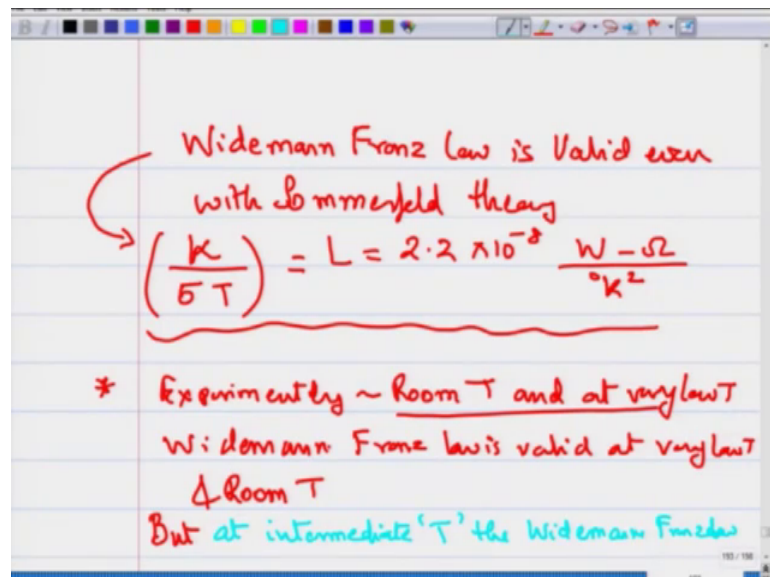
Sigma is equal to $n e^2 \tau / m$, you can use the Fermi velocity square as $2 E_F / m$ and this actually comes out from $\frac{1}{2} m v_F^2 = E_F$ Fermi energy. So therefore, that gives rise to v_F^2 is $2 E_F / m$. It is basically coming from here and the specific heat of the electron in the solid is $\frac{\pi^2}{3} g(E_F) k_B^2 T$ where, $g(E_F)$ is the density of states of the electrons at the Fermi energy which is $\frac{3}{2} \frac{n}{E_F}$.

So, you can put all of that here. So, this will be nothing else, but I am sorry this is $\frac{\pi^2}{3}$. So, $\frac{\pi^2}{3} \times \frac{3}{2} \frac{n}{E_F} \times k_B^2 T$. So, if you use all these expressions one for if you use this expression for C_v , substitute for v_F^2 as this and if you substitute for τ as $m / n e^2 \sigma$ into conductivity sigma divided by $n e^2$. All of these three, if you substitute in this expression for kappa tau of course, goes here and

the specific heat will actually come here. Then you will get an expression for kappa is equal to pi square by 3 k B square by e sigma the conductivity into the temperature.

Or, the thermal conductivity divided by sigma electrical conductivity into the temperature is a fundamental constant 3 which is k B square by E, E is the electronic charge. And this is of course, your Lorentz number and this is your statement of the Wiedemann Franz law. So, whether you look at Sommerfeld's theory also, even if you are looking at Sommerfeld's theory you are getting your Wiedemann Franz law validated.

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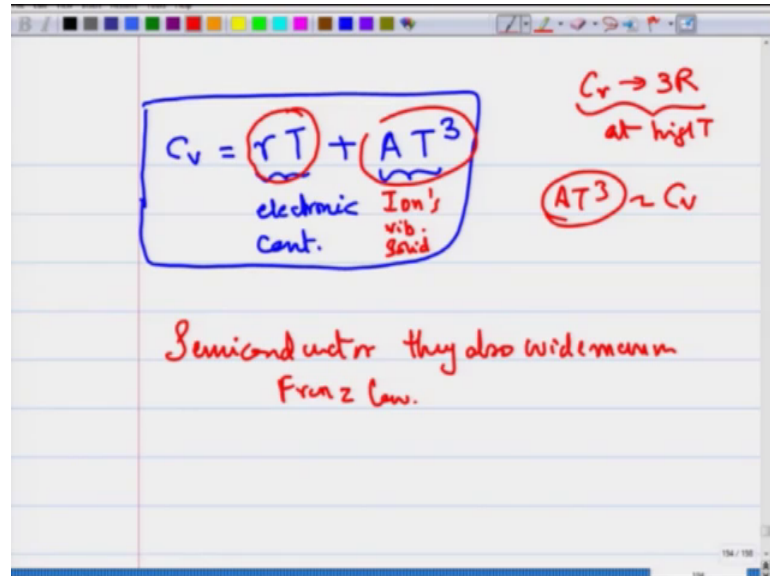


The Wiedemann Franz law is valid even within Sommerfeld's theory; namely the thermal conductivity divided by the electrical conductivity into the temperature is equal to a constant which is your Lorentz number. And, this is about 2.2 into 10 raise to minus 8 watt ohm divided by degree Kelvin square. This is nothing else, but your Wiedemann Franz law. So, even within the Sommerfeld's theory the Wiedemann Franz law is valid. Experimentally it is found that if you take the ratio of thermal conductivity divided by the electrical conductivity into the temperature it is constant and it works beautifully at room temperature and at very low temperature.

So, the Wiedemann Franz law is valid at very low temperature and room temperature. But, at intermediate temperatures the Wiedemann Franz law is not validated. It is if you

look at very high temperatures and very low temperatures the Wiedemann Franz law is valid, but at intermediate in between temperatures it is not valid.

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$$C_v = \gamma T + AT^3$$

electronic cont. Ion's vib. Solid

$C_v \rightarrow 3R$ at high T

$AT^3 \sim C_v$

Semiconductor they also Wiedemann Franz Law.

And, that happens because as I if you recall I had said that the specific heat has two contributions. One is the electronic contribution which we have seen from the Sommerfeld's theory and another contribution is because, of vibration of ions inside the solid ok. And, that is the ionic contribution to specific heat which is written as A times T cube. This is the general expression which you will come across later also, this will of course, be derived in a later half of the course using the vibration model of atoms inside the solid.

And so, your electronic contribution has two parts: one is the your specific heat of a solid has two contributions. One is the electronic contribution and the other is the contribution from ions vibrating in the solid and that has A T cube dependence. So, the specific heat has two contributions and at low temperatures of course, you have gamma times T as the contribution. And, the A T cube term is not seen at very low temperatures and at high temperature the specific heat becomes constant at a value which is 3R that will also be shown and this happens at high T.

But, at intermediate temperatures you have and A T cube term which actually contributes to your specific heat. And, that is why because of this T cube dependence your Wiedemann Franz law at intermediate temperatures is not followed. Another reason also

you will see that, if you go to other types of materials like semiconductors they also do not follow Wiedemann Franz law. So, although the Sommerfeld's model give us a another new way and a better way to study the conductivity thermal conductivity, electrical conductivity it still has its limitations.