Electronic Theory of Solids
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Lecture - 33
Susceptibility and Thermal Properties

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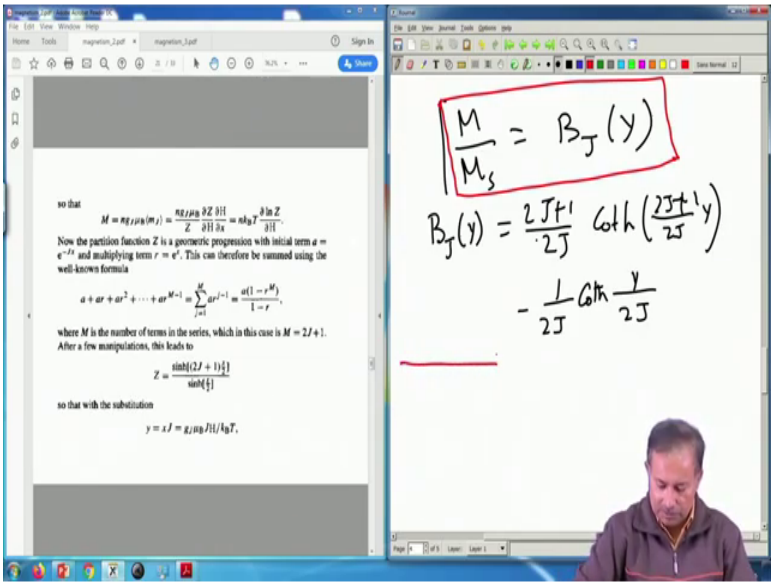

so that

$$M = n g_J \mu_B \langle m_J \rangle = \frac{n g_J \mu_B}{Z}\frac{\partial Z}{\partial \mathrm{H}}\frac{\partial \mathrm{H}}{\partial x} = n k_B T \frac{\partial \ln Z}{\partial \mathrm{H}}.$$

Now the partition function Z is a geometric progression with initial term $a = e^{-Jx}$ and multiplying term $r = e^x$. This can therefore be summed using the well-known formula

$$a + ar + ar^2 + \cdots + ar^{M-1} = \sum_{j=1}^{M} ar^{j-1} = \frac{a(1-r^M)}{1-r},$$

where M is the number of terms in the series, which in this case is $M = 2J+1$. After a few manipulations, this leads to

$$Z = \frac{\sinh[(2J+1)\frac{x}{2}]}{\sinh(\frac{x}{2})}$$

so that with the substitution

$$y = xJ = g_J \mu_B J \mathrm{H}/k_B T,$$

$$\boxed{\frac{M}{M_s} = B_J(y)}$$

$$B_J(y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} y\right) - \frac{1}{2J} \coth \frac{y}{2J}$$

So, we have been doing paramagnetism of free ions, free moments. And, then what we did is that we consider two cases: one is J equal to half. So, let me write it down.

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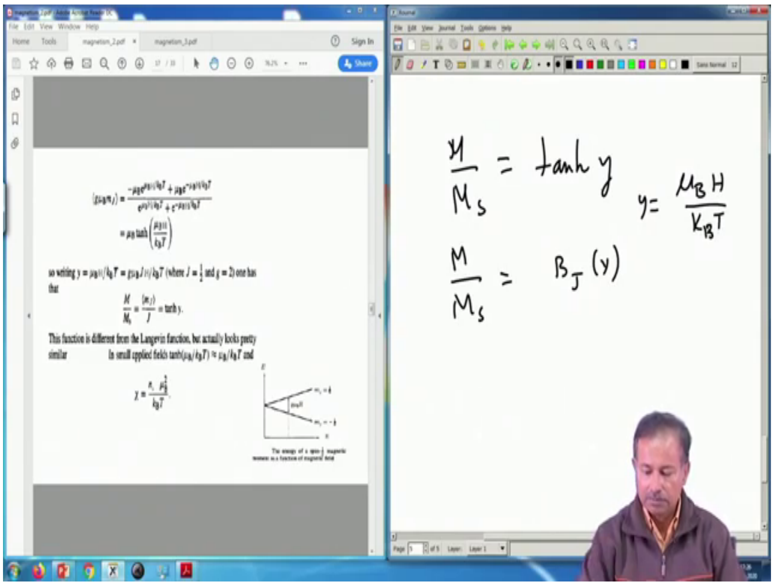

$$\langle \mu_B m_J \rangle = \frac{-\mu_B e^{\mu_B H/k_BT} + \mu_B e^{-\mu_B H/k_BT}}{e^{\mu_B H/k_BT} + e^{-\mu_B H/k_BT}}$$
$$= \mu_B \tanh\left(\frac{\mu_B H}{k_BT}\right)$$

so writing $y = \mu_B H/k_BT = g\mu_B J H/k_BT$ (where $J = \frac{1}{2}$ and $g = 2$) one has that

$$\frac{M}{M_s} = \frac{\langle m_J \rangle}{J} = \tanh y.$$

This function is different from the Langevin function, but actually looks pretty similar In small applied fields $\tanh(\mu_B/k_BT) \approx \mu_B/k_BT$ and

$$\chi = \frac{n_s \mu_B^2}{k_BT}.$$

The energy of a spin-$\frac{1}{2}$ magnetic moment as a function of magnetic field

$$\frac{M}{M_s} = \tanh y \qquad y = \frac{\mu_B H}{K_B T}$$

$$\frac{M}{M_s} = B_J(y)$$

So, there are two cases: one was J equal to half and the other one was so in J equal to any J. So, the two equations are M by M s equal to tan hyperbolic y and the other one is M by M s equal to B J of y ok. So, these are the two equations that you got. So, y equal to mu B H by k B T. So, this is the general J ok.

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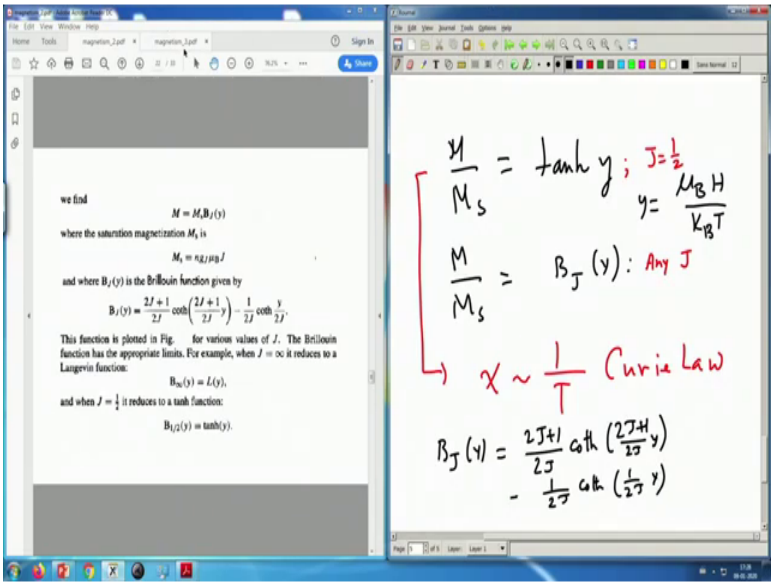

we find

$$M = M_s B_J(y)$$

where the saturation magnetization M_s is

$$M_s = n g_J \mu_B J$$

and where $B_J(y)$ is the Brillouin function given by

$$B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\frac{y}{2J}.$$

This function is plotted in Fig. for various values of J. The Brillouin function has the appropriate limits. For example, when $J = \infty$ it reduces to a Langevin function:

$$B_\infty(y) = L(y),$$

and when $J = \frac{1}{2}$ it reduces to a tanh function:

$$B_{1/2}(y) = \tanh(y).$$

$$\frac{M}{M_s} = \tanh y \;;\; J = \frac{1}{2} \qquad y = \frac{\mu_B H}{K_B T}$$

$$\frac{M}{M_s} = B_J(y) : \text{Any } J$$

$$\chi \sim \frac{1}{T} \quad \text{Curie Law}$$

$$B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}y\right)$$

So, for arbitrary J let me write any J and J equal to half. This dependence leads to so this one for example, gave us a susceptibility which was proportional to 1 over T. And this is actually the famous Curie Law obtained by Pierre Curie and so it carries his name with it it is named after him. And it is a very important law because it if you find in an experiment that your magnetic susceptibility of the system behaves like 1 over T then you know that there are these free spins, in its free moments in the system and so that means, there is there are free moments which are responding to your magnetic field. And these moments are not really interacting with each other.

Of course, spin exactly moment half. Moment and spin are just interchangeably used, so I often say spin, but I should stick to moment. But anyway if I say spin I mean moment. The thing is that, the Brillouin function as I wrote down is a fairly complicated looking function. It has this cot hyperbolic 2 J plus 1 by 2 J cot hyperbolic, again the same factor inside minus 1 by 2 J cot hyperbolic to 1 by 2 J into y ok.

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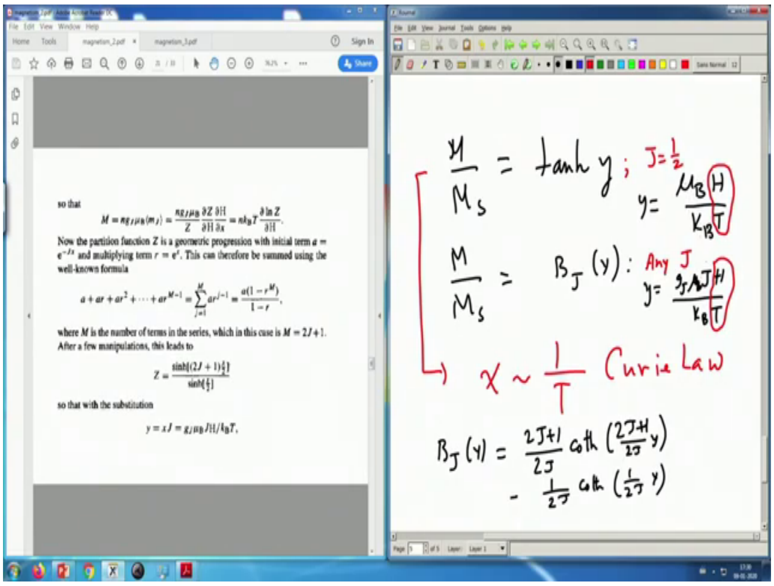

so that

$$M = ng_J\mu_B\langle m_J\rangle = \frac{ng_J\mu_B}{Z}\frac{\partial Z}{\partial H}\frac{\partial H}{\partial x} = nk_BT\frac{\partial \ln Z}{\partial H}.$$

Now the partition function Z is a geometric progression with initial term $a = e^{-Jx}$ and multiplying term $r = e^x$. This can therefore be summed using the well-known formula

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so that with the substitution

$$y = xJ = g_J\mu_B JH/k_BT,$$

$$\frac{M}{M_s} = \tanh y \; ; \quad J = \frac{1}{2} \quad y = \frac{\mu_B H}{K_B T}$$

$$\frac{M}{M_s} = B_J(y) : \quad \text{Any } J \quad y = \frac{g_J \mu_B J H}{K_B T}$$

$$\chi \sim \frac{1}{T} \quad \text{Curie Law}$$

$$B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}y\right)$$

Here y is of course has more factors g J mu B J H by k B T. This g J is called the land g factor. Remember your g factor that we used was 2, but this is not 2, this comes from atomic calculations. I will write down what it is, but not derive it here. This is obtainable in atomic calculations, because if it involves the it basically involves L, S and so on ok.

So, once we have that; there are two things you should remember that there is something called a Langevin Function which is obtainable from B at J equal to infinity. So, that is not something what we are using here. J equal to infinity actually gives you the classical limit of this calculation and you can check that you do get it. And the other is that J equal to half.

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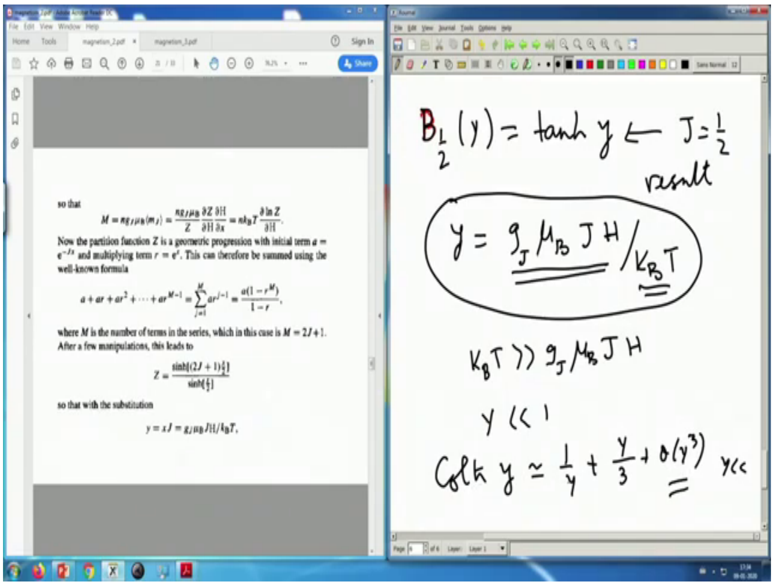

so that

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so that with the substitution

$$y = xJ = g_J\mu_B JH/k_BT,$$

$$B_{\frac{1}{2}}(y) = \tanh y \leftarrow J = \frac{1}{2}$$

result

$$y = \underline{\underline{g_J\mu_B JH}}/\underline{\underline{K_B}}T$$

$$K_BT \gg g_J\mu_B JH$$

$$y \ll 1$$

$$\coth y \simeq \frac{1}{y} + \frac{y}{3} + \underline{\underline{O(y^3)}} \quad y \ll$$

You can easily check that this B half of y you can just put J equal to half here and you can immediately find that it is tan hyperbolic y. So, this gives me back the result for J equal to half. So, M by M s equal to tan hyperbolic y. And these factors that we used here y factor will also become the same y factor that you got for d as J equal to half system. So, everything falls in place it has to as it has to ok.

Now, one can make an approximation. As I said the y that we wrote down here there are remember y equal to g J mu B J H divide by k B T ok. Now again these things mu B into H as I said gives you about something less than 1 degree. These factors will add a just another number small number, less than around 1 to 2 or less than 10 usually. And, so you are always at low temperatures in the; you are always at this scale the numerator has a scale which is at a low at which is equivalent to a low temperature; k B T typically is the room temperature for example or you can go down to liquid nitrogen temperature. If you want to which is 77 degree Kelvin, but it is always almost always unless you are very at very low temperatures less than a degree or few degrees or so.

This is much greater than g J mu B J H which implies that y is much less than 1, it is a very good approximation to do to find out the value of this. Otherwise you have to just plot and computers you can easily plot B J of y because the functional form is given in terms of cot hyperbolic.

Nevertheless, for analytical approach it is very important to get a formula get the dependences out with respect to H and temperature. So, it is much better to do this approximate calculation. And this approximation is fairly good ok. So, again the same way you can go ahead. And you remember that cot hyperbolic y for y much less than 1 is of the order of 1 over y plus 1 or y plus y by 3 plus higher order terms plus terms of order y q.

So, these can be neglected easily. And if you keep this then you will see that the result that you will get is interesting.

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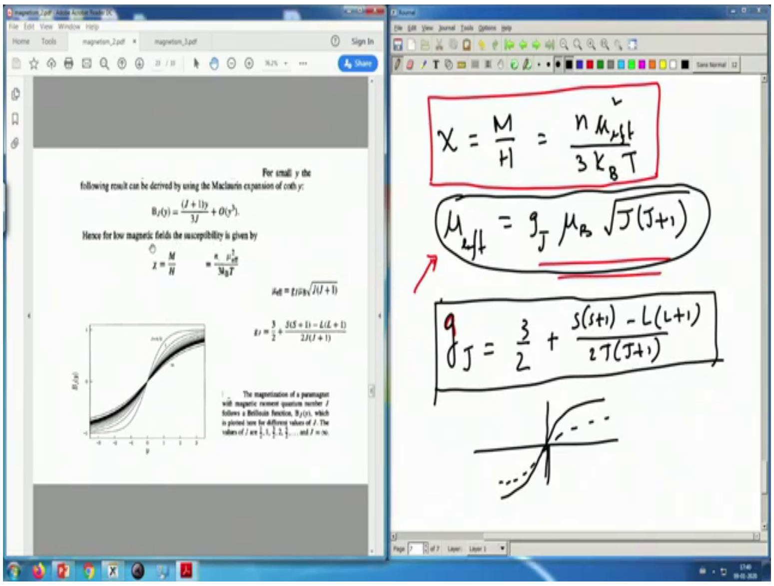

For small y the following result can be derived by using the Maclaurin expansion of coth y:

$$B_J(y) = \frac{(J+1)y}{3J} + O(y^3).$$

Hence for low magnetic fields the susceptibility is given by

$$\chi = \frac{M}{H} = \frac{n\mu_{\text{eff}}^2}{3k_BT}$$

$$\mu_{\text{eff}} = g_J\mu_B\sqrt{J(J+1)}$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

The magnetization of a paramagnet with magnetic moment quantum number J follows a Brillouin function, $B_J(y)$, which is plotted here for different values of J. The values of J are $\frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots$ and $J = \infty$.

$$\boxed{\chi = \frac{M}{H} = \frac{n\mu_{\text{eff}}^2}{3k_BT}}$$

$$\mu_{\text{eff}} = g_J\mu_B\sqrt{J(J+1)}$$

$$\boxed{g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}}$$

That, chi turns out to be chi which is equal to M by H is n mu effective some effective mu square by k B T; 3 k B T because of that three that I have. So, this is the result. Where of course, mu effective has all those factors: g J mu B and to root over J into J plus 1 ok.

So, my important relations this one. Of course, this mu effective is also important. If you remember I was showing you some p effective and p, so let me just try to see if I can go back few slides.

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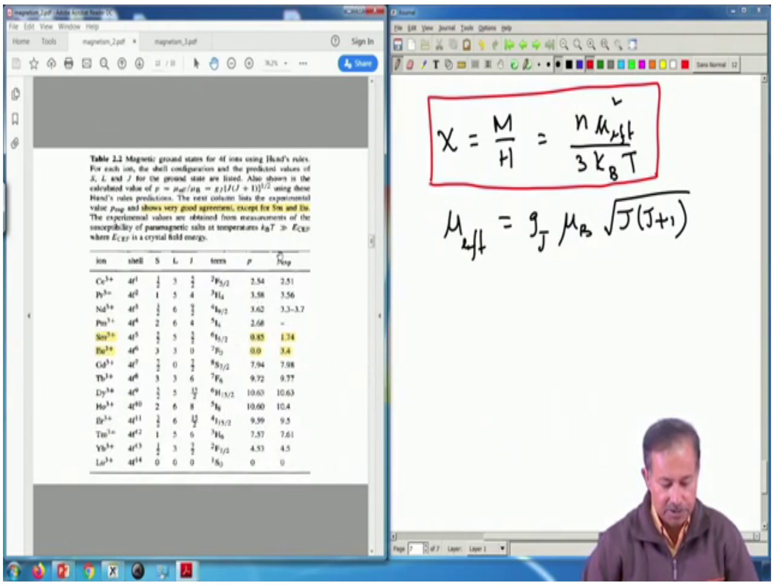

Table 2.2 Magnetic ground states for 4f ions using Hund's rules. For each ion, the shell configuration and the predicted values of S, L and J for the ground state are listed. Also shown is the calculated value of $p = \mu_{eff}/\mu_B = g_J[J(J+1)]^{1/2}$ using these Hund's rules predictions. The next column lists the experimental value p_{exp} and shows very good agreement, except for Sm and Eu. The experimental values are obtained from measurements of the susceptibility of paramagnetic salts at temperatures $k_BT \gg E_{CEF}$ where E_{CEF} is a crystal field energy.

ion	shell	S	L	J	term	p	p_{exp}
Ce^{3+}	$4f^1$	$\frac{1}{2}$	3	$\frac{5}{2}$	$^2F_{5/2}$	2.54	2.51
Pr^{3+}	$4f^2$	1	5	4	$^3H_4$	3.58	3.56
Nd^{3+}	$4f^3$	$\frac{3}{2}$	6	$\frac{9}{2}$	$^4I_{9/2}$	3.62	3.3–3.7
Pm^{3+}	$4f^4$	2	6	4	$^5I_4$	2.68	-
Sm^{3+}	$4f^5$	$\frac{5}{2}$	5	$\frac{5}{2}$	$^6H_{5/2}$	0.85	1.74
Eu^{3+}	$4f^6$	3	3	0	$^7F_0$	0.0	3.4
Gd^{3+}	$4f^7$	$\frac{7}{2}$	0	$\frac{7}{2}$	$^8S_{7/2}$	7.94	7.98
Tb^{3+}	$4f^8$	3	3	6	$^7F_6$	9.72	9.77
Dy^{3+}	$4f^9$	$\frac{5}{2}$	5	$\frac{15}{2}$	$^6H_{15/2}$	10.63	10.63
Ho^{3+}	$4f^{10}$	2	6	8	$^5I_8$	10.60	10.4
Er^{3+}	$4f^{11}$	$\frac{3}{2}$	6	$\frac{15}{2}$	$^4I_{15/2}$	9.59	9.5
Tm^{3+}	$4f^{12}$	1	5	6	$^3H_6$	7.57	7.61
Yb^{3+}	$4f^{13}$	$\frac{1}{2}$	3	$\frac{7}{2}$	$^2F_{7/2}$	4.53	4.5
Lu^{3+}	$4f^{14}$	0	0	0	$^1S_0$	0	0

$$\boxed{\chi = \frac{M}{H} = \frac{n\mu_{eff}^2}{3k_BT}}$$

$$\mu_{eff} = g_J \mu_B \sqrt{J(J+1)}$$

Remember this p and p effect experimental we were showing these similarly one actually here in experiments one actually calculates. And one can figure out the value of mu effective, and one can compare this mu effective with this number to check if the. So, experimentally you just plot it with respect to 1 by k B T for example, and then you know that the coefficient should be n mu effective square by 3.

So, n is no now more or the density is known and then of course mu effective can be easily figured out from that as. So, from that then you can go back and find out this effective value of J or so on. So, that is that is a standard practice people do. And then compare these with the estimated values.

So, here for example, g J is given for you. Its g J is a long formula s into s plus 1 minus L into L plus 1 by 2 J into J plus 1. So, if it is for example, take L equal to 0 s equal to half, then if L equal to 0 then J equal to s, then you will just have half from here 3 by 2 plus half is two which is the original g 0 remember.

So, of course, once you have this coupling between L and S and then of course you cannot do this; I mean the total J j sub J g sub J deviates somewhat from two and that is this formula. Now, this is just an atomic physics calculation and you can find out in any books, if you want to. But for all practical purposes you do not need to experimentally you determine this quantity and then compare with your estimates ok.

So, I mean g J values are tabulated for many of these elements. So, you can also use that many of the ions and elements, you can use those as well.

Now, what is in important is this picture. This, remember this picture that M by M s that we got.

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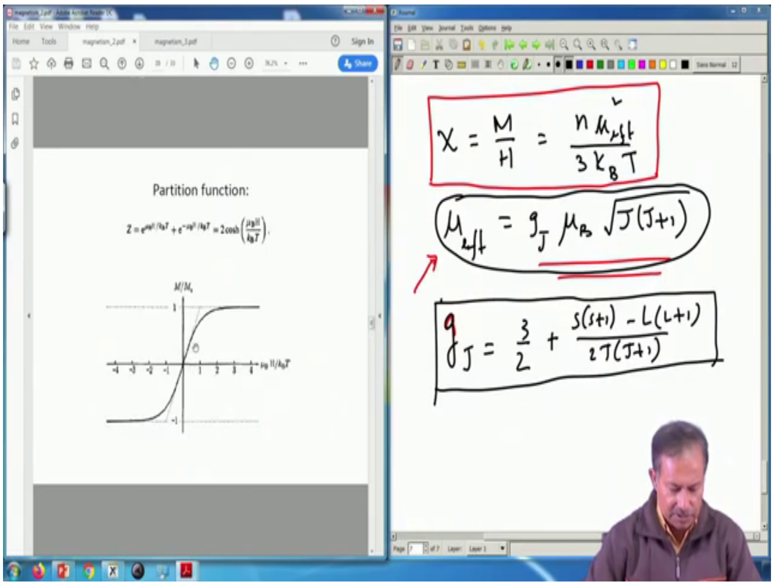

Partition function:

$$Z = e^{\mu_B H/k_B T} + e^{-\mu_B H/k_B T} = 2\cosh\left(\frac{\mu_B H}{k_B T}\right).$$

$$\chi = \frac{M}{H} = \frac{n\mu_{eff}^2}{3k_B T}$$

$$\mu_{eff} = g_J \mu_B \sqrt{J(J+1)}$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Now, that was a tan hyperbolic kind of picture. Look at B J sub B J of y that also looks somewhat like the same picture; I mean it has to be because after all you have at J equal to half it has to go back to that picture. At J equal to infinity of course, it is the slope is much less. And so, then between J equal to half and J equal to infinity is a dense set of lines. So, as J increases the line basically goes down. So, as J increases for low J it is like this and at higher J it just goes down like this.

Now again if you if you find that that the relation between chi and T is still 1 by t.

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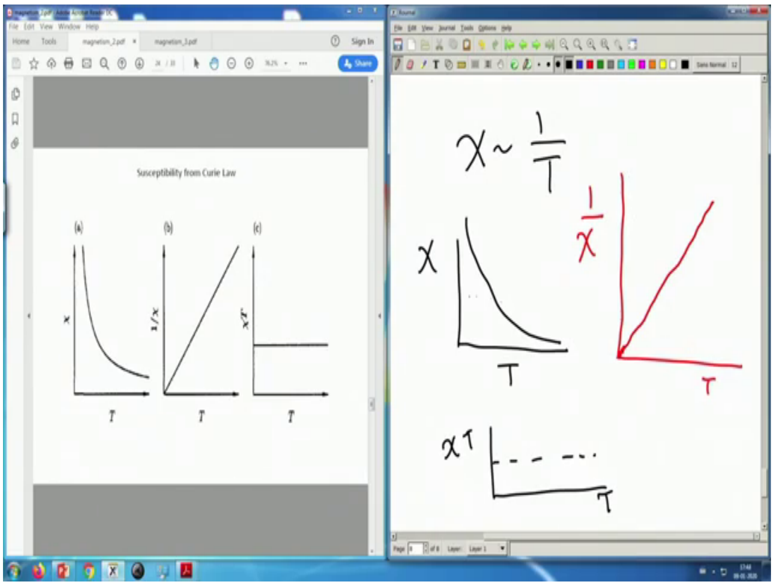

So, that is an important message from here chi is still 1 by T. So, as I said if you have free moments in the system and if you are finding from your experiment that chi goes as 1 over T, then you can be rest assured that there are free moments in the system. So, this is the famous Curie Law in magnetism and that is followed more or less nicely by paramagnetic systems where there are free moments. Of course, there will be deviations and we will discuss those when we come to them.

So, this is susceptibility from Curie's Law. So, I can plot this as with chi versus T which is a hyperbola. Usually, people plot this is the plot that is most common 1 by chi versus T which is a straight line. And the slope gives you these those quantities that are in front of this mu effective square and so on; n mu effective square by 3 k B.

The interesting thing is that; so the slope gives actually the inverse of that you are plotting 1 by chi with T. So, anyway the point is that this straight line figure and this straight line picture with the line cutting the T the origin is a very famous picture that is a telltale signature of magnetic paramagnetic system. But of course, this whole treatment that we did this approximate approximation of course breaks down at very low temperature.

So, this passing through the origin it should be taken with some care. In real systems it may not happen as I have just shown and that you have to actually go through. The formula will of course, give you a picture like this, but you should be careful here. And as I will show that there are systems basically at very low temperature systems, magnetic systems order and that ordering prevents this kind of a passing through this behavior gets changed. So, the divergence at 0 temperature does not survive in real systems, where other effects come and cut it off.

Now of course, you can also plot, this is also done in some cases some people do this, they in some papers you will find chi times T plotted because it then it becomes a constant ok. So, these are various ways people plot, but the message from all of them is simple and similar and the same basically. And as I said this is the most common plot the red one is the most common plot, here the middle one for example is the most common plot that you will this middle one; the B that you will see.

So, what did we achieve? We achieve something called the basically we derived Curie's Law from very simple minded statistical mechanics calculations. Where we assume that these magnetic ions are just now we are replacing them by free moments; free moments these moments interact with magnetic field and they also get thermalized at a finite temperature.

So, these two effects are taken care of in a statistical mechanical calculation, where we did the usual calculation of the either you directly calculate the average; or you can also calculate the partition function from which you take derivatives to calculate the derivative of the log of partition function to calculate physical quantities like magnetization and susceptibility.

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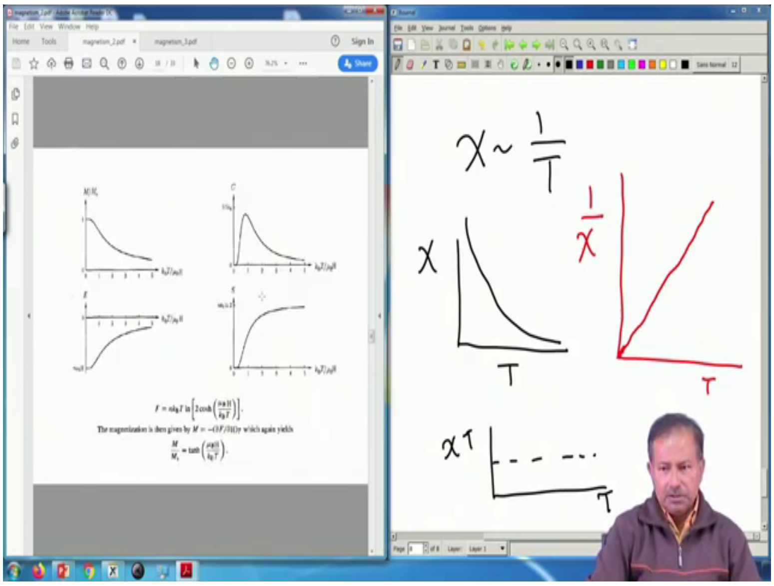

$$F = -nk_BT\ln\left[2\cosh\left(\frac{\mu_B H}{k_BT}\right)\right].$$

The magnetization is then given by $M = -(\partial F/\partial H)_T$ which again yields

$$\frac{M}{M_s} = \tanh\left(\frac{\mu_B H}{k_BT}\right).$$

The important pictures that I showed at this magnetization, magnetization saturates at low temperature and then it becomes thermalized at high temperatures. Low and high are of course mu B H sets scale which is a very low scale though in terms of temperatures about a degree or less. And so, any temperature reasonable temperature or room temperature is fairly high temperature.

Then, I also showed that the energy is it starts with minus mu B times the number of ions or moments times H, but it then goes towards 0 as the system thermalizes . So, the energy increases as you the entropic contribution to the free to the; this is the energy its is increases. Then of course, free energy will you have to calculate the free energy to calculate every physical quantities like M and so on at finite temperature.

But if you just calculate the energy, the energy goes towards approaches towards 0 at high temperature. Then of course, is this specific heat which is fairly interesting. This kind of a specific heat picture tells us that there is there are two levels in the system and the there is a peak. And of course, it is consistent with the third law of thermodynamics which dictates that it goes to 0 as the temperature goes down to 0. And then at high temperature of course, the system thermalizes and there is almost specific heat goes down to 0; very small value at large temperatures.

And this again is the entropy. And of course entropy and specific it you know are related in thermodynamics, one is the integral of the other with a factor of T. And the entropy can be counted here just from simple physical arguments moments is that every spin in this treatment for example it was J equal to half.

So every spin has, every moment has two states to access. It can be at high temperature it is easy for it to access both the states, cannot you cannot really if temperature is so large much larger than k mu B into H then these the moments will freely go between these two states. So, they are so they each of them will have two states to access. So, n of them will have 2 to the power n and then take a log multiplied by k B and that is your entropy. And of course then divide by volume to get the entropy density.

So, this is the principle. But then this actually tells us if you get a curve like this, in for example at finite J you can see that this will just be 2 J plus 1 instead of 2 you will get 2 J plus 1. And that is again telling us that the there are 2 J plus 1 states from minus J 2 plus J and these states are all accessed if your temperature is fairly high compared to this the span of states, the range of energies of these states. And then the moments will access all of them and their entropy will go to 2 J plus 1. Then again 2 J plus 1 to the power n then take a log and again you will get log n k B log 2 J plus 1. From this you can actually figure out the value the moment that is contributing to the entropy.

Besides, if your actual entropy will have other components. It will have components from electrons, from phonons and so on. So this one, if you have a component which is log of 2 J plus 1 then you know that there is a spin which is contributing, this moment which is contributing which value is J. And that is a very nice way to find out that a there is a this is called the magnetic entropy contribution in a solid. And at very low temperatures where the other entropies become quenched they are very small then this starts dominating.

For example in an insulator the electronic entropy will be small, then at very low temperatures the phonon entropy contribution will also be very small, and then this will pick up. But then it should not be close to 0, should not be as so small that it goes down to 0. So, very low temperature of course, you will not access all the states, so that you will not get 2 J plus 1. So, there is a tradeoff. I mean you have to know what you are doing when you do these experiments.

Then we did the calculation for finite J and a finite J calculation is straightforward, it is just that you do not get a simple formula like tan hyperbolic y, but you get a formula. So, you just sum this series to calculate your partition function with r equal to e to the power x and starting with a equal to e to the minus J x. And use this formula to calculate your partition function. And at the end of the day you will get a partition function like this, correspondingly you will get a magnetization which is derivative of the log of the partition function its a free energy basically. And with respect to H this that will give you M, where M s M by M s M s is this quantity which is where all the spins are saturated ok.

So, then the Brillouin function you can plot or you can approximate at temperatures much higher than this. Basically, y is much less than 1 in this limit where your magnetic energies are much smaller than the k, thermal energies in that limit you can expand you can do it. And I just wrote down the expansion and x plus 1 by x plus 1 third x is what cot hyperbolic x gives you for low x.

And then you will get a B J y you will have an approximate value J plus 1 into y by 3 J plus some y q order terms. Forget those terms, neglect them and your chi is M by H which is n mu square by 3 k B t where mu there is a mu effective mu effective; n mu effective square by 3 k B T which is this ok. And for this is where the plot is for J equal to half to J equal to infinity. You have the series of plots for B J of y and that gives you the formula. But necessarily, what is necessary is this Curie’s Law that is what we are after and that is what we get.

So, this is the free moment contribution to susceptibility. Susceptibility coming from free moments and then and that is 1 over k B T again, and this 1 by T dependence is experimentally plotted in this fashion.