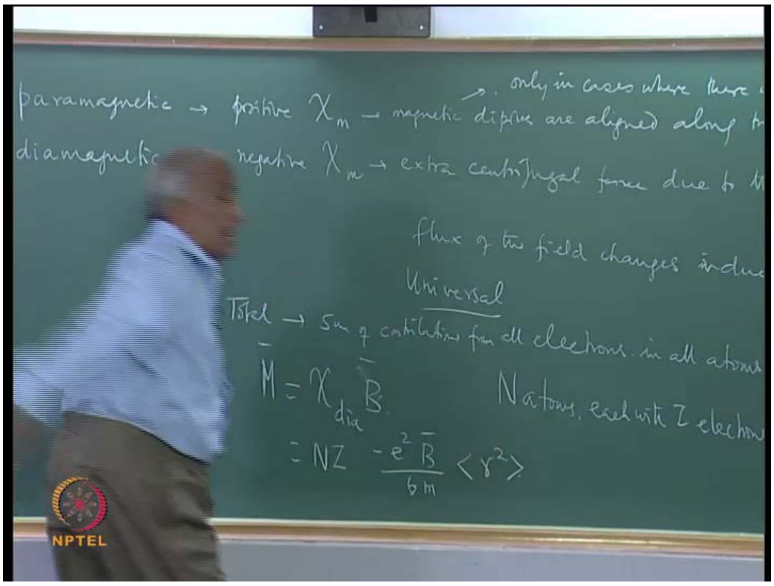
Condensed Matter Physics
Prof. G. Rangarajan
Department of Physics
Indian Institute of Technology, Madras

Lecture - 20
Paramagnetism of Transition Metal and Rare Earth Ions

In the last lecture, we saw how the energy of an electron in an applied magnetic field consists of magnetic comes of different kinds one is a paramagnetic term.

(Refer Slide Time: 00:40)



paramagnetic → positive χ_m → magnetic dipoles are aligned along th → only in cases where there

diamagnetic negative χ_m → extra centrifugal force due to th

flux of the field changes induc

Universal

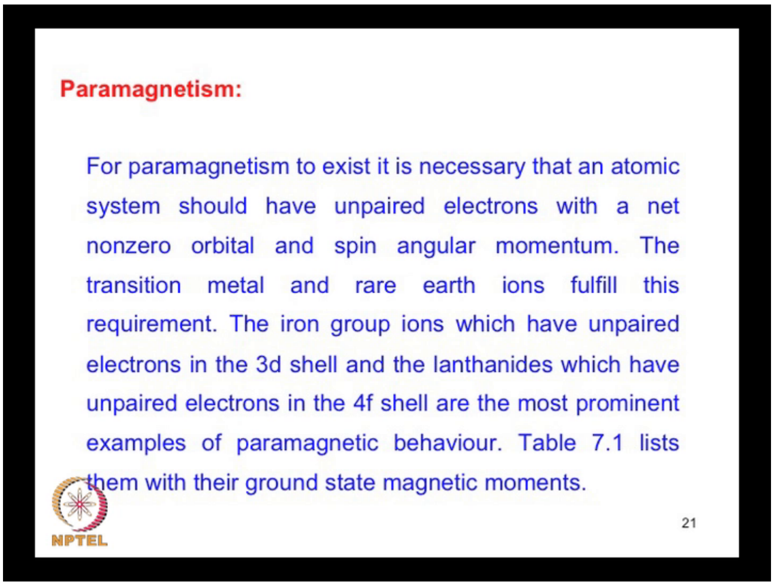
Total → Sum of contributions from all electrons in all atoms

$\bar{M} = \chi_{dia} \bar{B}$ N atoms, each with Z electron

$= NZ \frac{-e^2 \bar{B}}{6m} \langle r^2 \rangle$

And the other it is a diamagnetic paramagnetic term correspondence to positive magnetic susceptibility in the sense that the magnetic dipoles are alien along the applied magnetic field.

(Refer Slide Time: 01:10)



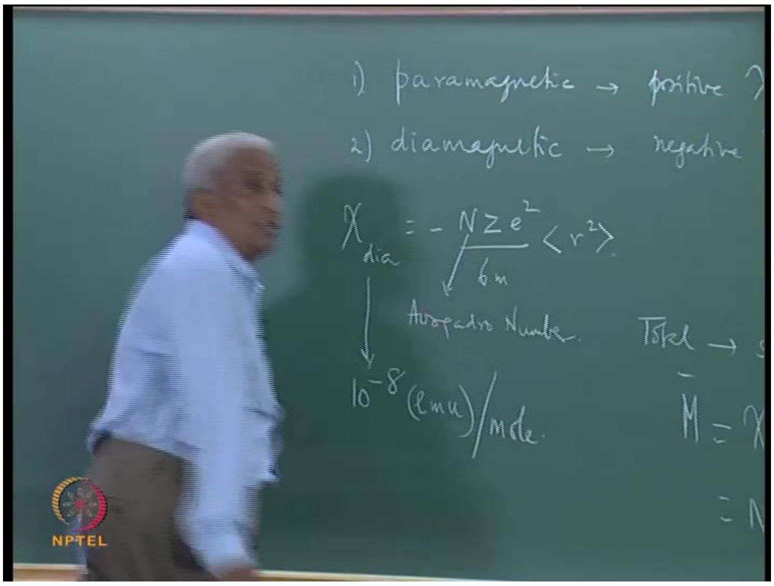
Paramagnetism:

For paramagnetism to exist it is necessary that an atomic system should have unpaired electrons with a net nonzero orbital and spin angular momentum. The transition metal and rare earth ions fulfill this requirement. The iron group ions which have unpaired electrons in the 3d shell and the lanthanides which have unpaired electrons in the 4f shell are the most prominent examples of paramagnetic behaviour. Table 7.1 lists them with their ground state magnetic moments.

Whereas the diamagnetic term arises from a negative magnetic susceptibility and this is due to the extra centrifugal term centrifugal force due to the magnetic field on the electron in anatomic are molecular orbital. So, this causes the magnetic flux associate in the field the change changes and this induces inducing an e m f according to Lenz law in electromagnet. So, this is since this e m f is a bacterium which is opposing the influencer field in therefore, it as a negative sign that gives you the negative diamagnetic susceptibility. This effect is universal the diamagnetism occurs in all substances, whereas paramagnetism occurs only in cases where there is an unpaired electron giving rise to a net magnetic dipole moment which has to orient along the field.

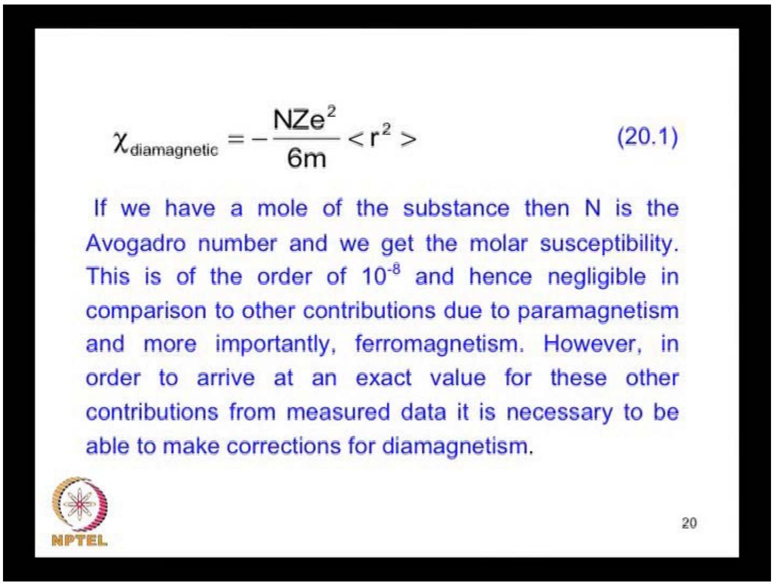
So, this does not occur in all situations where as diamagnetism always occurs the total diamagnetic susceptibility is obtained by summing up the contributions from all the electrons total is some of contributions from all electrons and then in all atoms are molecules in a given quantity of the material. So, the magnetization is then xi diamagnetic types h are the where b is the in magnetic induction. So, if you have n atoms each with z electrons because the atom with an atomic numbers z will have z electrons then the a m is n z times the contribution which is minus e squared b by 6 m times as we saw last time. So, where r square is a average value of square of the atomic radius orbital radius.

(Refer Slide Time: 06:23)



So, thus we get x i dia s minus n z e square like 6 m times of r square. So, n is of course, the allocator number.

(Refer Slide Time: 06:27)



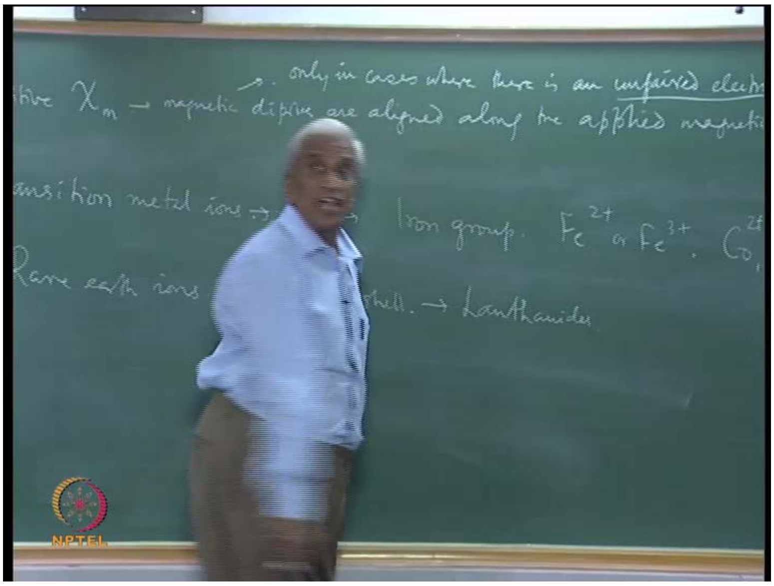
$$\chi_{diamagnetic} = -\frac{NZe^2}{6m} < r^2 > \qquad (20.1)$$

If we have a mole of the substance then N is the Avogadro number and we get the molar susceptibility. This is of the order of 10^{-8} and hence negligible in comparison to other contributions due to paramagnetism and more importantly, ferromagnetism. However, in order to arrive at an exact value for these other contributions from measured data it is necessary to be able to make corrections for diamagnetism.

If we are taking about the molar diamagnetic susceptibility and this is of the order of ten to 4 minus eight in more substance therefore, is an extremely small value per mole. So, this is a even though it is present a very wherein all the materials this is extremely small in comparison to the contribution from paramagnetism or ferromagnetism. Therefore, we usually do not feel it we do not talk about, but in general for accurate work you have to take to the diamagnetism before determining calculating the paramagnetic are ferromagnetic contributions.

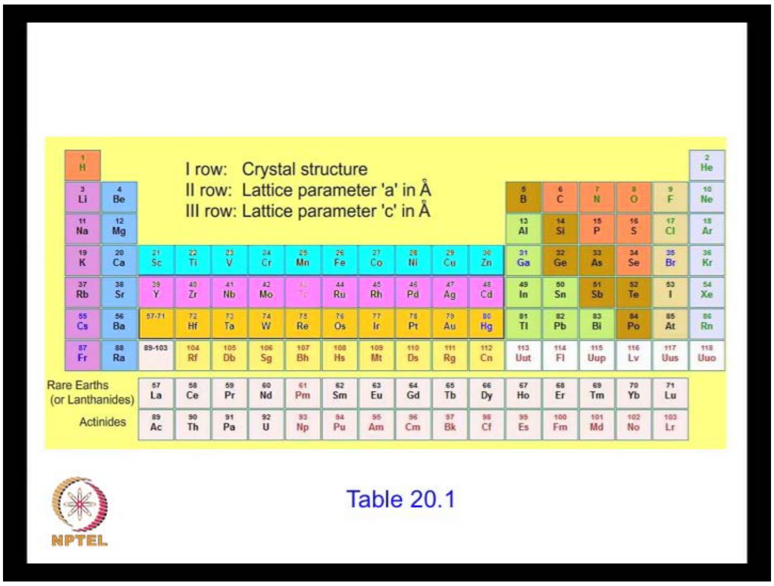
Next, we consider paramagnetism, as we said it is necessary to have an unpaired electron in the atom or molecule. In order to give rise to a net orbital angular momentum non-zero orbital or of spin angular momentum only when there is an non-zero net orbital and or spin angular momentum, then only you will have a net dipole magnetic dipole moment which gives rise to a paramagnetic effect. So, what kinds of systems are there which have such a possibility which are the systems in the there is a non-zero, orbital or spin angular momentum given rise given by unpaired electron spins. So, this is the question.

(Refer Slide Time: 09:11)



So, why you look at the periodic table a Fairlyman's, we find so-called transition metal ions corresponding to the feeling of 3 d shells’ are even 4 d shells and so on or rare an ions corresponding to if 4 f shells.

(Refer Slide Time: 09:35)



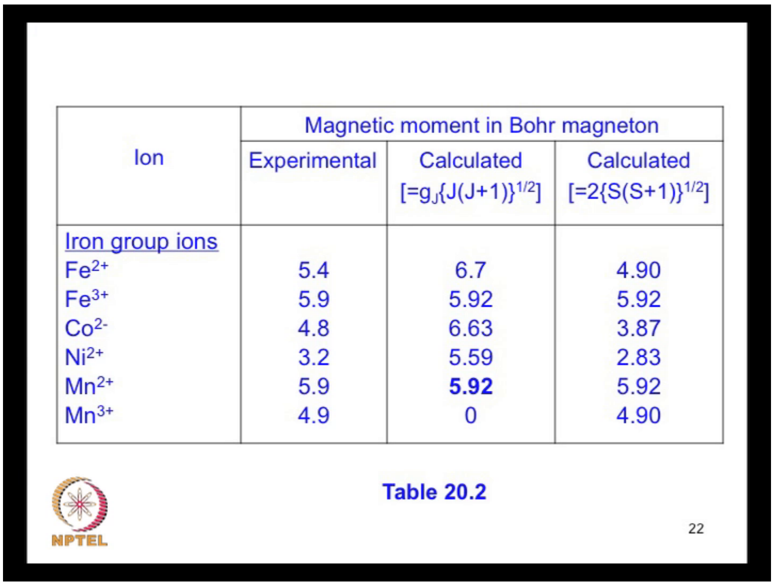
I row: Crystal structure
II row: Lattice parameter 'a' in Å
III row: Lattice parameter 'c' in Å

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Rare Earths (or Lanthanides)		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
Actinides		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Table 20.1

So, these are the ions this 3 d ions or also known as the iron group ions because the iron F e 2 plus or F e 3 plus is an important member of this group. So, are the other magnetic ferromagnetic ions such as cobalt nickel and so on. So nickel two plus nickel three-plus nickel plus also. So, these are the various ions and the fact rare the ions are known as the lanthanides. So, they correspond to the progressive filly on the 4 f ship and they are the most prominent examples of paramagnetic here.

(Refer Slide Time: 10:43)

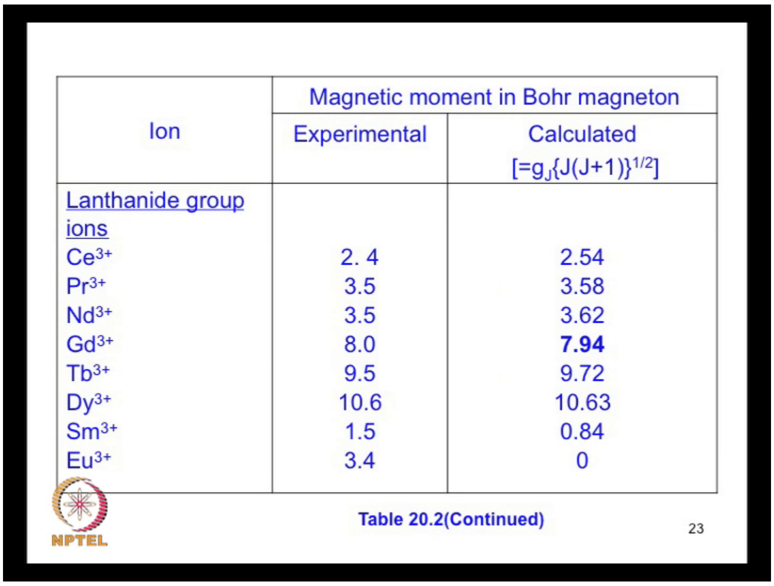


Ion	Magnetic moment in Bohr magneton		
	Experimental	Calculated $[=g_J\{J(J+1)\}^{1/2}]$	Calculated $[=2\{S(S+1)\}^{1/2}]$
Iron group ions			
Fe^{2+}	5.4	6.7	4.90
Fe^{3+}	5.9	5.92	5.92
Co^{2-}	4.8	6.63	3.87
Ni^{2+}	3.2	5.59	2.83
Mn^{2+}	5.9	**5.92**	5.92
Mn^{3+}	4.9	0	4.90

Table 20.2

So, the next table summarizes this the giving the magnetic moment in bore magnetrons both experimental and calculated values.

(Refer Slide Time: 10:54)

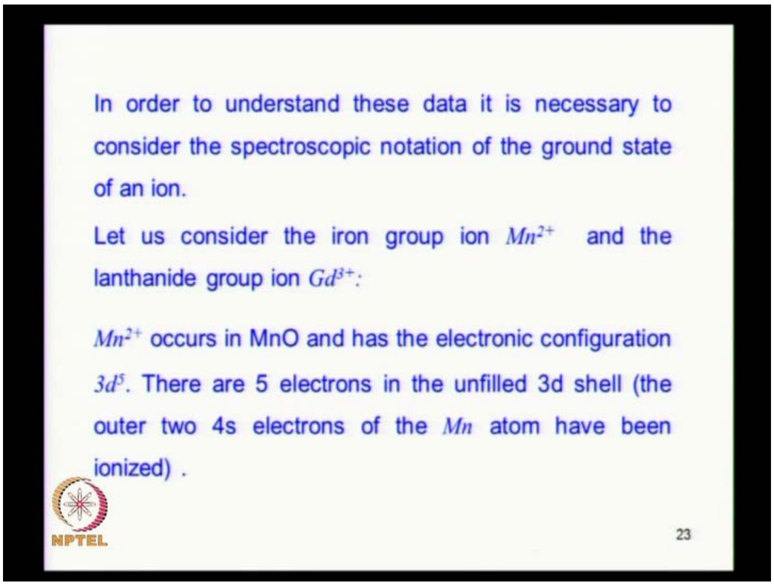


Ion	Magnetic moment in Bohr magneton	
	Experimental	Calculated $[=g_J\{J(J+1)\}^{1/2}]$
Lanthanide group ions		
Ce^{3+}	2. 4	2.54
Pr^{3+}	3.5	3.58
Nd^{3+}	3.5	3.62
Gd^{3+}	8.0	**7.94**
Tb^{3+}	9.5	9.72
Dy^{3+}	10.6	10.63
Sm^{3+}	1.5	0.84
Eu^{3+}	3.4	0

Table 20.2(Continued)

For the different typical members the ion ions group 3 the transition ion as well as the lanthanides are the ions.

(Refer Slide Time: 11:08)



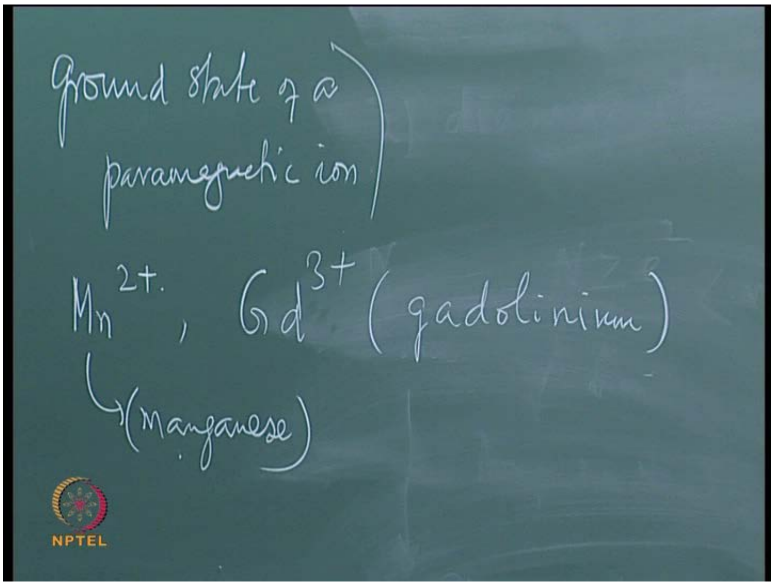
In order to understand these data it is necessary to consider the spectroscopic notation of the ground state of an ion.

Let us consider the iron group ion Mn^{2+} and the lanthanide group ion Gd^{3+}:

Mn^{2+} occurs in MnO and has the electronic configuration $3d^5$. There are 5 electrons in the unfilled 3d shell (the outer two 4s electrons of the Mn atom have been ionized) .

In order to understand this paramagnetic behavior it is necessary for as to consider this spectroscopic notation of the ground state of an ion.

(Refer Slide Time: 11:21)



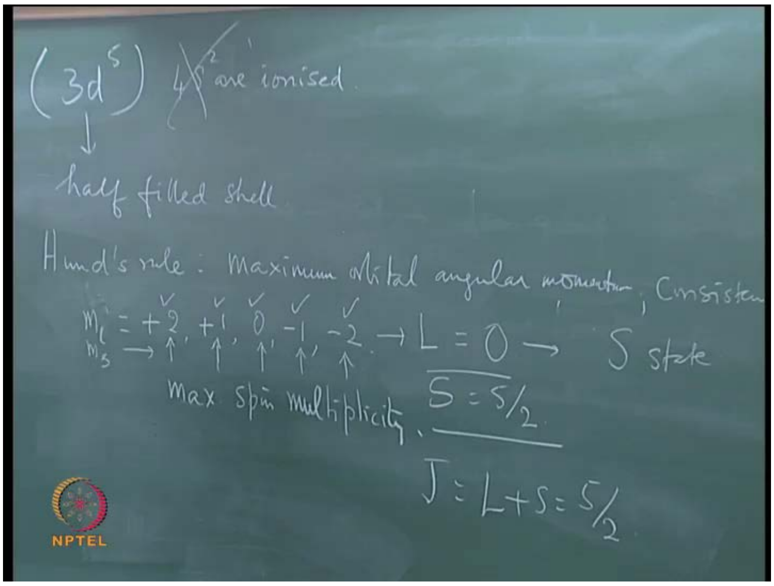
Ground state of a paramagnetic ion

Mn^{2+}, Gd^{3+} (gadolinium)

↳ (manganese)

How do you determine the ground state and that is what will determine the corresponding paramagnetic moment. For example, let us consider a particularly simple example of manganese to plus and similarly for the lanthanide group let us take get a gadolinium 3 plus.

(Refer Slide Time: 12:29)



$(3d^5)$ $\cancel{4s^2}$ are ionised

↓

half filled shell

Hund's rule : Maximum orbital angular momentum, Consisten

$$m_l = \overset{\checkmark}{+2}, \overset{\checkmark}{+1}, \overset{\checkmark}{0}, \overset{\checkmark}{-1}, \overset{\checkmark}{-2} \rightarrow L = 0 \rightarrow S \text{ state}$$

$$m_s \rightarrow \uparrow, \uparrow, \uparrow, \uparrow, \uparrow$$

max spin multiplicity. $\overline{S = 5/2}$

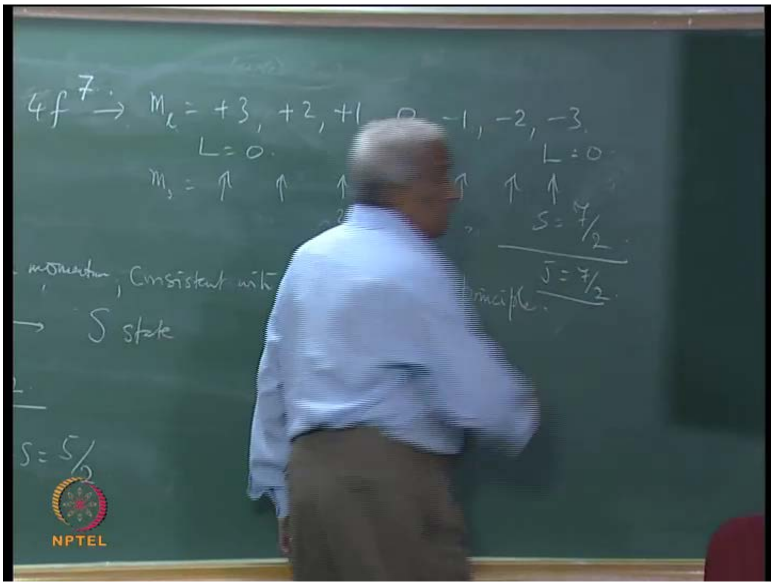
$J = L + S = 5/2$

So, if you consider the manganese ion from the atomic number of manganese, we can easily find that this corresponds to a configuration. The electron configuration with an outer more shall in which there are 5 unpaired electrons in the outermost 3 d shell a typical example of this is manganese oxide m no they manganese occurs in the two plus stage. So, there are 5 electrons in the un feel the 3 d shell the outer to 4 s 2 are ionized m n 2 plus. So, these go out leaving these in the unfilled outermost shell it is the behavior of the 5 electrons that determines the magnetic behavior of manganese ion in general the 3 d shell can have ten electrons. So, these a half filled shell.

So, according to whom all the electrons will be found in such stage. So, as to have the maximum once ruled use you maxi- mum orbital angular momentum. So, as not to violate the Pauli principle consistent with the Pauli exclusion principle, here we have already seen in what is Pauli exclusion principle according to Pauli exclusion in principle here no two electrons having all quantum numbers identical can occupy the same quantum state. In other words, applied to the manganese to plus for which there are different states things there are five electrons and these additional.

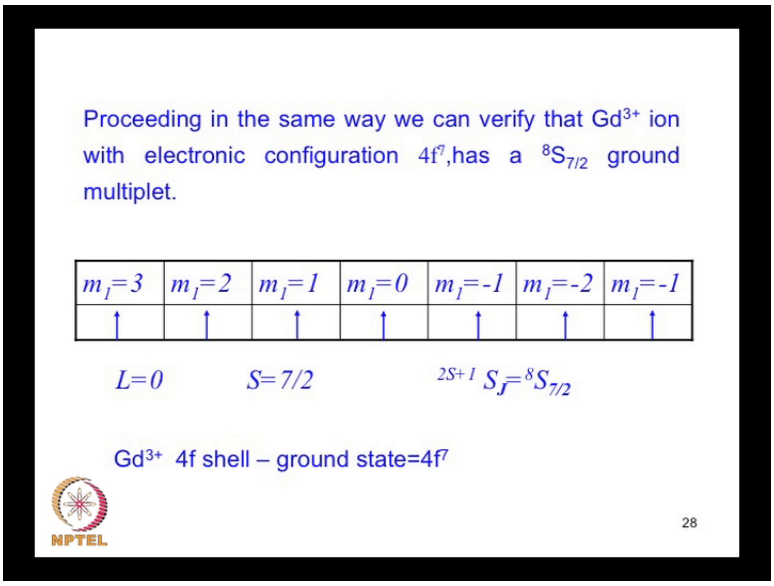
So, you have the possibility plus to plus 1 0 minus 1 and minus 2. So, this gives me these are various m l vales for the orbital angular momentum which are possible. So, all these or filled by an electron since there are five state each of these is filled. So, I have so that the total orbital angular momentum because if they if the another electron is put into these it can have only spin down. So, we must have l equal to the total some of this is zero. So, that you can have a maximum spin multiplicity we want to have spin orientation this upward arrow corresponds to m s is equal to plus r these are the m l and these are the m s. So, I have s equal to 5 by 2. So, I have maximum spin and consistent with that I have l equal to 0 which is s state l equal to 0 corresponds to an sj and the j the total angular momentum which is al plus s s 5 by 2. So, the ground multi plate has j equal to 5 by 2. So, if you look at the ground state these is be the ground state for them n 2 plus ions.

(Refer Slide Time: 17:08)



Now, in the same way we can find that gadolinium 3 plus which has a 4 f 7 configuration in the outer shell outermost and un filled shell. So, since there is a possibility of 14 electrons in the f-shell therefore, the again have a half filled shell. And similarly, we can have m l is equal to plus 3 plus two plus 1 0 minus 1 minus two minus 3 giving l equal to 0 and m s c is up spin up spin up spin up in up spin giving to s equal to 7 by 2. So, we have an a state again with a j equal to l equal to 0. So, j is 7 by 2, so that would be the spectroscopic state of gadolinium 3 plus ion no having determined the ground-state of the ion.

(Refer Slide Time: 18:35)



Proceeding in the same way we can verify that Gd^{3+} ion with electronic configuration $4f^7$,has a $^8S_{7/2}$ ground multiplet.

$m_l=3$	$m_l=2$	$m_l=1$	$m_l=0$	$m_l=-1$	$m_l=-2$	$m_l=-1$
↑	↑	↑	↑	↑	↑	↑

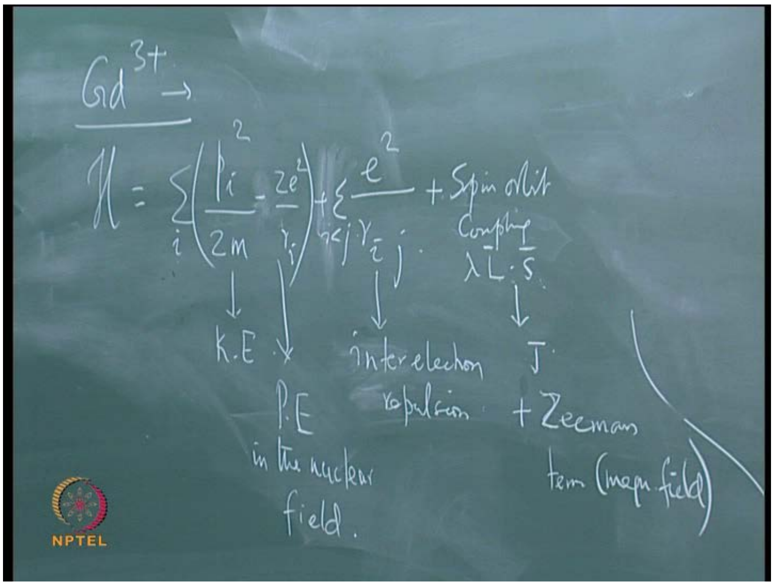
$L=0$ $S=7/2$ $^{2S+1}S_J = {}^8S_{7/2}$

Gd^{3+} 4f shell – ground state=$4f^7$

NPTEL

We can we have to now proceed to find the g factor up this ion it is g factor which will determine the magnetic moment. So, in the case of the gadolinium 3 plus this situation is somewhat simpler.

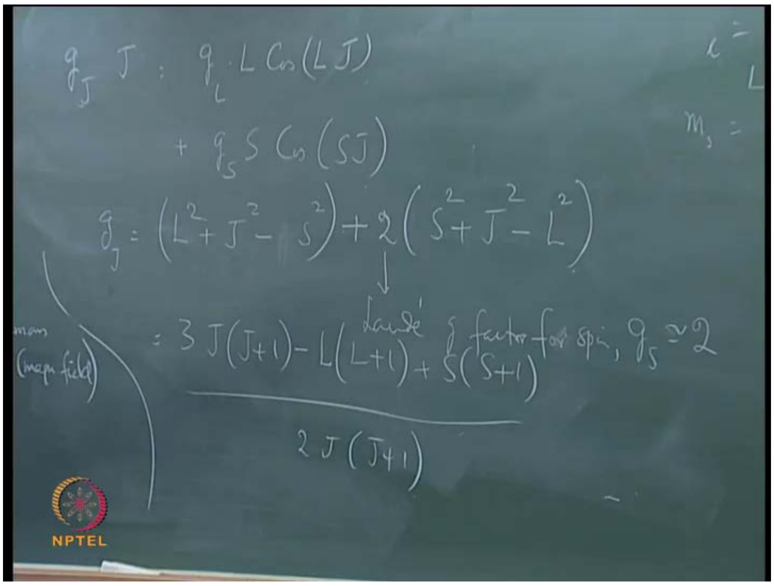
(Refer Slide Time: 18:58)



Because in order to determine these, we have to proceed by considering the Hamiltonian at the electron a many electron atom which has the following terms. This is the kinetic energy term pi square by 2 m summed over all the different electrons which are labeled by the denoted by this label I then you have I am leaving out the 1 by 4 by epsilon naught etcetera. So, that I have this is the kinetic energy term this is the potential energy term I have also this is the potential energy in the nuclear nuclear field coulomb field as a nucleus. So, this is minus and then I have plus sigma i less than j this is the inter electron coupling or repulsion.

So, beyond this, we have various terms, the most important is this; spin orbit coupling which as the formed lambda l dot s. So, if the sped not be coupling the sufficiently strong I am writing it in descending order of the strength of the various interactions. So, if these coupling is strong this gives the coupling between l and s use you as a certain j as the total angular momentum. So, that it is this angular momentum which interact with an applied magnetic field Zeeman term due to a magnetic field. So, in order to find this, we have the homes rules we have applied the homes rules and now we can proceed to find the zee factor.

(Refer Slide Time: 21:59)



$$g_J\, J = g_L \cdot L \cos(LJ) + g_S\, S \cos(SJ)$$

$$g_J = (L^2 + J^2 - S^2) + \underset{\downarrow}{2}(S^2 + J^2 - L^2)$$

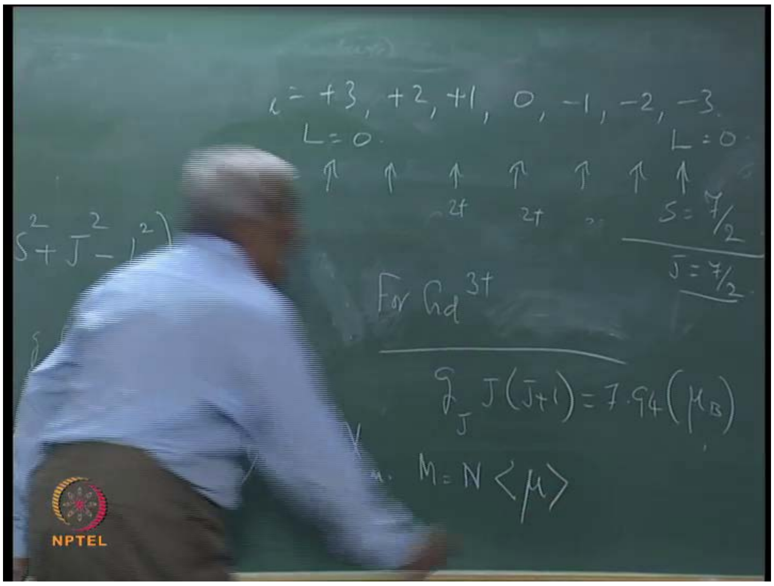
Landé g factor for spin, $g_S \simeq 2$

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

So, how do we go about doing this we have you according to the g J g J is the g factor associated with the total angular momentum J this given by g L into L cross L J plus g sin to s cause s J. So, this is the projection of the contribution from the orbital angular momentum this is the contribution from the spin angular momentum. Now g J is given by 1 plus are L square plus J square minus 2 s square minus s square times plus 22 into s square plus j square minus l square this two comes, because they landed g factor for spin which we write as g s is approximately two.

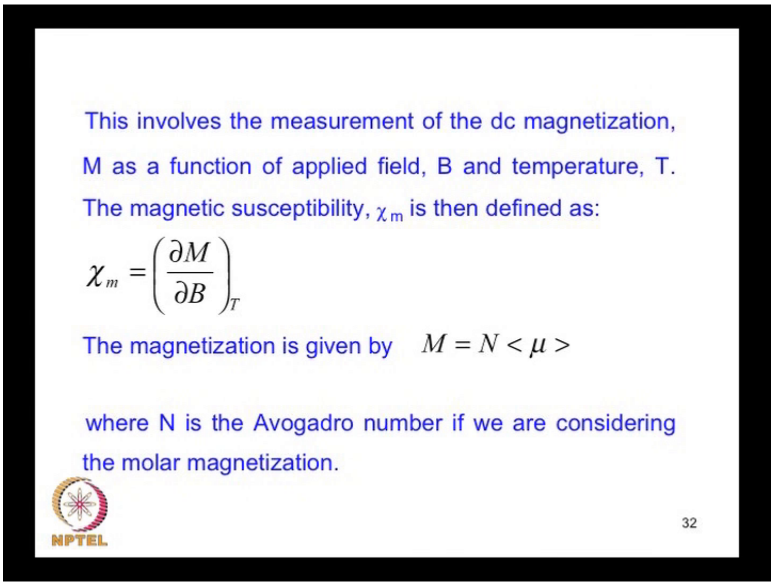
So, if you take these two to together you get the net J as 3 j into J plus 1 minus L into plus 1 plus s into s plus 1 by 2 j into J plus 1 that is the expression for the G factor associated with an angular momentum J. Your for every square of the angular momentum operator, we have replaced it by the corresponding Eigen value, which is j into j plus 1 for j square l into l plus 1 into for l square s into s plus for s square. So, using this since we know the l s and j we can calculate the g value.

(Refer Slide Time: 24:31)



If you substitute these values we get a g value of 7.94 for the gadolinium not g j g j into j into j plus-one which is the angular momentum which 7.94 bore magnetrons. So, this how we calculate the magnetic moment of a given paramagnetic ion know how do we experimentally determine it we experimentally determine it by measuring the magnetization in an applied magnetic field. So, that dm by db use you xi m the paramagnetic susceptibility is given by d m by d p, where the magnetization these n u the mu is the average magnetic moment individual magnetic moment, and n is the number of ions. If it is a mole of the substance, this number is alligator number.

(Refer Slide Time: 26:03)



This involves the measurement of the dc magnetization, M as a function of applied field, B and temperature, T. The magnetic susceptibility, χ_m is then defined as:

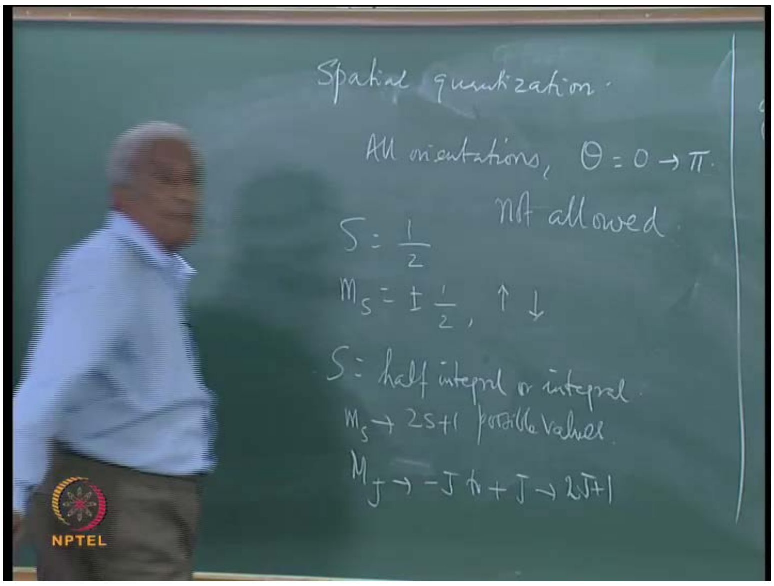
$$\chi_m = \left(\frac{\partial M}{\partial B}\right)_T$$

The magnetization is given by $M = N < \mu >$

where N is the Avogadro number if we are considering the molar magnetization.

The average magnetic moment has now to be calculated in order to make a theoretical calculation of the magnetic susceptibility and then we can compare the experimentally determined values. In order to do this, we have to compare this by a recalling our discussion of the orientational polarization. In the case of a dialectic material, a para-dielectric material, where you have a number of electric dipoles distributed in different orientations in an applied electric field this was classically treated by a using Boltzmann statistics the various orientation. So, if the electric dipole with respect to the applied electric field ranges from 0 to pi, the angle theta goes from 0 to pi. All these orientations where allowed the main difference our argument in this case proceed. In the same way, we will calculate the statistical average of the dipole moment of the paramagnetic ion by a fight averaging 8 over all that all the allowed orientations in the case of paramagnetic dipole.

(Refer Slide Time: 27:31)



Spatial quantization.

All orientations, $\Theta = 0 \rightarrow \pi$.

not allowed

$S = \frac{1}{2}$

$m_s = \pm \frac{1}{2}$, ↑ ↓

S = half integral or integral.

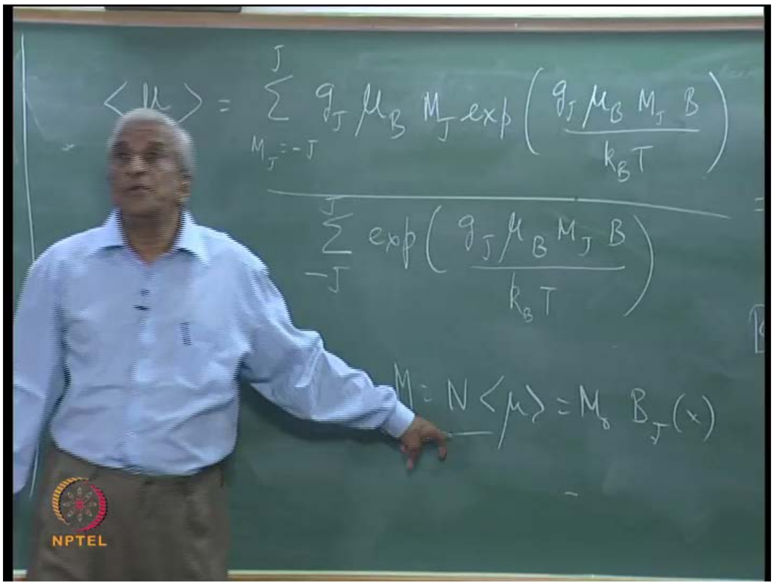
$m_s \rightarrow 2s+1$ possible values

$M_J \rightarrow -J \hbar + J \rightarrow 2J+1$

The only thing is in the magnetic case, you have spatial quantization which means that all orientations are not allowed corresponding to theta equal to 0 to pi are not allowed only certain discrete orientation are allowed. For example, in the case of have a spin off you have m s equals to plus minus half, these are usually denoted by an up and down arrow; that means, the dipole is either aligned parallel to the applied magnetic field or it is aligned anti parallel to the applied.

So, you have one only two such orientations possible for us spin half. This spin can only be half-integral in general or integral corresponding to a given s value m s has two s plus 1 value possible values. And these two s plus 1 orientations will have different energies is applied magnetic field. And we make a statistical average of a magnetic moment over these two s plus or ion one orientations from for example, plus for example, if you have m j then this goes from minus j to plus j which is 2 j plus 1. So, this is what we have to do in order to the calculate the average. So, let us calculate this.

(Refer Slide Time: 29:35)

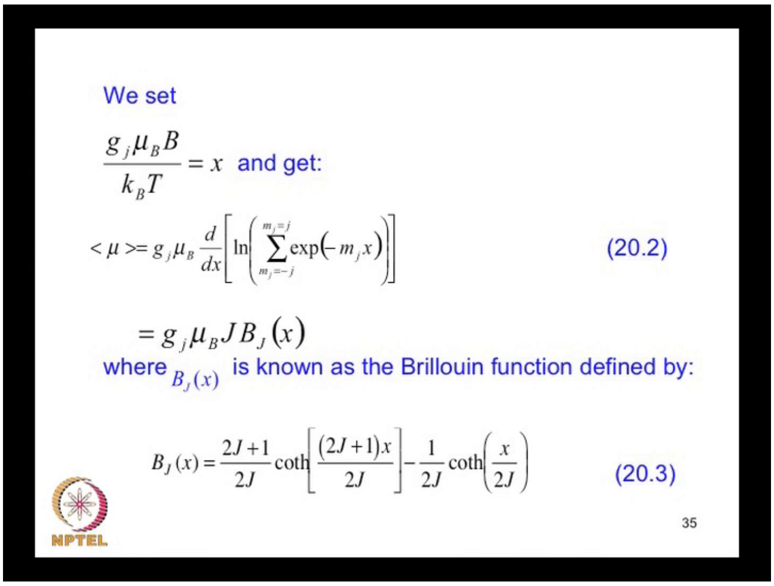


$$\langle \mu \rangle = \frac{\sum_{M_J=-J}^{J} g_J \mu_B M_J \exp\left(\frac{g_J \mu_B M_J B}{k_B T}\right)}{\sum_{-J}^{J} \exp\left(\frac{g_J \mu_B M_J B}{k_B T}\right)}$$

$$M = N\langle \mu \rangle = M_0 B_J(x)$$

So, the average moment mu these some statistical some over g j mu b b e exponential well this can be written as m j because you have mu b b dot j. So, that gives you n j exponential g j mu b m j b write by k be t by sigma over m j equal to minus j two-plus j divide by. So, that gives you the net average magnetic moment for short hand let us write g j mu b m j by k b t b as x just for short hand. So, that we can write this and doing the calculation it turns out that we arrive at g j mu b b j of x times j. So, this is the average where this b j of x is known as the brown function the explicit farm of this bro in function is as follows.

(Refer Slide Time: 31:47)



We set

$$\frac{g_j \mu_B B}{k_B T} = x$$ and get:

$$< \mu >= g_j \mu_B \frac{d}{dx}\left[\ln\left(\sum_{m_j=-j}^{m_j=j} \exp\left(-m_j x\right)\right)\right] \qquad (20.2)$$

$$= g_j \mu_B J B_J(x)$$

where $B_J(x)$ is known as the Brillouin function defined by:

$$B_J(x) = \frac{2J+1}{2J}\coth\left[\frac{(2J+1)x}{2J}\right] - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \qquad (20.3)$$

What do the below in function associated with a given j value b j f x e 2 j plus 1 by 2 j s quartet of 2 j plus x by 2 minus plus 1 by plus j quartet of x by 2, so this is minus 1. So, this is for Brillouin function, it is rather easy to make this substitution and arrived this form.

(Refer Slide Time: 32:39)

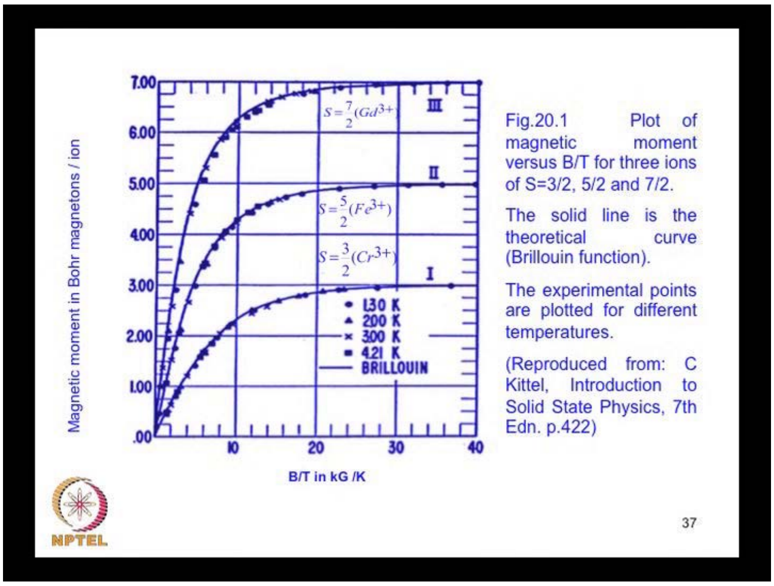


Fig.20.1 Plot of magnetic moment versus B/T for three ions of S=3/2, 5/2 and 7/2.

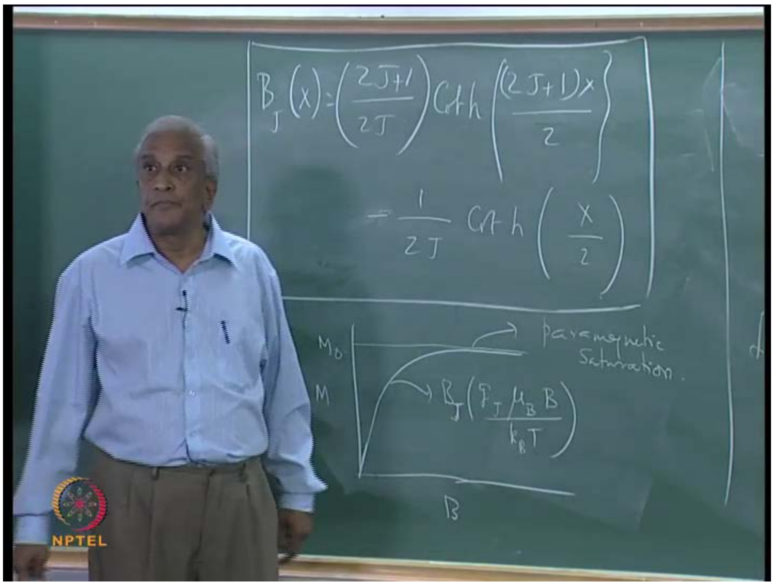
The solid line is the theoretical curve (Brillouin function).

The experimental points are plotted for different temperatures.

(Reproduced from: C Kittel, Introduction to Solid State Physics, 7th Edn. p.422)

So, this is the form of the Brillouin function which enters the expression of the magnetic moment. So, for a given j value and again d value and so on, m can be written which is n mu can be written as m naught b j of x where m naught is a saturation value the maximum value maximum possible value when all the n spins are aligned parallel to the applied nagnetic field. So, we can show the experiment graphically show the variation of the m j associated with a given j value for different choices of different magnetic moments.

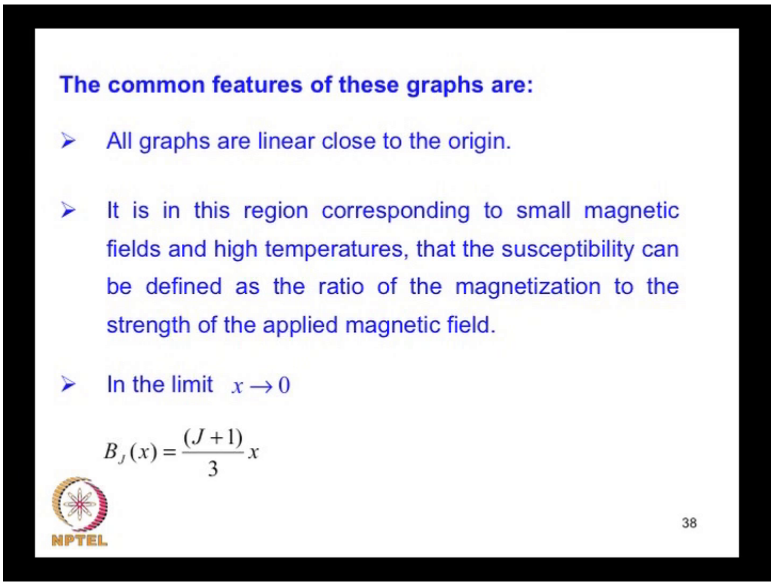
(Refer Slide Time: 33:28)



So, the overall variation as a formed like this m verses b goes like this. So, that is the n naught. So, this is the b j of x b j of x where x is g j mu bb by k b t. So, we can see several features all the v a given magnetization always approaches a saturation. So, this the phenomenon of paramagnetic saturation it approaches a constant value at high enough a field. So, once you have the field which is sufficiently strong that all the dipoles get lined up along the field then you cannot increase the magnetic moment beyond that value. So, that is why you reach maximum value and close to the origin. This is linear and then it is slowly becomes non-linear and ends to this saturation value which is determined by this over all behavior is determined by this argument brillouin function which basically involves the applied strengths and the applied field and the temperature.

So, either you can have a very high magnetic field are you can go to a very low temperature in both cases the value of x is very high. So, that will give you the saturation. So, that is the overall behavior you have. So, all the graphs can be shown to be linear close to the origin this is the region corresponding to small applied magnetic field and high temperatures this is where the susceptibility can be defined as the ratio the magnetization to the string the applied magnetic field. So, in the limit when x tends to 0 very close to the origin we can show that b j effects tends to the value j into j plus 1 by 3 j plus 1 into x by 3.

(Refer Slide Time: 36:22)



The common features of these graphs are:

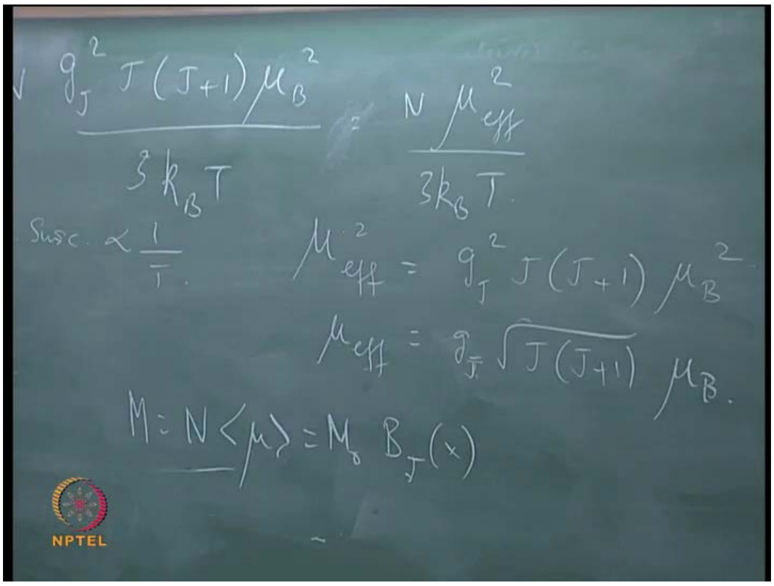
- All graphs are linear close to the origin.
- It is in this region corresponding to small magnetic fields and high temperatures, that the susceptibility can be defined as the ratio of the magnetization to the strength of the applied magnetic field.
- In the limit $x \to 0$

$$B_J(x) = \frac{(J+1)}{3}x$$

38

So, this slope up this is just j plus 1 by 3. So, the xi n the magnetic susceptibility, which is defined as the ratio the magnetization to the applied field becomes in the liner region.

(Refer Slide Time: 36:44)



$$\frac{g_J^2 J(J+1)\mu_B^2}{3k_BT} = \frac{N\mu_{eff}^2}{3k_BT}$$

Susc. $\propto \frac{1}{T}$.

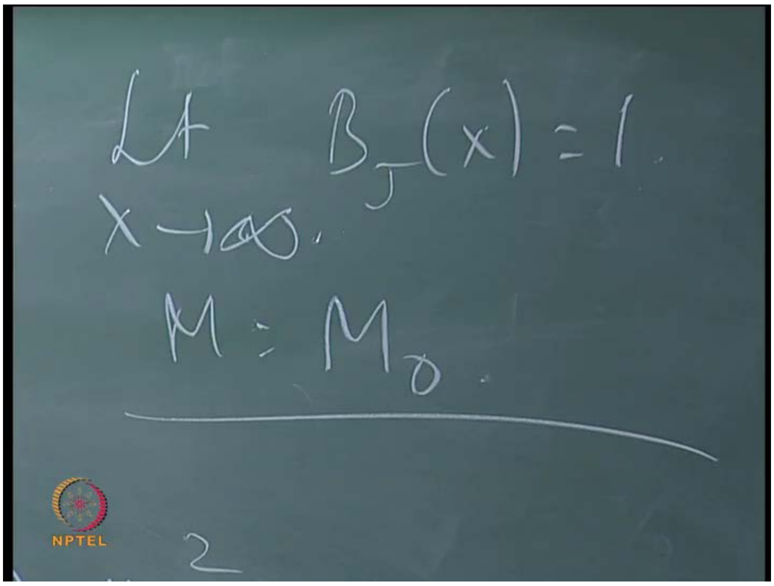
$$\mu_{eff}^2 = g_J^2 J(J+1)\mu_B^2$$

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

$$M = N\langle\mu\rangle = M_0 B_J(x)$$

So, this gives me a susceptibility paramagnetic susceptibility which is inversely proportional to the absolute temperature. So, them effective magnetic moment s given by n mu effective square by 3 k b t. So, this is g j square j into j plus 1 mu b square and that is mu effective is therefore, g j root j into j plus 1 bold magnetism. So, we can calculate the effective magnetic moment once you know the g j the g factor and the j value. So, this can be calculated as we have already seen the case of the gadolinium 3 plus ion. So, this is the in this for this orientation this susceptibility the paramagnetic susceptibility there is some there is the dialectic orientational susceptibility in the case of the polar molecules for sufficiently i fields and or low temperature.

(Refer Slide Time: 38:45)



$$\lim_{x \to \infty} B_J(x) = 1.$$

$$M = M_0.$$

2

When this spin alignment in the field is complete we can easily see that limit extending to infinity b j of x is one. So, that m will become m naught the saturation value. So, the x i at low temperatures goes as c e by t there c is a constant known as curly constant it as the value n mu effective square by 3 k b. So, if you substitute all these values the zero-point one two 4 one into p effective square the p effective is the effective are a bold magnetrons number which we calculated a 7.94 in the case of gather in 3 plus. So, we have in general a diamagnetic and paramagnetic susceptibility.

(Refer Slide Time: 40:00)

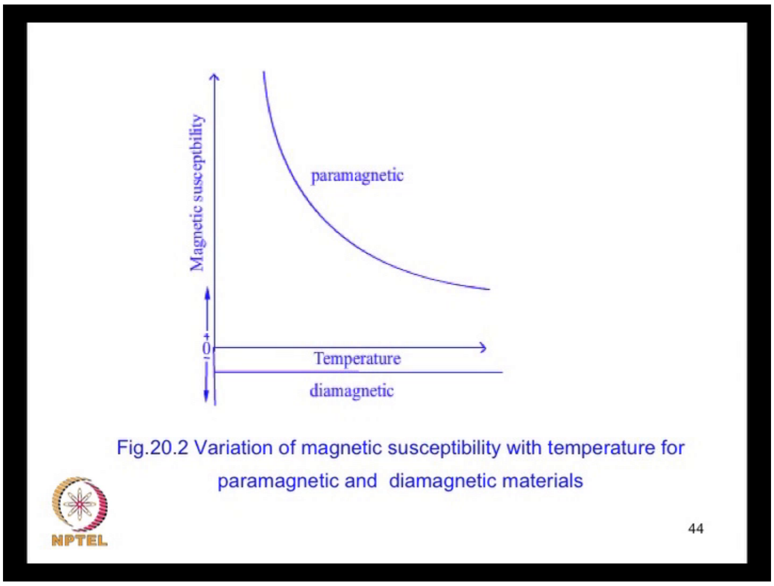
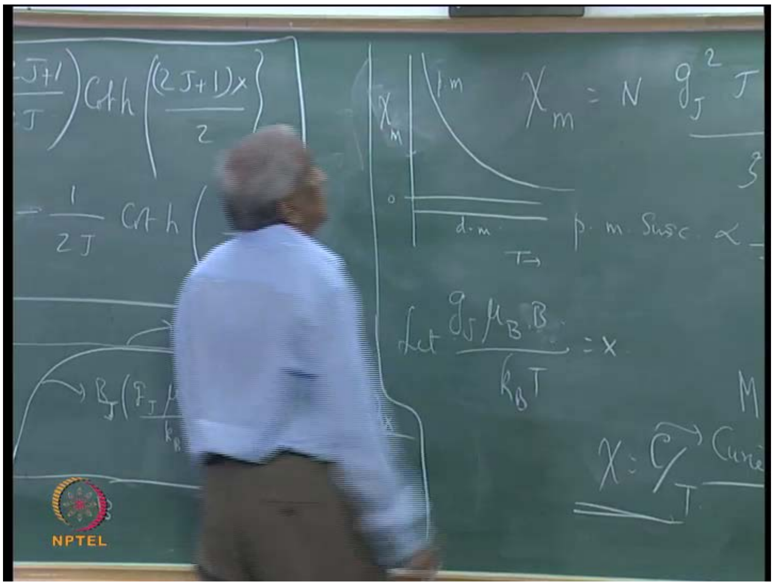


Fig.20.2 Variation of magnetic susceptibility with temperature for paramagnetic and diamagnetic materials

So, the next figure shows both these contributions the magnetic susceptibility which always includes a diamagnetic contribution and in the case of system with unpaired magnetic ions unpaired electrons. It also has a paramagnetic contribution and the paramagnetic contribution is positive and goes as susceptibility, this is zero.

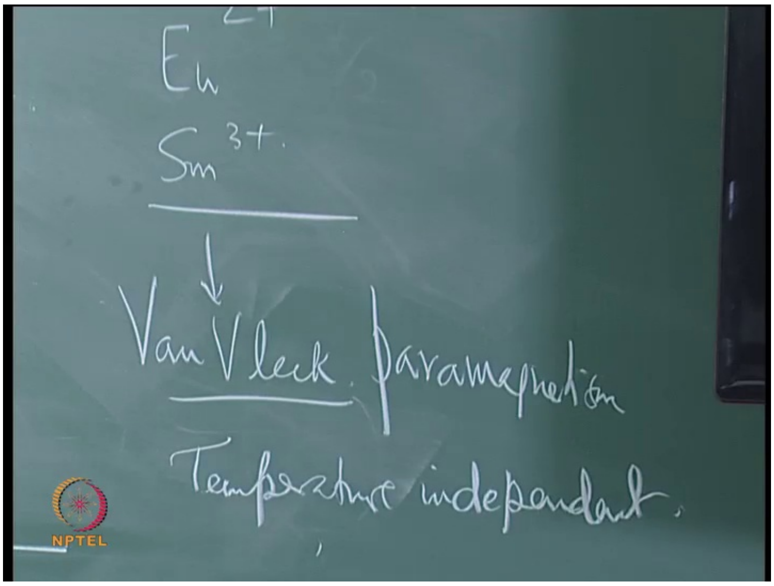
(Refer Slide Time: 40:24)



So, the paramagnetic contribution goes like this corresponding to this C by T variation, this is paramagnetic and there is a small negative diamagnetic. The total susceptibility is the some of these too of the function temperature these are the inverse 1 by t which gives you a hyperbolic defenders. For example, if you take x i inverse it is t by c. So, if you plot inverse susceptibility one by x i as a functionally the absolute temperature you will get a straight line who will slope is one by c from which you can determine the effective magnetron number.

So, this is how we compare calculate the theoretical value and compare it with experimentally measured susceptibility, whereas so this comparison the show in in a table yeah yeah this is able you can see that most of the rare the ions the comparison between the experimental and calculated values is quite satisfactory. Whereas this is not the greatest it is in iron –grouped ions, there is a fundamental reason for that, but before going to that let us consider the rare.

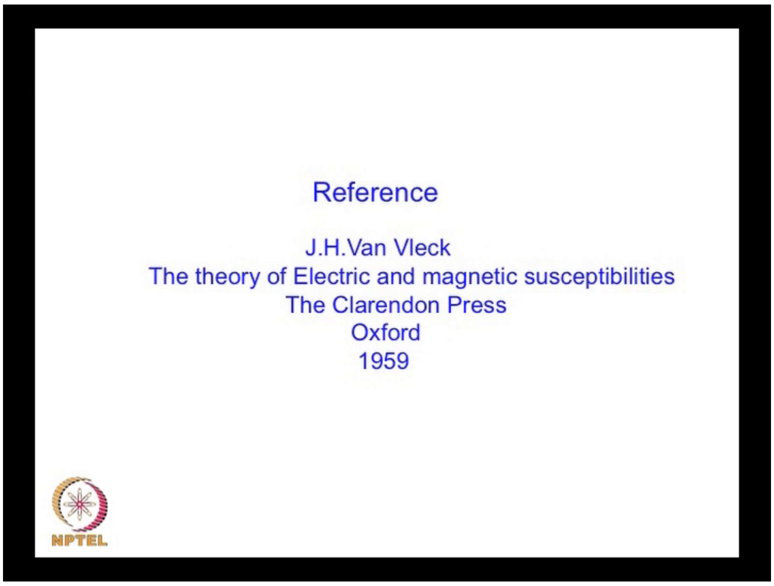
(Refer Slide Time: 42:11)



The ion in the case of europium 3 plus and samarium 3 plus, the agreement is poor as you can see from the table. This is because this was accounted for value then black. The reason for this departure, this disagreement between the experimental and calculated value at you in the case of europium and samarium is because these two ions have not only ground multiplied, but an excited multiplied close to the ground multiplied. So, you have a ground multiplied with an excited multiplied. And our assumption has been that at sufficiently no temperature, all day on are practically in the ground state and there is the excited-state is sufficiently for a way that there is no admixture of the excited and the state in to the ground state. Otherwise, the excite as a state will have a different magnetic moment if there is an ad mixed this will also makes with is ground state magnetic moment. And this is precisely what happens in the cases of europium and samarium and because of this admixture of the excited state if looking to the ground state because of the relatively small separation between the ground state and excited state.

So, this can mix with this that is what changes the magnetic moment value that contributes to what is known as Van-Vleck paramagnetism, which is temperature independent unlike the curie para magnetism which is dependent inversely on the temperature, it depends what on 1 by T. Well, we have to consider the iron -grouped ions where you know that the agreement between the experimental and calculated values in the following this procedure is rather poor. And there is a very deep fundamental reason, for this which has do with the nature of the 3 d ion in comparison to the 4 f ion, we will see this in the next lecture.

(Refer Slide Time: 44:46)



Reference

J.H.Van Vleck
The theory of Electric and magnetic susceptibilities
The Clarendon Press
Oxford
1959