Solid State Physics
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Lecture - 64
Magnetic Property of Solid (Contd.)

So, far we have discussed about the paramagnetism; this classical theory Paramagnetism.

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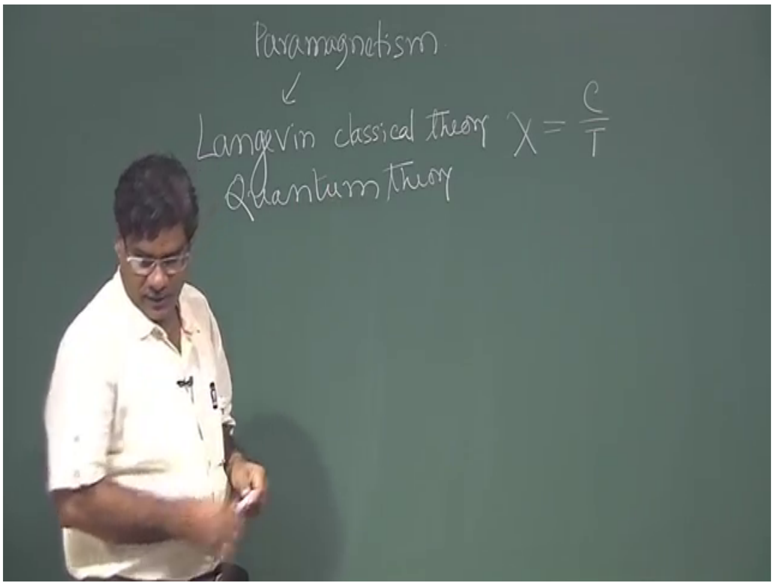

So, this Langevin classical theory, as well as this quantum theory, and we will get the same result its chi is equal to C by T. And as I mentioned that in case of quantum theory what we got this P effective; effective number of board magneto.

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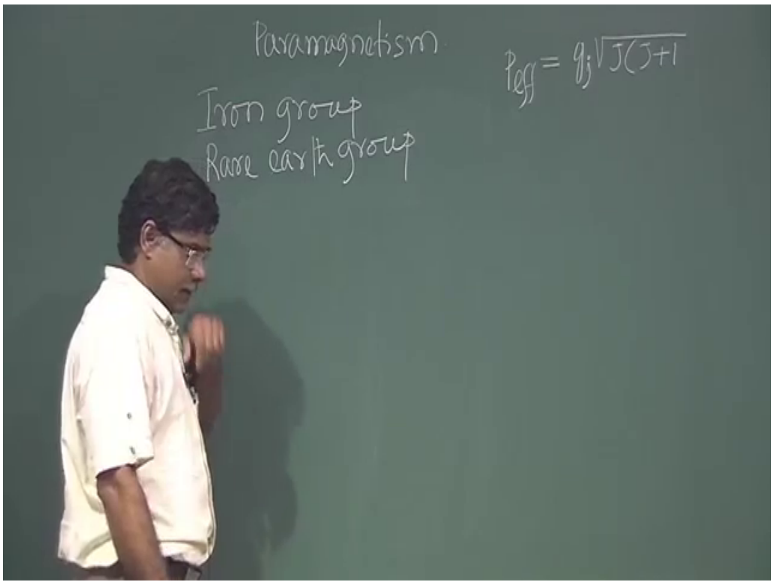

So, that P effective it was g J square root of J J plus 1. So, that is the effective number of board magnetum.

So, then if you multiply mu v that will be the magnetic moment mu attest with each attest with each of atoms or ions. So, if you if you do experiment on this solved Para magnetic solved of iron group and the rare earth group rare earth group; which one is iron group and which one is rare earth group. So, if you see the periodic table I will show you if you see the periodic table.

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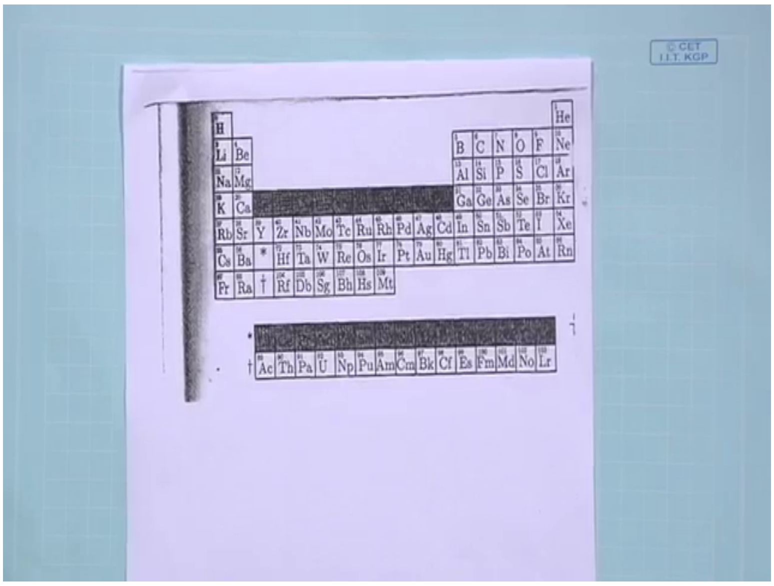

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	†	Rf	Db	Sg	Bh	Hs	Mt									

*	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
†	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

So, see in this periodic table. So, this one is you cannot see what are the elements this one is iron group transition metal.

So, here 3 d orbitals are having unfilled electrons and this one is rare earth group lanthanide group right. So, this one is having unfilled 4 f electron. So, these two group this I am this rare earth group if you take salt of rare earth group and if you take salt of this transition metal group iron group.

So, I think this figure may be you can see this scandium then titanium benadium right then chromium then this one is manganese iron cobalt nickel right then copper zinc. So, here starting for 3 d one electron to 3 d 10 electron and here starting from I think cerium is having f 1 electron cerium is having a f 1 electron and then f 1 then f 2 f 3. So, this is the r b m ok.

So, these are having the electron in f cell 4 f cell; so this unfilled cell. So, L this unfilled cell these are 3 d electronics and four f electrons responsible for dipole moment magnetic dipole moment permanent dipole moment. So, if you take salt and measures do the experiment and measure find out this P effective value? So, what is observed? So, this one is effective board magnet from number for iron for iron group irons.

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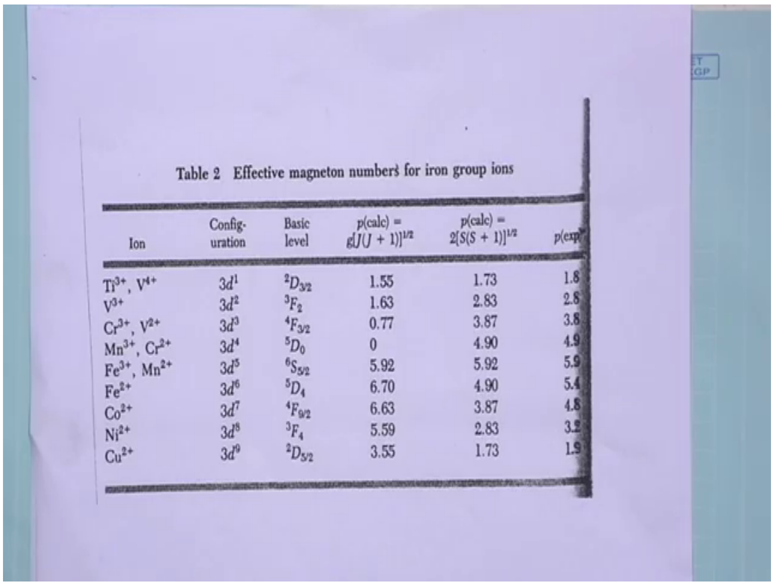

Table 2 Effective magneton numbers for iron group ions

Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{calc}) = 2[S(S+1)]^{1/2}$	p(exp
Ti^{3+}, V^{4+}	$3d^1$	$^2D_{3/2}$	1.55	1.73	1.8
V^{3+}	$3d^2$	$^3F_2$	1.63	2.83	2.8
Cr^{3+}, V^{2+}	$3d^3$	$^4F_{3/2}$	0.77	3.87	3.8
Mn^{3+}, Cr^{2+}	$3d^4$	$^5D_0$	0	4.90	4.9
Fe^{3+}, Mn^{2+}	$3d^5$	$^6S_{5/2}$	5.92	5.92	5.9
Fe^{2+}	$3d^6$	$^5D_4$	6.70	4.90	5.4
Co^{2+}	$3d^7$	$^4F_{9/2}$	6.63	3.87	4.8
Ni^{2+}	$3d^8$	$^3F_4$	5.59	2.83	3.2
Cu^{2+}	$3d^9$	$^2D_{5/2}$	3.55	1.73	1.9

So, here you see these are the just iron in terms of iron it is written. So, all are having 3 d 1, 3 d 2, 3 d 3, 3 d 4 this electrons are 3 d 9 in copper 2 plus and these are the spectroscopic term at ground state.

What is the spectroscopic term? That is written here and for these P effective if you calculate if you know the L S J value, then we can calculate P effective? So, these are the value. So, if you consider J the total angular quantum number; so then if you calculate P effective. So, this is the number and if you consider only spin angular moment, if you neglect the orbital angular momentum then you are getting P effective is this one. Now you see this experimentally this value is found this. So, here you can see the experimental values are close to this P effective, that is, 2 is S plus 1 to the power half. So, with this P effective value are close. So, here you can see this is 3.55 this is 1.73, but 1.9 this is in case of nickel ion 5.59.

This is 2.83 and this 3.2. So, it is close to this when only this when only this pin angular momentum is considered L is 0. So, in that case these P effective values are close to this. So, so from here so, just I will calculate one and show you let me take I think I can take for you this just one example if I take iron 2 plus or 3 plus this iron. In this case, let us take iron 2 plus, in this case J value no I think it will be interesting if I take iron 3 plus, if I take iron 3 plus. So, in case of iron 3 plus this electron configuration is 3 d 5.

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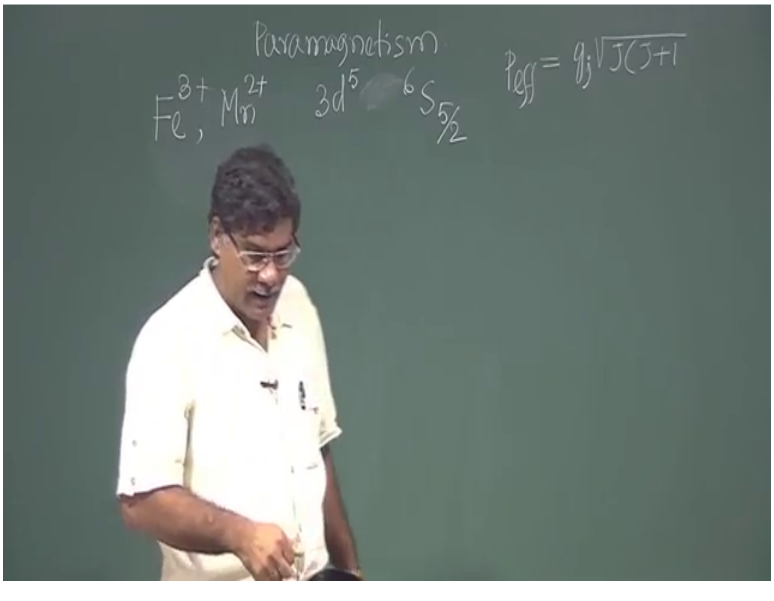

So, if I consider just iron; iron 3 plus and this manganese 2 plus. So, both are having the same number of the electrons. So, this 3 d pi and 4 S 2 that is has done for this ionized it.

So, this will not be there and so, actually for iron this is d 6 4 S 2. So, this 2 electron and this 1 electron from d it is. So, that is 3 plus. So, (Refer Time: 10:19) these 3 d 5 manganese 3 d 5 4 days to. So, these 2 plus. So, these 2 electrons has ionized. So, in this case what is basic spectroscopic term? It is basic spectroscopic term it is 6 S 5 by 2. So, I will tell you the meaning, and then P calculated value is 5.92 and in this case also it is 5.92. So, then it will not be interesting in both cases it is same, because L will be 0 in this case. So, then let me take this iron 2 plus, let me take iron 2 plus iron 2 plus.

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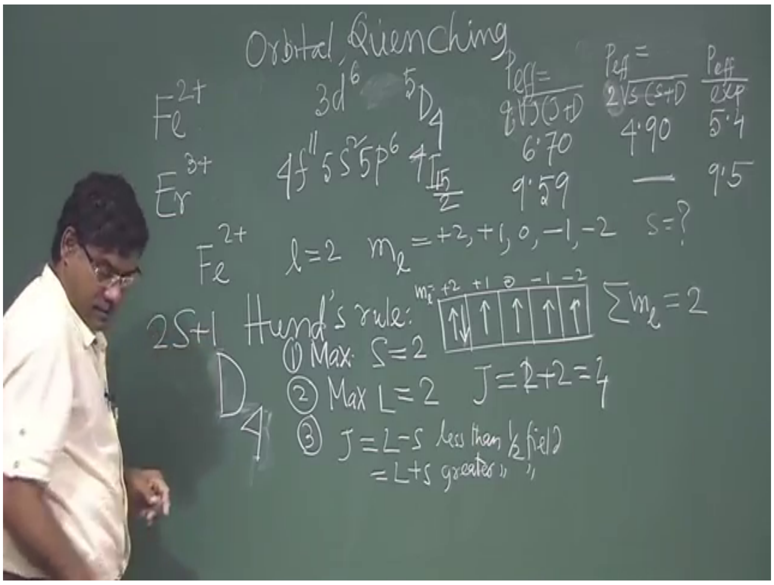

So, in this case 3 d 3 d 6 3 d 6 electron; so only 4 S 2 electrons ionized; so then basic this 5 d 4, 5 d 4 this will be 5 d 4 spectroscopic term will be 5 d 4 5 d 4 right 5 d 4 and this value will getting 6.7 calculate value, using this formula we are getting 6.70 and if you calc consider this S P effective I think I will write P effective equal to g J square root of J a plus 1. So, this value I am getting 6.70 and P effective if I calculate g S that is basically two g S 2 square root of S; S plus 1.

So, this value is coming 4.90 and experimental is found that it is it is 5.4 experimentally P experiment P effective experiment, that is 5.4 yes 5.4 right. So, these the data. So, this from Petal book, that I am showing from Petal book. So, I will calculate one. So, you should calculate the others and check it and then in case of rare earth solved.

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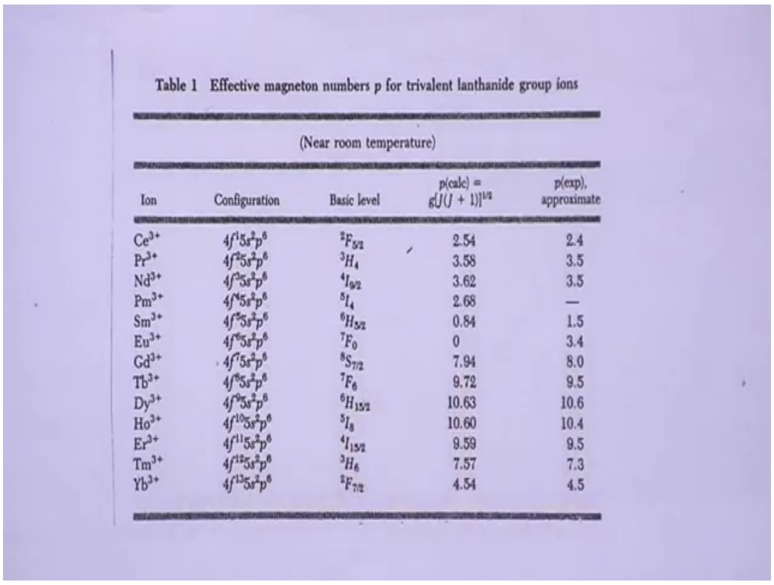

Table 1 Effective magneton numbers p for trivalent lanthanide group ions

(Near room temperature)

Ion	Configuration	Basic level	p(calc) = $g[J(J+1)]^{1/2}$	p(exp), approximate
Ce^{3+}	$4f^1 5s^2 p^6$	$^2F_{5/2}$	2.54	2.4
Pr^{3+}	$4f^2 5s^2 p^6$	$^3H_4$	3.58	3.5
Nd^{3+}	$4f^3 5s^2 p^6$	$^4I_{9/2}$	3.62	3.5
Pm^{3+}	$4f^4 5s^2 p^6$	$^5I_4$	2.68	—
Sm^{3+}	$4f^5 5s^2 p^6$	$^6H_{5/2}$	0.84	1.5
Eu^{3+}	$4f^6 5s^2 p^6$	$^7F_0$	0	3.4
Gd^{3+}	$4f^7 5s^2 p^6$	$^8S_{7/2}$	7.94	8.0
Tb^{3+}	$4f^8 5s^2 p^6$	$^7F_6$	9.72	9.5
Dy^{3+}	$4f^9 5s^2 p^6$	$^6H_{15/2}$	10.63	10.6
Ho^{3+}	$4f^{10} 5s^2 p^6$	$^5I_8$	10.60	10.4
Er^{3+}	$4f^{11} 5s^2 p^6$	$^4I_{15/2}$	9.59	9.5
Tm^{3+}	$4f^{12} 5s^2 p^6$	$^3H_6$	7.57	7.3
Yb^{3+}	$4f^{13} 5s^2 p^6$	$^2F_{7/2}$	4.54	4.5

You can see in case of rare earth solved, you can see this; this P calculated that is g J square root of J J plus 1. So, what are values? We have calculated value is there. So, experimentally what about value we got we can all are matching well all are matching well. So, like say gadolinium. So, this one see it is calculated 7.94 and this experimentally 8.0; so good agreement and erbium year 3 plus erbium. So, years you can see this calculated value 9.59 and experimental 9.5; so will calculate this one erbium.

E r erbium 3 plus erbium so, it is electronic configuration is 4 F 11 and I have 5 S 2, 5 P 6 and then we spectroscopic term this spectroscopic term is 4 I 15 by 2 and this calculated value 9.59, this 9.59, and this is 9.5. So, this is not calculated because all value are will matching with this with this one g J square root of J, J plus 1. Now, question is that why there is a difference in calculated value and effective experimental value of P effective. In case of iron group ions whereas, where rare earth iron the matching with this is quite good. So, the reason what is the reason behind it. So, that we want to find out. So, basically in this case iron group.

This a L is not contributing, only a S is contributing in this case J equal to S L equal to 0 L is not contributing, but in rare earth case it is L is contributing. Orbital motion is contributing to the magnetic moment. So, what is the reason? So, that we want to find out. So, that is called what about the reason that is called quenching orbital quenching it is called orbital quenching. Orbital is not responding to the magnetic field as if it is in active. So, it is not rotating it is as if it is fixed it is inactive it is not rotating with magnetic field. When we are applying magnetic field, orbital angular momentum is not following the magnetic field it is inactive it is fixed it is not responding to the magnetic field. So, that is called orbital quenching. So, this orbital quenching is responsible for this difference rare earth and iron group. So, we discuss later on why in this case orbital quenching is happening in iron group whereas, this rare earth group it is orbital quenching is not happening.

So, that we will discuss later, but let me should I calculate this. So, this how this 3 d 6, 4 S 2 for iron atom so, that he can hopefully can write the electronic configuration and from there you can get this one in case of erbium ion also you can find out this electronic configuration. Now, atoms have this electronic configuration, in case of say iron I have so in case of iron 2 plus iron, because 4 S 2 these two electrons have done. So, that is 4 S 2. So, is close sub cell so its L is J is 0?

So, you do not bother. So, whatever here unfilled one 3 d 6 electron? So, it has so if you find out this total L and this total S for this. So, you will have few number of L a possible few number of S are possible and then few number of J will possible for us for the J will be possible. So, these are the different possible steps of this irons or atoms right; it can stay in different states having different energy, because J values are different energy will be different right. Now so out of these different states which one is down state which one is down state for any imperial electric whatever the atoms electric configuration you are seeing.

So, for each for each atom if you calculate this L S J value so, you will have a set of number of these values and; that means, there are different states different energy levels and that atom can stay in any of them, but which one is the lowest energy state that is called ground state. So, that we have to find out. So, that is the spectroscopic term this one. So, this represents the down state of the atom right; how to get that down state of hat atom. So, that Hums rule; Hums rule tells that this let us do it and so this d 6 electron d means L equal to 2. So, it is it has m L it has m L equal to plus 2 plus 1 0 minus 1 minus 2 right. And then corresponding S here S what will be the S value? So, that one has to find out.

So, now Hums rule is telling, Hums rule this first rule is telling that you arrange. So, it has so, how many. So, here for L equal to two I have 5 ml value means 5 states right 5 states. So, you know this called d x y, d y z, d z x, d z square, d x square, minus x square probably get. So, so this is a 5 sub cells, although they are re generate. So, now electron be spin you put for so, I have 6 electron. So, you put spin of put this electron in such a way that it spin will be maximum. So, how to maximize the spin see if I put all spin of all spin off that they I can put, because without violating the Pauli Exclusion Principle. So, that I have put 5 and then one more I have to put, where I have to put anywhere I can put.

So, let us say here I will put. So, where to put this one then the second law tells. So, this first law is maximize first maximize S you put in such a way that this S will be maximum and then second law is telling, this then after keeping this S maximum. So, keep S maximum I can put this one here, here, here, here, here, here, here, right anywhere I can put, but second law is restricting that one. So, this m L value m L value for this case say plus 2 this is plus 1 this is 0 this is minus 1 this is minus 2 rights. So, this one where to put so this tell is second law then you should maximize l.

So, if I put here then I can put what is the l; L value for this combination. So, there is a summation of m L basically. So, before putting this summation of this 1 is 0 right; 0. Now this one if I put here. So, m L will be 0; if I put here m L will be 2 plus 2 right. So, then this will be the maximum this will be the maximum if I put it here. So, this m L to get the m L equal to 2.

L has to be 2 L has to be 2. So, in this case maximum S 1, 2, 3, 4. So, 4 into half so, it will be 2 L in this case it will be 2. So, summation of m L is to so to get if L is not close. So, m L value two will not get. So, this and third one is telling that if it is if less than half filled, then J they will L minus S, if it is greater than half filled say L will be J will be L plus S right. So, less than half filled and greater than half filled. So, it is greater than half filled, because half filled will be 5. So, it is 6. So, J will be L plus S. So, J will be it is telling J will be L plus S means 2 plus 2 equal to 4. So, L equal to 2 S equal to 2 and J equal to 4, that is, the L S J value is corresponding this corresponds to the ground state of this atom right. So this is the spectroscopic term how it is right how it is written. So, 2 S plus 1 multiplicity this is called multiplicity, then this L value L and then J value so; that means, here.

So, from here our L equal to 2 means D right. So, D we write L capital D and our J value is 4. So, J value is 4 and then S value 2; 2 means 5 right 2 into 2 plus 1.

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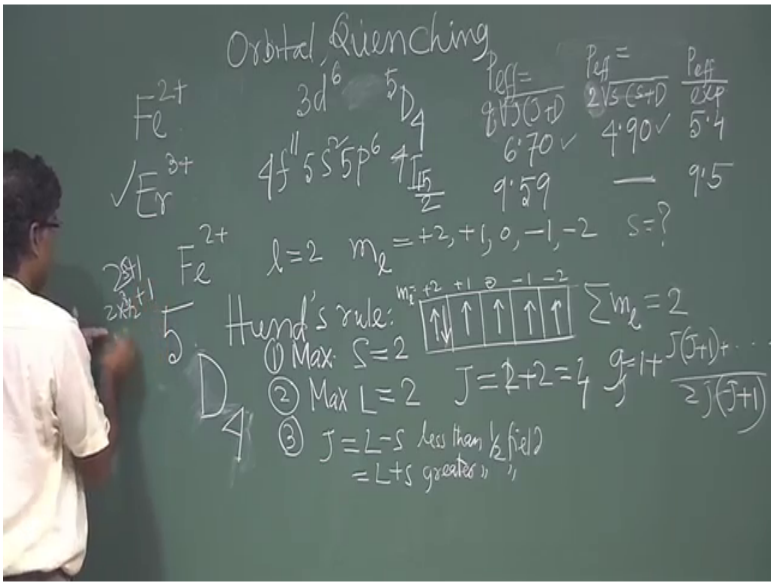

So, it will be 5. So, whatever; given in the book, that is I have taken in Peter book. So, from there you can see so this exactly I got same one. So, using Hums rule one can get this ground state of this of the atom or of the ion. So, now if you know the spectroscopic term, find out the spectrum for ground state. So, from there itself you will get L S J or opposite f you calculate L S J for ground state and then you can find out spectroscopic term. So, now, if you so if what is this you see this P effective for J; J is g J one has to calculate, what is g J? So, the J 1 plus J plus 1 right plus S plus 1 etcetera you know this two J, J pus 1 right J plus 1. So, you calculate it you calculate it if we calculate you will see these you will I am not I will not calculate it will take time.

So, but just you calculate and check it and then just check S; S equal to 2 here J equal to you take J equal to take 4 calculate this and then (Refer Time: 30:14) value and for this erbium this one just the way I have done. So, same way you should do this one. So, this f 11 means it will follow this J equal to L plus S and so for f means it will be 7 14 electrons it can take. So, it will be 7. So, you put 7. So, m L will be 0 and then you have additional 4. So, out of 4 so that unpaired electron spin of electron 3 will be there. So, 3 means half plus half plus half 3 by 2. So, S will be 3 by 2, then 2 S plus 1 right multiplicity 2 into S half S 3 by 2 plus 1. So, this 3 plus 1 4 so, exactly it is 4. So, you just calculate check it practices for other has shown you list.

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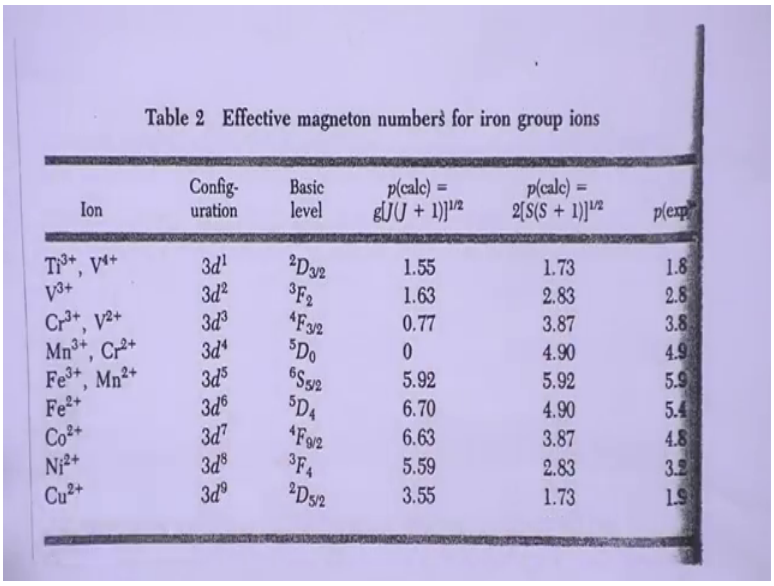

Table 2 Effective magneton numbers for iron group ions

Ion	Configuration	Basic level	p(calc) = $g[J(J+1)]^{1/2}$	p(calc) = $2[S(S+1)]^{1/2}$	p(exp
Ti^{3+}, V^{4+}	$3d^1$	$^2D_{3/2}$	1.55	1.73	1.8
V^{3+}	$3d^2$	$^3F_2$	1.63	2.83	2.8
Cr^{3+}, V^{2+}	$3d^3$	$^4F_{3/2}$	0.77	3.87	3.8
Mn^{3+}, Cr^{2+}	$3d^4$	$^5D_0$	0	4.90	4.9
Fe^{3+}, Mn^{2+}	$3d^5$	$^6S_{5/2}$	5.92	5.92	5.9
Fe^{2+}	$3d^6$	$^5D_4$	6.70	4.90	5.4
Co^{2+}	$3d^7$	$^4F_{9/2}$	6.63	3.87	4.8
Ni^{2+}	$3d^8$	$^3F_4$	5.59	2.83	3.2
Cu^{2+}	$3d^9$	$^2D_{5/2}$	3.55	1.73	1.9

So, for all you calculate this and another one is this term for iron group. So, just whatever this result is given just check it and it will be good practice for you. So, I think this is from this what we conclude that iron group solved of iron group it is paramagnetic, but from there whatever this P effective value we are getting. So, that is telling that L is quenched; L is not contributing in case rare earth it is not L is contributing with S and thus P J is the effective angular momentum and corresponding P effective value we are getting which agree with the explain to day that. So, now, what is the reason behind it why this orbital is quenched, ok.

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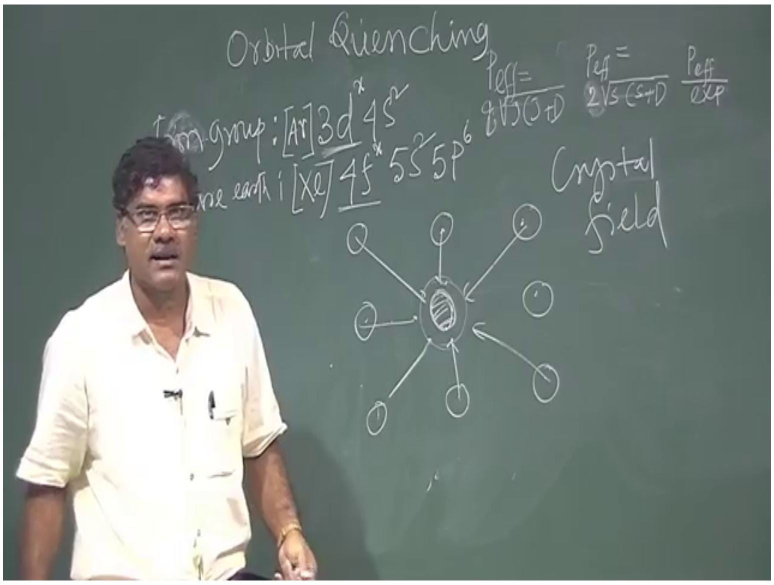

So, if you see the for iron group. So, electronic configuration is 3d.

So, I think in here you have what is the combination I think Argon, I think argon that one is argon, then 3d 4 S 2; 3d 4 S 2 right and for rare earth; I think I should right iron group and for rare earth what we got I think this is xenon yes and then you are getting I am writing x x number of electrons and then 5 S 2 of 5 P 6. So, if you look at this two. So, 3d as if this is the upper most cell whereas, these 4 f are quite inside, because outside this 5 P are there right 5 P 6 electrons are there. So, this cells is protected by this 5 P cell right. So, 5 P cell is electrons are there electrons are there and inside this 4 f right. In case of iron group 3d or outer most cell 3d or outer most cell. So, if now whatever so far whatever we have done to parametric for diametric just we have taken isolated like isolated atom no.

Because, we have not we have considered that there will not be interaction among the ions right among the dipole moment of the ions or atoms right. So, that is looks isolated parametric gas kind of things. But, that was not the realistic assumption, because this atoms iron and rare earth whatever this solid we are taking. So, this ions or atoms are in a solid right are in a solid ok.

So, if I consider this one this say iron ion or rare earth ions or whatever. So, here this there is a there will be influence of other resonance of this other neighbors you know other neighbors. So, it is basically the electrons electronic structure of these they have they are same also there is no problem. So, there will be it will generate this neighbors will generate some that is electric field when atoms are in a crystal. So, neighbors of this one will generate some electric field and that this. So, this is so this is under electric field. So, there will be effect of this electric fill on this ions right. So, this was not free it is not free. So, means it has no effect with the there is no effect on this from the from the neighbors it is not the case there is effect. So, that is called crystal field that is called crystal field.

Now, due to this crystal field, why this crystal form where this coming this and it is electro static nature, so this due to this crystal field this type of some influence from the neighbor on these. So, this S is electronic structure effective these cells are effective right which you have contributing the magnetic moments. So, they are effective. So, now, in this case since it is outer outside it is outside right.

So, this effect this will be affected more these this cell will be affected more than these, because these f cell is contributing to the magnetic moment f cell, but f cell is there and outside that P shell is there you know P cell is there. So, from this field it is in some extend it is protected. So, it not reaching to this 4 f shell in f shell and not getting this stuff right. So, that is the reason, why in this case that whatever is whatever calculation we have done considering the isolated ions.

So, as if this rare earth one this is looks like isolated, because it is not having any effect from the surrounding where as this iron group it is having the effect from the surrounding. So, due to this crystal field it is affecting the d shell. So, what are happens what happens two may happen.

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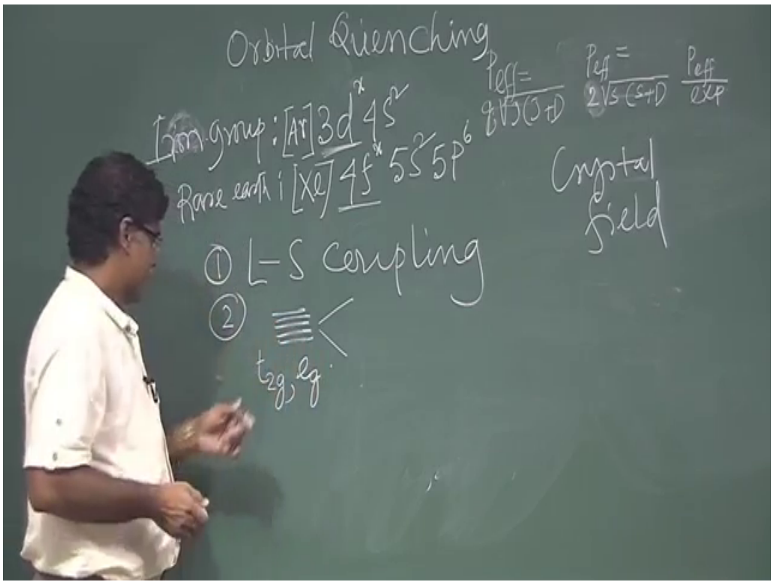

Two things may happen one is L S coupling, L S coupling will break right and second is this energy levels 5 m L right; if L equal to 2 5 m L this energy level they are degenerate and due to this crystal field this degeneracy is removed. So, generally it tells this here 5 are there in case of d shell. So, it is retain t 2 g and e g in this two group; so t 2 g and e g how it is defined. So, this distribution of this angular distribution of the charge you know angular charge is distribution of the electronics charge in the shell d shell.

So, as I told that d x x, d x y, d y z, d z square. So, these indicates the so I will show you I will show you see in case of S shell this is spherical symmetry of the charge.

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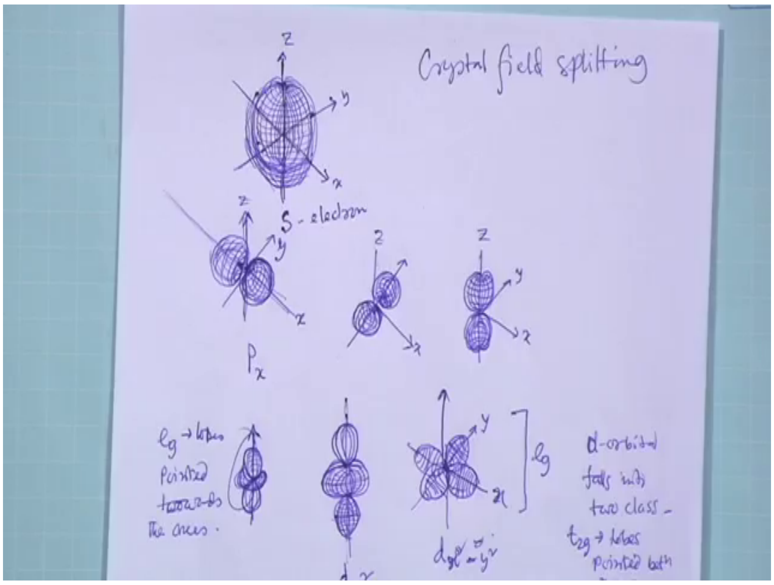

So, I have done. So, here it will take time to draw. So, that is why. So, this S shell for P x, P y, P z, P x along this loops along the x direction, this one along the y direction, this one along the z direction, right.

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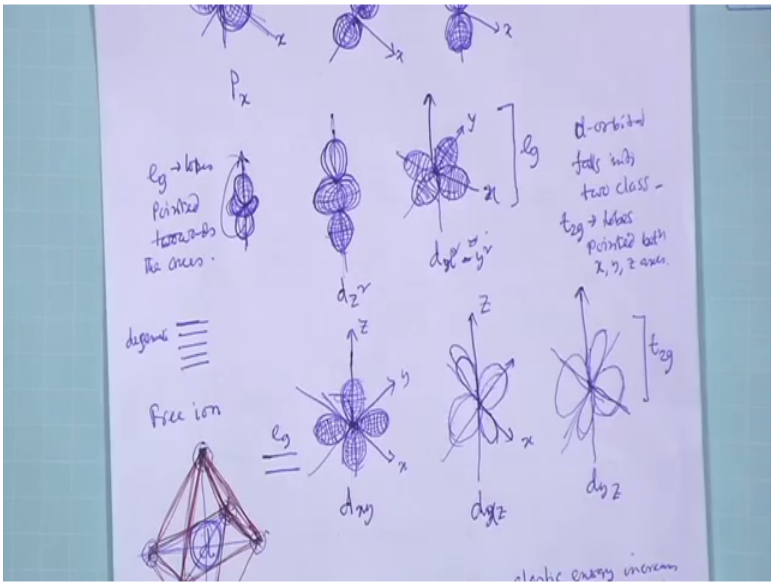

Similarly, in case of d there are 5, in case of d there are 5 yes there are 5. So, this is d z square. So, it is along the z axis along the z axis and this is d x square v minus y square. So, this is this along the x axis and along the y axis this low lops are along y direction d x y mean it is between x and y axis. So, it is not along the x axis or the y axis, but it S in this plane and it is along the between this two axis. So, in this case also five also same this d x z, d y z.

So, this the t 2 J that is defined that where these electrons that charges distribution angular distribution is not pointed towards the axis. And other one is easy e g where this electronics are distribution charge distribution angular distribution is pointed towards the axis. So, that is why it is e g. So, two groups are there. So, or so without applying medical if you apply will be there they are split it that you know gamins splitting right without applying magnetic field due to crystal field this two are separated this two types are separated.

So, here I think it is which one is higher that I have to see, ok.

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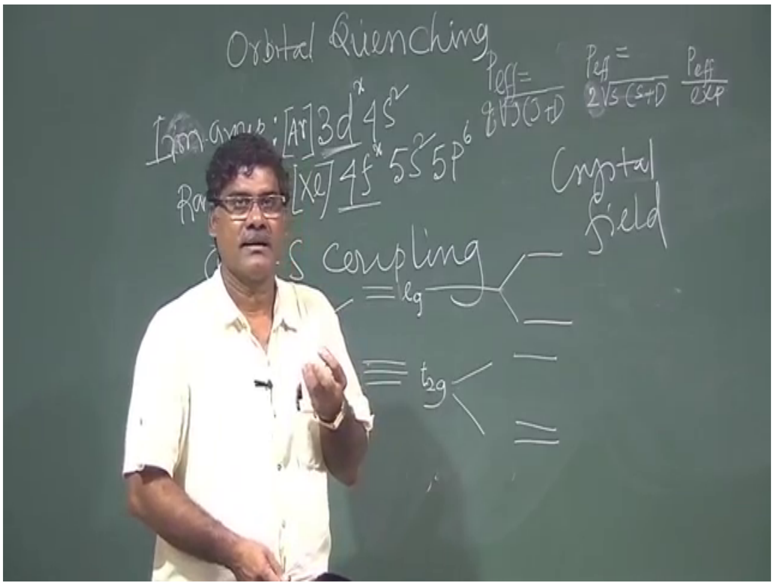

So, that is t 2 g is higher and no e g is higher. So, this will be e g and this will be t 2 g. So, this nomenclature now again what happens this sometimes what happen. So, they take types of bonding you know these tetrahedral and octahedral most of the case it take octahedral. So, which one is octahedral which one is tetrahedral that I can probably I can tell you, so I have come here. So this is the octahedral you know. So, means these ions d shell that ions I do not no ions you see here and then it is surrounded by say oxygen.

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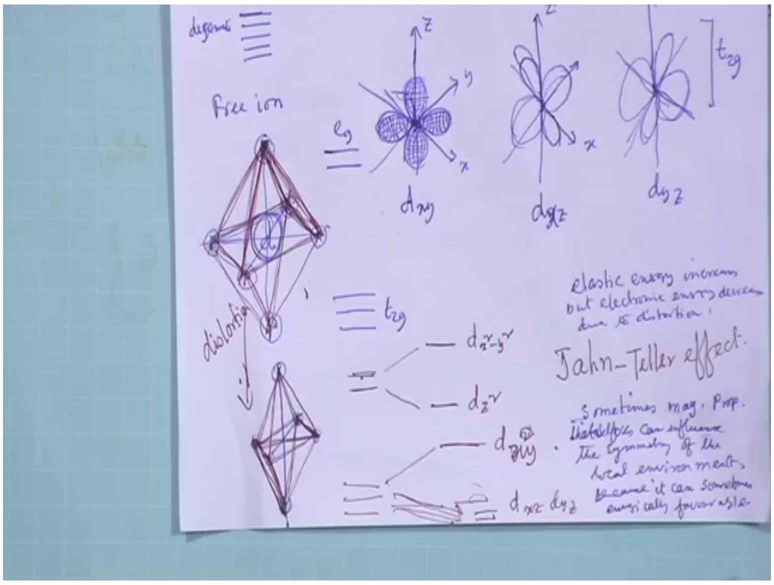

elastic energy increases but electronic energy decreases due to distortion.

Jahn-Teller effect.

Sometimes mag. Prop. can influence the symmetry of the local environments because it can sometimes energically favourable.

So, this f e 2 o 3 or f e 3 o 4 so this type of in that case, so tetrahedral and octahedral two kinds are there here it is called octahedral, because it has you can see (Refer Time: 44:58) and tetra heddle it looks like this.

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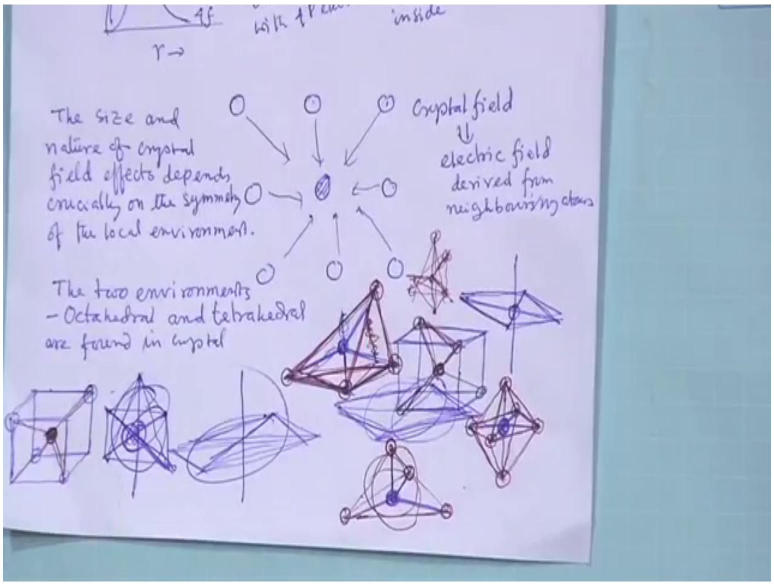

The size and nature of crystal field effects depends crucially on the symmetry of the local environment.

The two environments - Octahedral and tetrahedral are found in crystal

I have drawn here it looks like this tetra heddle as if you can consider this cubic; cubic shell. So, in middle that your ion and this surrounding this may be oxygen or some other attest with this one some bonding. So, this is the octahedral. So, this if I draw it is a say this one. So, this three I think so this is in middle and this three are the say oxygen. So, in this case, it will have four phase set it will have four phase set tetra means 4 octal means 8. So, that is why it is called tetrahedral.

So, this type so in which embedment your ions is there. So, whether it is in tetrahedral or it is octahedral. So, that is the effect of surrounding on the ion. So, that change is the change is some time affects the orbital which is associated with the magnetic moment. So, this is the reason of crystal field and due to crystal field there is a splitting there is a degeneracy is removed and this one what happens sometimes this what about tetrahedral I showed you tetrahedral so this tetrahedral sometimes it is distorted you know automatically distorted where this is distorted may be elastic energy increased, but its electronic energy decrease, so that this total energy of the system will be lower.

So, to minimize the energy of the system sometimes happen, it happen that system distorted itself and because of this distortion then again degeneracy again, further it may remove it may be move and it happens that in this case is this removed. And in this case also degeneracy is removed here one and here this. So, only these two are degenerated. So, they are separated. So, which one so this one I think d I have written d x square minus (Refer Time: 46:43) and the d z square. So, whatever things is important here just I want to say that this in crystal, this ions which is contributing the magnetic moment. So, that is affected by the environment b the neighbors.

So, by the crystal it is different situation is different than the isolated ions. So, because of whatever moment I have calculated by whatever calculated also isolated ion. So, result is different, because of this crystal field and that is the reason of quenching orbital quenching.

So, I will stop here.

Thank you.