Electronic Theory of Solids
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Lecture – 36
Paramagnetism of metals

Hello, we are working on this conduction electron Paramagnetism.

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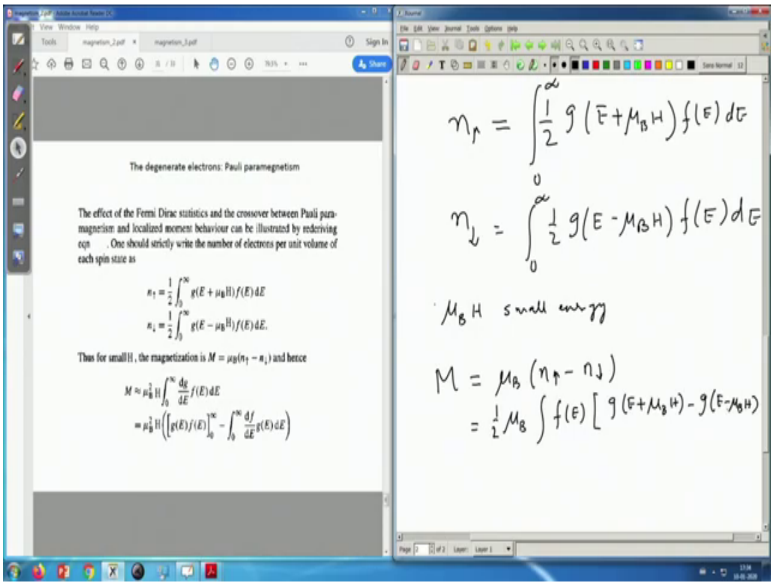

The degenerate electrons: Pauli paramegnetism

The effect of the Fermi Dirac statistics and the crossover between Pauli paramagnetism and localized moment behaviour can be illustrated by rederiving eqn . One should strictly write the number of electrons per unit volume of each spin state as

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Thus for small H, the magnetization is $M = \mu_B(n_\uparrow - n_\downarrow)$ and hence

$$M \approx \mu_B^2 H\int_0^\infty \frac{dg}{dE}f(E)\,dE$$
$$= \mu_B^2 H\left(\left[g(E)f(E)\right]_0^\infty - \int_0^\infty \frac{df}{dE}g(E)\,dE\right)$$

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$\mu_B H$ small energy

$$M = \mu_B(n_\uparrow - n_\downarrow)$$
$$= \frac{1}{2}\mu_B \int f(E)\left[g(E+\mu_B H) - g(E-\mu_B H)\right.$$

And, what we have shown is that the density of states can be written as for the up electron the total number of up electrons can be written as half of the original density of states E plus mu B into H. So, original density of states at E plus mu B H times the Fermi function integrated from 0 to infinity. So, that is my n up. Similarly, n down is half of g E, but E at minus mu B H f E d E ok. So, this is the relation.

Now, as we mentioned that mu B H is much is a small number small energy compared to the electronic energies that we are talking about and soon we will see that we are only interested close to Fermi level. So, for so, mu B H is an exceedingly small number compared to that less than even 100 in most cases. So, in that case we can just do a Taylor expansion before that let me just write down the expression for M; M is mu B into n up minus n down which is then mu B half of f E g of E plus mu B H minus g of E minus mu B H times d of E.

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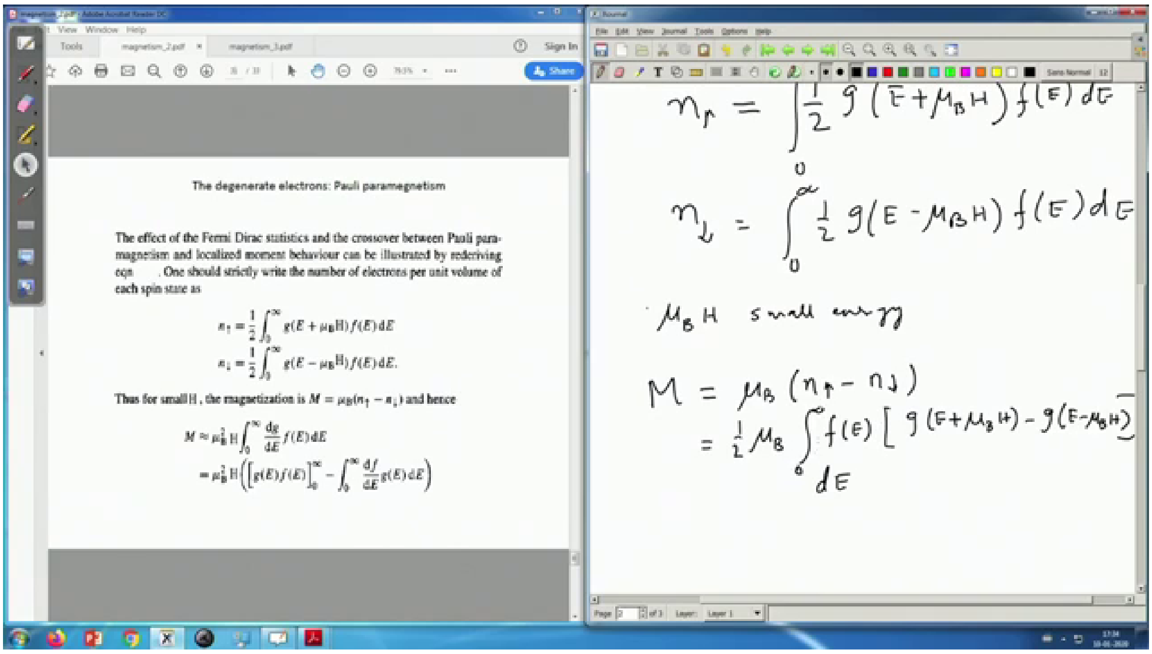
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$$n_\uparrow = \int_0 \frac{1}{2} g(E+\mu_B H) f(E)\, dE$$

$$n_\downarrow = \int_0^\infty \frac{1}{2} g(E-\mu_B H) f(E)\, dE$$

$\mu_B H$ small energy

$$M = \mu_B (n_\uparrow - n_\downarrow)$$
$$= \frac{1}{2}\mu_B \int_0^\infty f(E)\left[g(E+\mu_B H) - g(E-\mu_B H)\right] dE$$

So, this is my integral that I have to consider. Now, this is from 0 to infinity.

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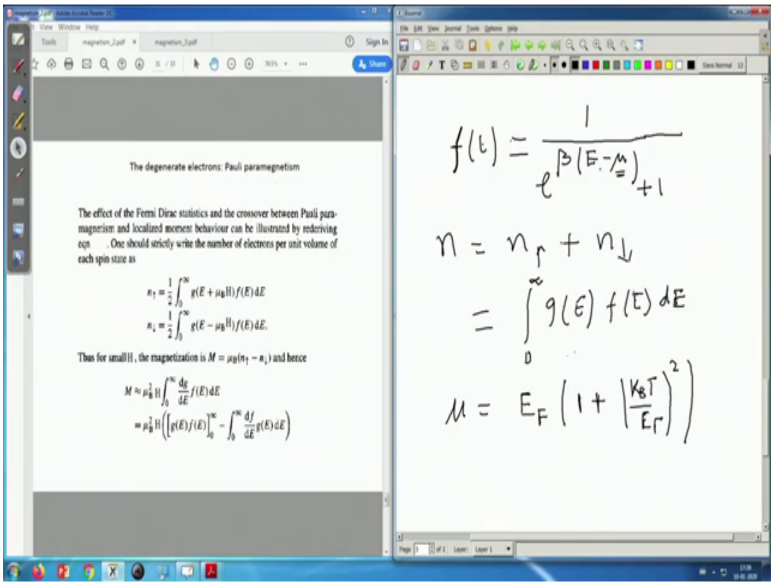
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$$= \mu_B^2 H\left(\left[g(E)f(E)\right]_0^\infty - \int_0^\infty \frac{df}{dE} g(E)\,dE\right)$$

$$f(E) = \frac{1}{e^{\beta(E-\mu)}+1}$$

$$n = n_\uparrow + n_\downarrow$$
$$= \int_0^\infty g(E) f(E)\, dE$$

$$\mu = E_F\left(1 + \left(\frac{K_B T}{E_F}\right)^2\right)$$

There is one more thing I wanted to bring to a notice is that f of E equal to 1 over E to the power beta E minus mu plus 1. So, this is my Fermi function. So, they remember that there is a mu sitting here in the Fermi function. Now, we are in this calculation for example, we have assumed that for both n up and both n down we are using the same Fermi function, but it is it is not completely question, in the sense that we have to also see that the mu has not changed when you put the magnetic field for.

So, then so, for n up and n down you can use whether for the case with magnetic field which is what makes n up and n down different in that case mu may have also change. And so, then we have to argue and reason that mu has not change at least to first order in the chemical potential mu has not changed to first order in mu B H when the field is present. So, it is the same values.

So, remember we are using the same value that we had for the case with H equal to 0. The same mu is being used for both n up and n down and in the entire calculation. f E is not different when H equal to 0 and H not equal to 0, but that is not completely correct, but there is an argument I can give which tells you that it is to first order that is the same. So, let us just look at the value of n total number.

Total number is n up plus n down. Now, if you look at this is g E from here from this calculation you can easily see that this is g E f E just use the n up and n down that I got in the previous page then you will land up with this equation ok. So, this is a remember this equation is the same as the one that you had obtained if you did not have a field. So, this equation is just that there was as if there is no field and is the number total number even without the field.

So, so that means, to first order which is where we did the Taylor expansion there is absolutely no change in the chemical potential. So, that is kind of an argument that tells you that the chemical potential remains the same. For so, which you know is that from Somerfield theory we remember that it is 1 plus K B T by E F square right. So, that remains whatever it is to first order in mu B H the magnetic field has not changed; the chemical potential to first order in mu B H ok.

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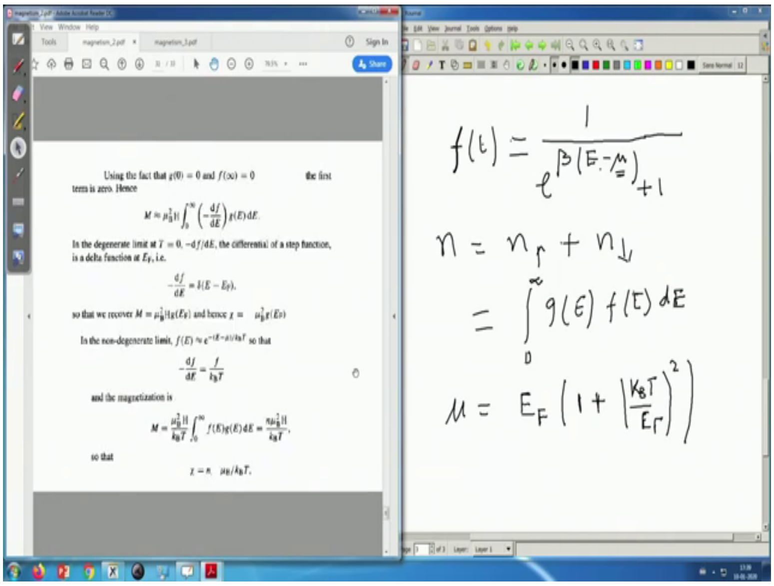

Using the fact that $g(0) = 0$ and $f(\infty) = 0$ the first term is zero. Hence

$$M \approx \mu_B^2 H \int_0^\infty \left(-\frac{df}{dE}\right) g(E)\, dE.$$

In the degenerate limit at $T = 0$, $-df/dE$, the differential of a step function, is a delta function at E_F, i.e.

$$-\frac{df}{dE} = \delta(E - E_F).$$

so that we recover $M = \mu_B^2 H g(E_F)$ and hence $\chi = \mu_B^2 g(E_F)$

In the non-degenerate limit, $f(E) \approx e^{-(E-\mu)/k_B T}$ so that

$$-\frac{df}{dE} = \frac{f}{k_B T}$$

and the magnetization is

$$M = \frac{\mu_B^2 H}{k_B T} \int_0^\infty f(E) g(E)\, dE = \frac{n \mu_B^2 H}{k_B T},$$

so that

$$\chi = n \mu_B / k_B T.$$

$$f(t) = \frac{1}{e^{\beta(E-\mu)}+1}$$

$$n = n_\uparrow + n_\downarrow$$

$$= \int_0^\infty g(E)\, f(E)\, dE$$

$$\mu = E_F\left(1 + \left(\frac{K_B T}{E_F}\right)^2\right)$$

I mean that is a side issue, but then one can just go ahead and do this integral which is here this is the one we are after. So, these two if you just subtract if you do a Taylor expansion and subtract, then what will you get is this term.

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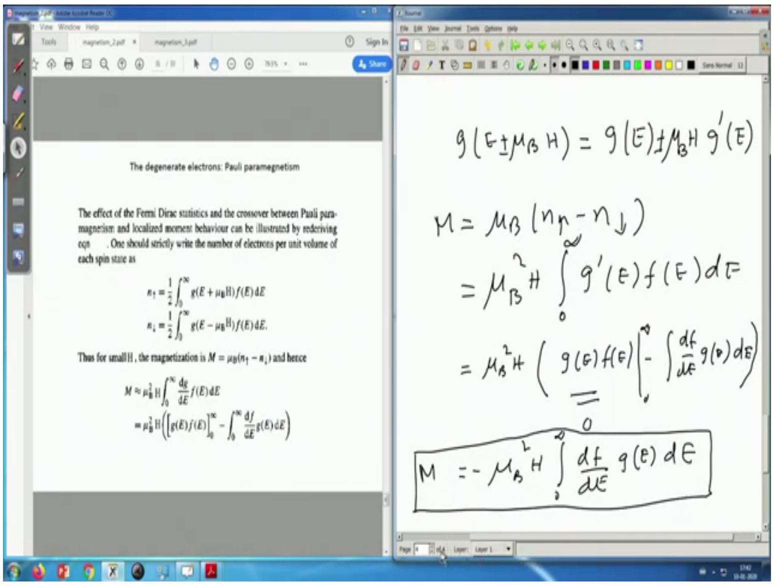

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$$g(E \pm \mu_B H) = g(E) \pm \mu_B H\, g'(E)$$

$$M = \mu_B (n_\uparrow - n_\downarrow)$$

$$= \mu_B^2 H \int_0^\infty g'(E) f(E)\, dE$$

$$= \mu_B^2 H \Big(\underbrace{g(E) f(E) \Big|_0^\infty}_{0} - \int_0^\infty \frac{df}{dE} g(E)\, dE \Big)$$

$$\boxed{M = -\mu_B^2 H \int_0^\infty \frac{df}{dE} g(E)\, dE}$$

So, , g E plus mu B H can be then Taylor expanded as I said since mu B H is very small g E plus mu B H into g prime of E derivative. So, this is plus minus. So, this also I can make plus minus. So, you finally, get this expression for m which is mu B times n up minus which is mu

B into n up minus n down and that gives you mu B square into H coming from here this half will get cancelled and give you 1 and you will have g E g prime E f E d E, ok.

So, this is the result that we have. Now, we just have to evaluate this integral. Remember that I can do a integration by parts which is shown here. So, let me just use it look at this integration by part you can see that this is equal to. So, this is equal to mu B square H into g E f E evaluated at 0 at infinity minus d f d E g E d E, right. So, that is the integrational part, but now these look at this g E is 0 at 0 and f E is 0 at infinity. So, this term basically goes to 0. So, all we have is minus mu B square into H d f d E times g E times d E to infinity. So, that is the integral we have to calculate.

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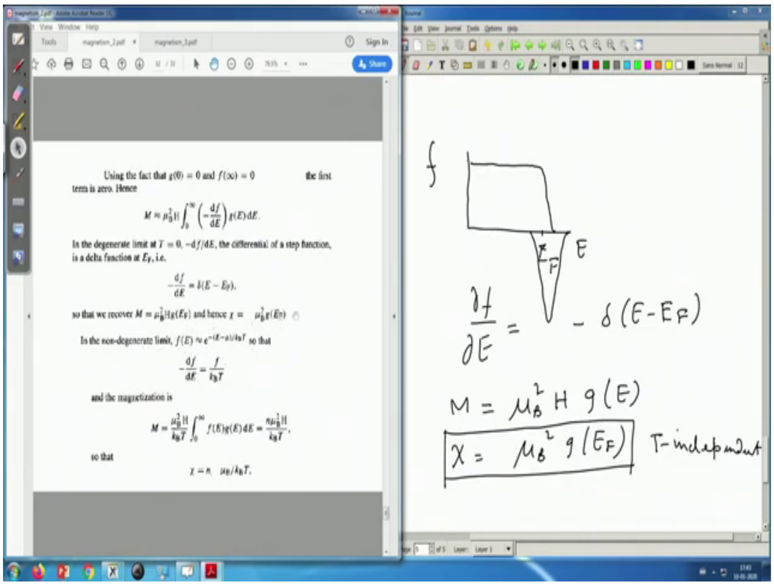

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so that

$$\chi = n \mu_B / k_B T.$$

$$\frac{\partial f}{\partial E} = -\delta(E - E_F)$$

$$M = \mu_B^2 H g(E)$$

$$\boxed{\chi = \mu_B^2 g(E_F)}$$ T-independent

Now, here again we make this quite reasonable approximation that d f d E is a function like this f is a function like this right at any finite temperature there is a slight deviation around E f.

So, at 0 temperature for example, this is just a finite drop here vertical drop. So, del f del E can be approximated fairly well by a delta function around E f ok. So, del f del E can be approximated by a delta function at E F except everywhere else it is 0 it is flat and then that is exactly what has been done and once you put that in this value then you only pick up the value at g is evaluated now only at f. And, that gives you the previous result that m equal to mu B square H into g of E f. So, chi equal to mu B square g of E F ok.

This is the result then we got from a much more elaborate calculation, but the result is the same and it is T independent T independent ok. The other interesting thing that as an aside one can mention is that if you if you are working in the non-degenerate limit like at very high temperature then of course, your Fermi function will be replaced by a Boltzmann function again and you can do this for yourself you can check that minus del f d f d E now is f by k B T and magnetization therefore, comes out to be n mu B square H.

So, the susceptibility is n mu B square by k B T. So, which is the result that we obtained for the classical for the case where the moments were independent in the non-degenerate case which is the Curie result.

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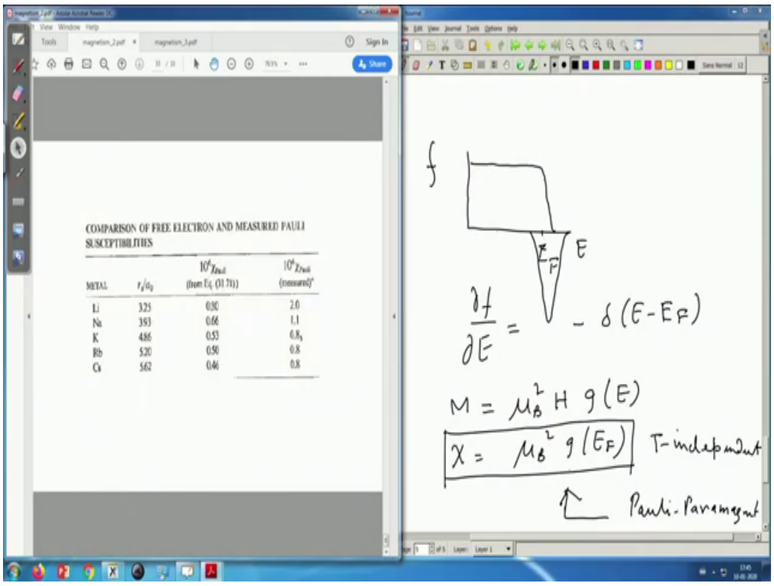

COMPARISON OF FREE ELECTRON AND MEASURED PAULI SUSCEPTIBILITIES

METAL	r_s/a_0	$10^6\chi_{Pauli}$ (from Eq. (31.71))	$10^6\chi_{Pauli}$ (measured)^a
Li	3.25	0.80	2.0
Na	3.93	0.66	1.1
K	4.86	0.53	0.8_5
Rb	5.20	0.50	0.8
Cs	5.62	0.46	0.8

$$\frac{\partial f}{\partial E} = -\delta(E-E_F)$$

$$M = \mu_B^2 H\, g(E)$$

$$\boxed{\chi = \mu_B^2\, g(E_F)}$$ T-independent

Pauli-Paramagnet

So, the Curie result is obtainable from the Pauli result in the limit when the system is non-degenerate. Of course, a real conduction when a metal is never non-degenerate and you have to work in the degenerate limit which is what gives us this result. So, this is T independent. So, this is extremely important in the sense this is called Pauli paramagnetism; Pauli was the person who first derived this.

One thing is if you if you see the result here the agreement between experiment and the theory is not. So, good as we had it for Curie's law or for diamagnetic contributions the reason for that many fold, but as you can see this there are many other contributions that come in a in a in the susceptibility of a metal.

And, one contribution that is important to note is just by in passing I mentioned that there is of course, a diamagnetic contribution that exists that always exists.

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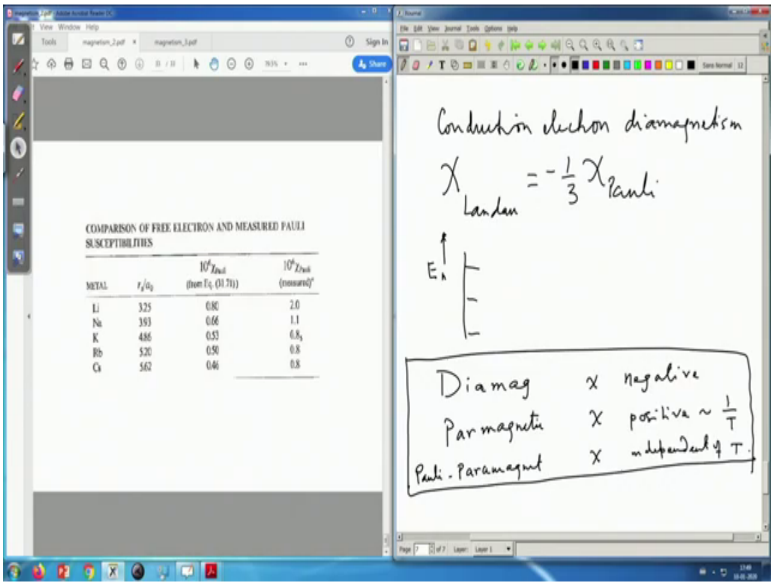

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Conduction electron diamagnetism

$$\chi_{Landau} = -\frac{1}{3}\chi_{Pauli}$$

E_n

Diamag χ negative

Parmagnetic χ positive $\sim \frac{1}{T}$

Pauli-Paramagnet χ independent of T.

And, if you have a conduction electron then conduction electron of course, also have a diamagnetic contribution right. So, and this is not easy to calculate and this was calculated diamagnetism and this was calculated by Landau and so, it is opposite to the field. It will oppose the field of course. So, with a negative sign and susceptibility Landau is about one third with the minus sign of course, chi Pauli.

So, this will have to be also accounted for and so, the theory Landau's Landau actually calculate it, but remember this is significant we had already noticed such effects when we did integer quantum hall effect where you had this levels which are quantized right. So, E was E sub n was quantized and typically the landaus susceptibilities appear when you have to take account when at very large fields and very low temperatures then of course, you will see these contributions coming up.

So, that is the story of susceptibility in a in several cases one is paramagnetic insulators and the other is metals. And in the other case where there is no paramagnetic susceptibility, then you had a diamagnetic sustainability which is for example, E naught gas solids and so on.

So, what we studied so far is there is a diamagnetic contribution, then paramagnetic contribution; so, chi is negative. So, paramagnetic; so, chi positive and, so, if you have independent paramagnets, then the chi is also going as independent ions, independent moments. Then you have chi going as one by T then you have Pauli paramagnet which is what conduction electrons do magnet which is chi is independent of chi positive of course, independent of temperature.

So, these are things that we studied and we can make experiments compared with experiments and basically these are all that one looks for. Of course, there are these other situations like one electron paramagnetism and all which are there you have to just remember that they are there, also Landau susceptibility is also there, diamagnetic susceptibility in a metal.

So, all those issues that are there, but main issue that one really deals with in real systems are these response of moments from a system of free nearly free moments or in a degenerate system degenerate moments and that is what the subject is and the other interesting thing that I am going now is where there is spontaneous magnetization.

So, all this we have discussed is that the magnetization is induced by the field whereas, the r systems like iron, cobalt, nickel where the magnetization is spontaneous. The systems is spontaneously magnetized, you do not have to put a field to magnetize it and that is what we will start discussing from this moment onwards.

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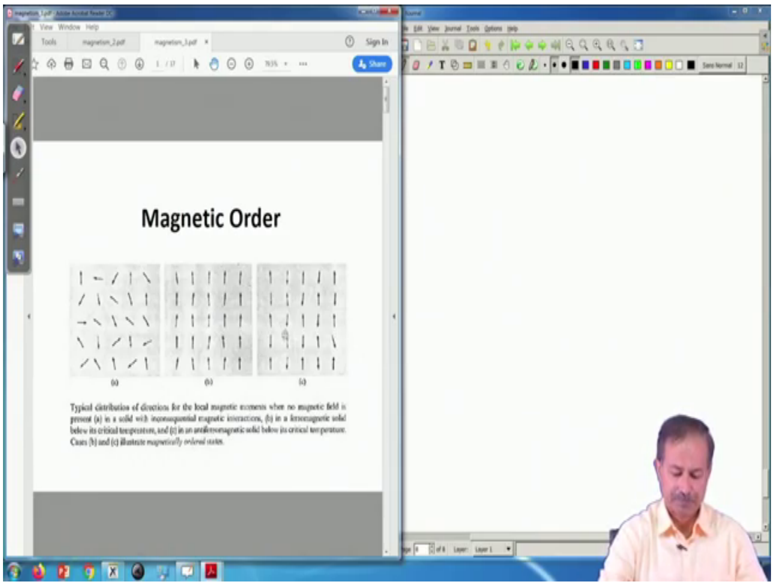

Magnetic Order

Typical distribution of directions for the local magnetic moments when no magnetic field is present (a) in a solid with inconsequential magnetic interactions, (b) in a ferromagnetic solid below its critical temperature, and (c) in an antiferromagnetic solid below its critical temperature. Cases (b) and (c) illustrate *magnetically ordered states*.

So, let me just introduce you first to what these systems are all about. So, this is about magnetic order ok. So, magnetic order is as I mentioned in my first class that on magnetism that magnetic order is was seen long back about 600 BC and the name magnet came from a place called magnesia apparently somewhere in Turkey. And, that there were there were minerals there, which were magnetic and that was extracted and used as used to attract iron and so on.

So, these magnetic materials as such magnetism where the magnetism exists spontaneously is in use for a long time ok. So, what kind of magnets can you have magnetic order? This for example, is of course; you need moments to have order. These moments have to order to give you magnetic order. The moments can be ordered by the field which is what in paramagnet what happens.

So, whereas, they can be ferromagnetic there is something called ferromagnet where you have all the magnetic moments are more or less aligned. And, large chunks of magnetic moments are aligned and if all of them aligned in the same direction then you will finally, pick up you will have a spontaneously magnetized system; it has a magnetic moments spontaneously.

There are other systems also different kinds of magnets which are like for example, anti-ferromagnet which is shown here.

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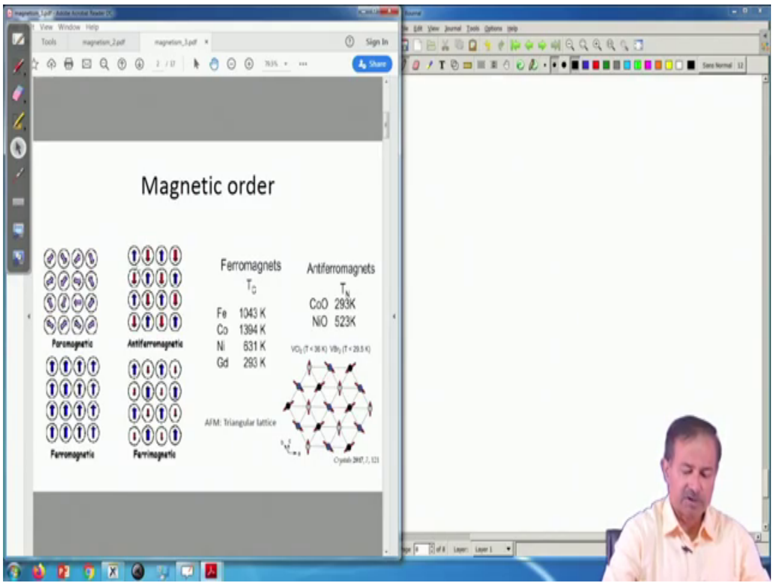

Magnetic order

Ferromagnets	T_C
Fe	1043 K
Co	1394 K
Ni	631 K
Gd	293 K

Antiferromagnets	T_N
CoO	293K
NiO	523K

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I will show a another picture next for example, this. This is a cartoon picture though, but it is it depicts what the situation is. In a paramagnet for example, you have moments of course, free moments, but these moments are completely random randomly oriented. And, there is nothing that orders them and they do not talk to each other. There is no interaction between two moments and they remain disordered.

Now, this if you if you measure the moment at a particular site, there at a particular ion for example, you will pick up a moment, but if you find out the total magnetization of the system you will not find any moment that is what paramagnet does. Whereas in a ferromagnet, which is the bottom left you will find that all the moments are more or less aligned.

At very low temperatures they are all aligned at finite temperature of course, there are these fluctuations due to due to thermal disorder and, but still to a fairly large temperature they are they remain order and they show magnetic long range magnetic. This is called long range magnetic order the magnetic order persist over an entire macroscopic range of the system.

There is also this strange kind of order which is called the antiferromagnet whereas you can see a blue spin is up and the blue red spin is down. So, every spin has its nearest neighbours down. So, the neighbouring spin of a spin up are all down the neighbouring spin of a down spin are all up. Now, this is one kind of antiferromagnet there are other kinds also ah, but I will show the pictures as we go on. But, this if you if you just look at it you can immediately see that if I sum the moments of magnetization coming from each of these tiny moments, the sum will still be 0.

So, an antiferromagnet has no net moment whereas, a ferromagnet has a large net moment. Although in both cases there is an order. This is also an order, the antiferromagnetic order is also a long range order because if this is up the blue spin at the top left is up then I know what is the direction of any other spin at anywhere in this lattice as far as you go. If this is the arrangement then I can tell you what the arrangement what the spin at a particular side is, knowing any particular arrangement the direction of moment at any particular side. So, that means, there is a long range order.

This is called as a special kind of material which is it shows again a long range order where the up spin and the down spins do not cancel each other. In this picture the blue spins are larger, the red spins are smaller. This is like an antiferromagnet here, but it is that the net moment if you sum the sum of the blues will be more much more than the sum of the red. So, it will show up with a finite magnetic moment like a ferromagnet; but much less because this partly cancelled by the red moments.

So, that is that is what this ferrimagnet does. This is again a long range order all these are except for the paramagnet. These three are all long range order. There are different kinds also more complicated ones, but these are the ones I am showing as time goes on we may see some other.

Now, these ferromagnets for example, there are this ferromagnets available in nature elemental ferromagnets iron, cobalt, nickel for example, is very well known. These look at the transition temperature. What is this transition temperature? The transition temperature is as I said is the where the disorder due to thermal fluctuations cancels the scale of energy that gives you the ordering.

So, so, suppose you take this ferromagnet on the left as you start raising the temperature at some point the thermal disorder will be such that it will start behaving like a all spins will now every spin will become independent and sort of independent they fluctuate. And, the temperature is large and their fluctuations are such that the overall net magnetic moment vanishes. So, if you it will be like a paramagnet, it is looks like a paramagnet then because the H spin takes random direction because of the fluctuations. They keep on fluctuating.

So, at any at finite temperature of course, every spin every spin has to fluctuate and if the directions cancel out over all it becomes disordered, then you will not find any moment. So, the point at which the spontaneous moment vanishes at that temperature is called the transition temperature. So, it makes a transition ferromagnet to a paramagnet. Cobalt has even higher 1394 degree Kelvin. So, it is like more than 1100 degree centigrade.

So, these are these tell you that that there is a large energy scale fairly large thousands of degrees at least a 1000 degree in iron and cobalt that forces the spins to align. So, this scale of energy that the temperature has to overcome to misalign them is about 1000 degree; that means, the scale of energy that aligns them is about 1000 degree.

So, this is not a small amount of energy this is much bigger than the for example, Debye temperature in a system which is typically few 100 degrees and that means, you have to find out where this energy comes from. And, that is one of the major tasks in condense matter as to find out the right energy scales from the interactions that are present in the system and the mechanics that drives it which is quantum mechanics in this case.

There are antiferromagnets also. These are oxides for example, cobalt oxide, nickel oxide. These are well known antiferromagnets, there are many more that is these are where the transition temperature is very high. Now, conventionally the transition temperature of an antiferromagnet is written as T sub N; N stands for Louis Néel. Néel was the first person who described this antiferromagnets and in honour of his name it is one does not call it T sub C, it is called T sub N for an antiferromagnet.

Now, here is an interesting example which is a triangular lattice. Look at the order of the magnetic moment I mean the directions of the magnetic moments. These are actually this is also long range order; because if you look at this red this spin for example, this top left, this is repeating here again this is repeating here again. So, along this line all spins are have the same direction. Similarly, along this line all spins have the same direction.

So, and if you if this is a particular type of antiferromagnetic order. There is no net spin is still going to be 0, but you can see how this ordering. So, the spins rotate by 120 degree if you go from here to here to the next one and then the next one is another 120 degree and then you come back to 360 degree back. So, this over a triangle you have this 120 degree angle between every two spins. So, this is another very interesting order. It happens in vanadium chloride, vanadium bromide and many other systems not too many, but some other systems also. So, this is an antiferromagnetic order on a triangular lattice.

So, this all this we will start discussing from the next class.