Neutron Scattering for Condensed Matter Studies
Professor Saibal Basu
Department of Physics
Homi Bhabha National Institute
Week 5 Lecture 14A

Keywords, Diamagnet, Paramagnet, Ferromagnet, Antiferromagnet, Curie temperature, Ordered magnetic state, Hund's law, Transition elements, Rare earth elements

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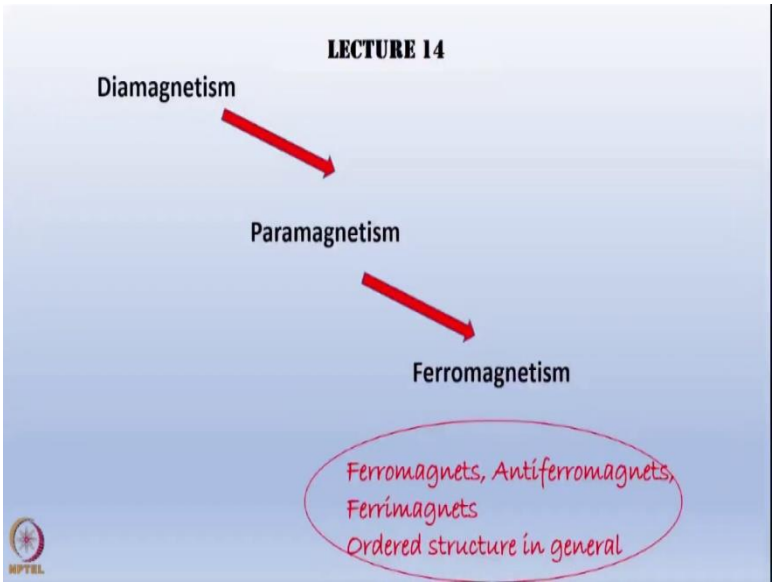

In this module, we will discuss magnetism in solids. This is a part of the module in which I will be teaching you how to do magnetic neutron diffraction but before that we need to understand various kinds of magnetism that you find in solids and a brief introduction will be necessary before we get into neutron diffraction. We know that primarily there are three kinds of magnetisms in solids: diamagnetism, paramagnetism and ferromagnetism.

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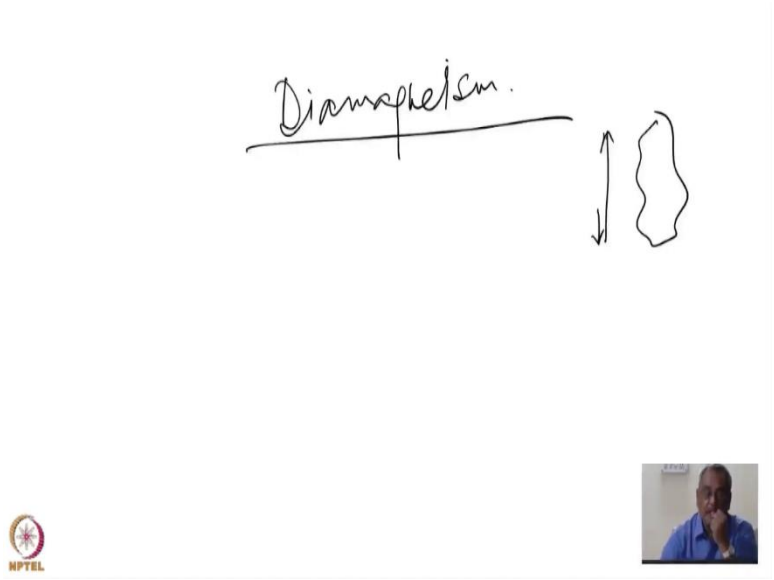

I will start with Diamagnetism. Diamagnetism is an inherent property of all materials, as diamagnetism comes from the fact that every electron orbit is a magnet. This is inherent in every material and this opposes any applied magnetic field. That means whenever I apply a magnetic field on any material, diamagnetism will try to opposite it. So, every material is inherently diamagnetic. I will give you very briefly a classical theory of diamagnetism which comes from Lenz's law.

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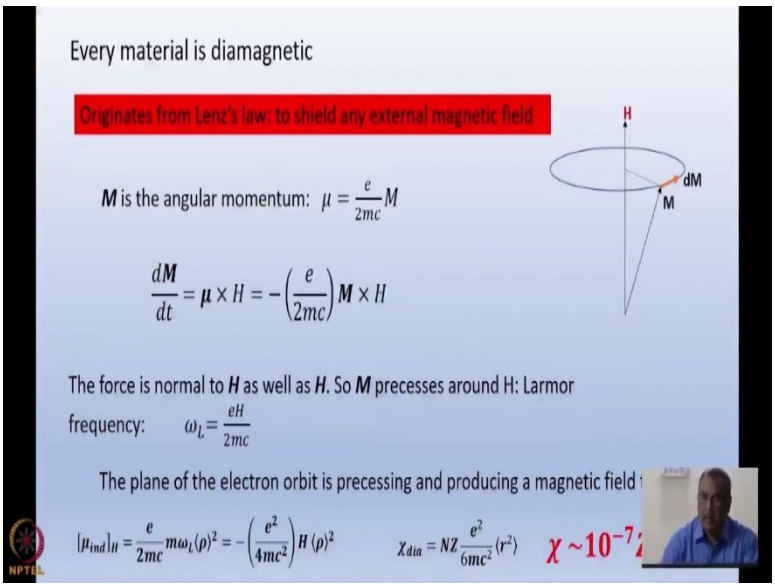

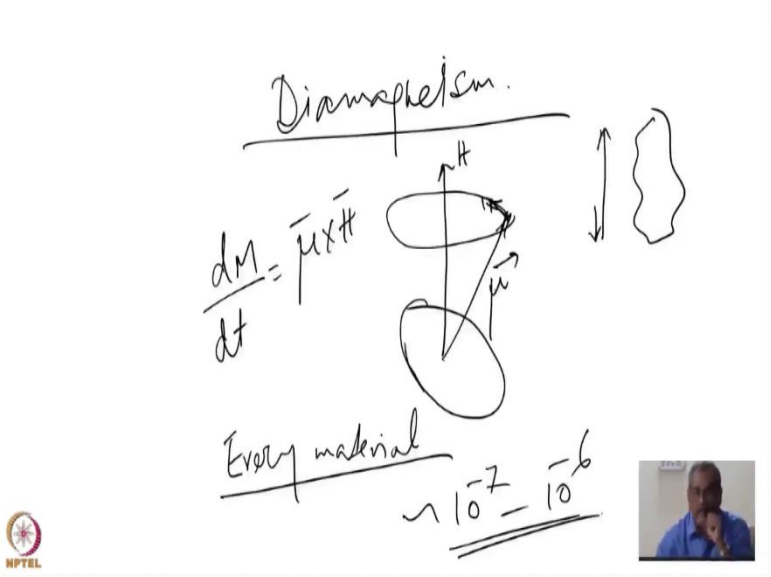

Every electron with angular momentum *M* has a magnetic moment $\mu = \frac{e}{2mc}M$. In the picture, *H* is the magnetic field that you applied on a material and *'M'* is the angular momentum for an electron in an orbit in the shown directions. Then the electron will tend to precess around the magnetic field and this precision is given by Larmor frequency, the rate of change of magnetic moment. You can see that it is coming as a cross product of the μ of the electron and the applied magnetic field *H*. Hence, for this system

$$\frac{dM}{dt} = \mu \times H$$

a vector cross product. Hence, it is perpendicular to both *H* and the magnetic moment which is basically due to rotation of electron in an orbit. Now I can add up this magnetic fields orbit by orbit and calculate the diamagnetism in the material. The Larmor frequency is, $\omega_L = \frac{eH}{2mc}$.

The electron orbit is precising and producing a magnetic field to oppose this applied field *H* and then the μ_{ind} given by $\frac{e}{2mc}m\omega_L\langle\rho\rangle^2$, it is a classical Lenz's law, here $\langle\rho\rangle^2$ the average radius of an orbit. Taking average radius of all the orbits and this comes typically as $\langle r\rangle^2$NZ, *N* is the number of electrons in the orbits and *Z* is the atomic number of the material. With this, diamagnetic susceptibility comes out to be

$$\chi_{dia} = \frac{e^2}{6mc^2}NZ\langle r\rangle^2$$

It has got a low value about 10^{-7}Z which is around 10^{-6} if I multiply it with the value of *Z*. It means every material every material has a part in magnetism which is of the order 10^{-7}- 10^{-6}

depending on the number of electrons in its atomic orbits which opposes a magnetic field. But over and above I also have atoms which have got unfilled electrons in their shells.

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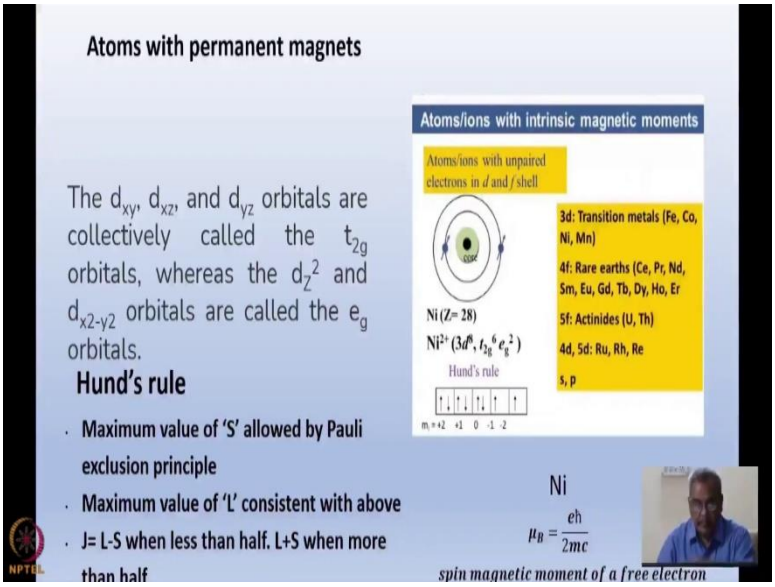

Going one step ahead, there are 3*d* transition metals such as Fe, Co, Ni which have unpaired electrons in *d* shells. Ni^{2+} is $3d^8$ that means in the third orbit in the *d* shell, there are 8 electrons. Before I try to evaluate the magnetic moment of this, I can say that if there are unfilled shells then there will be magnetic moment. If all the shells are filled then you know every sub orbit, as I shown here, they will have 2 electrons each and overall, the magnetic moment will be 0. We need Hund's rule for the filling of electrons in an orbit. Hund's rule says, maximum value of *S* allowed by Pauli exclusion principle, maximum value of *L* consistent with the maximum value of S allowed by Pauli exclusion and if the shell is less than half filled then J = L-S and J = L+S when more than half filled.

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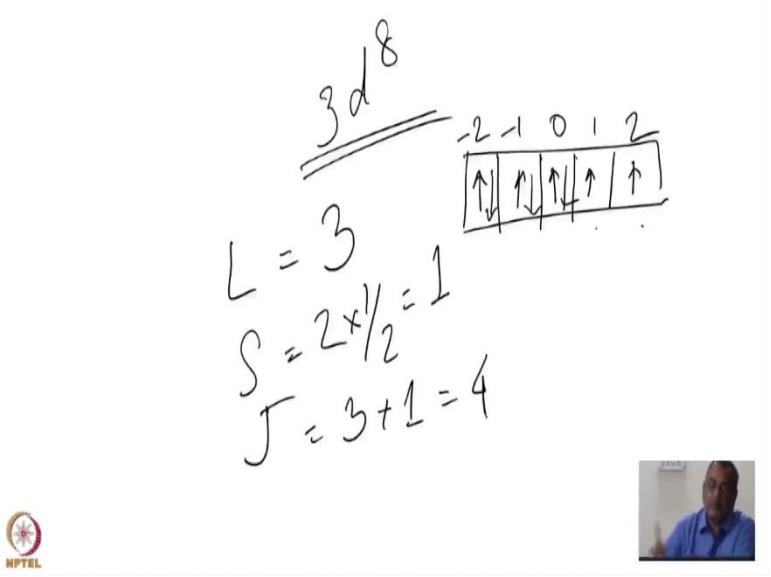

I will do it for Ni -3d^8. *d*-shell can accommodate maximum 10 electrons. Let me just draw the shells here with 2, 1, 0, -1, -2 l_z values. I have got 8 electrons. First let me put all of them in one in each orbital because this is the best possible configuration coulombically. But now I have to put three more and I have to maximize my L value. So, then I put three more in these three shells with 2, 1, 0 l_z values. That means now *L* value will be 2+1 = 3, *S* value is 2 × ½ = 1. And, as the shell is more than half filled so *J* value will be 3 + 1 = 4.

We have drawn in the same way. Then due to splitting of d orbit by crystal field it split into t_{2g} and e_g orbitals, and here t_{2g} has got 6 electrons and e_g has got 2 electrons. This gives me the ground state of nickel with two unfilled electrons.

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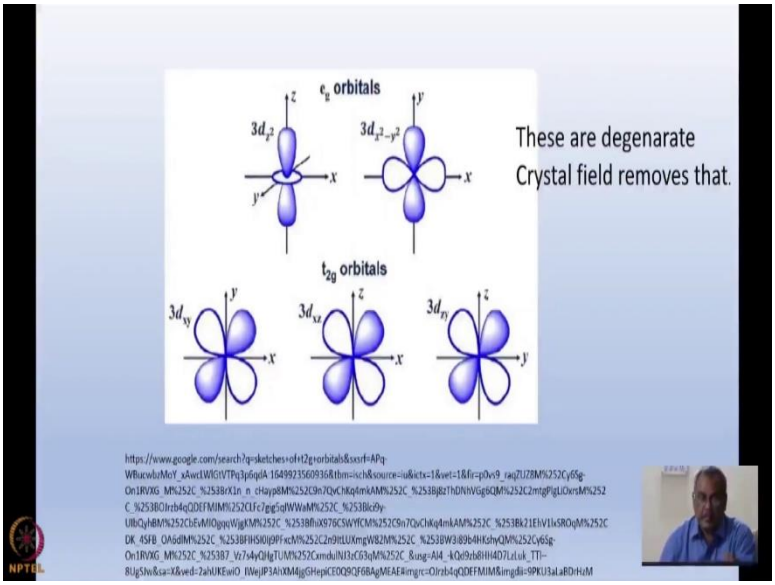

The orbitals which I mentioned their actual physical drawing is like this. They are $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{z^2}$ and $3d_{x^2-y^2}$. These are actually degenerate if I take an independent neutral atom but when you put the same electronic orbitals inside a crystal then depending on the crystal field which is highly directional, this degeneracy of energy is lifted in the crystal and once this degeneration is lifted then you have to put electrons accordingly in these orbitals.

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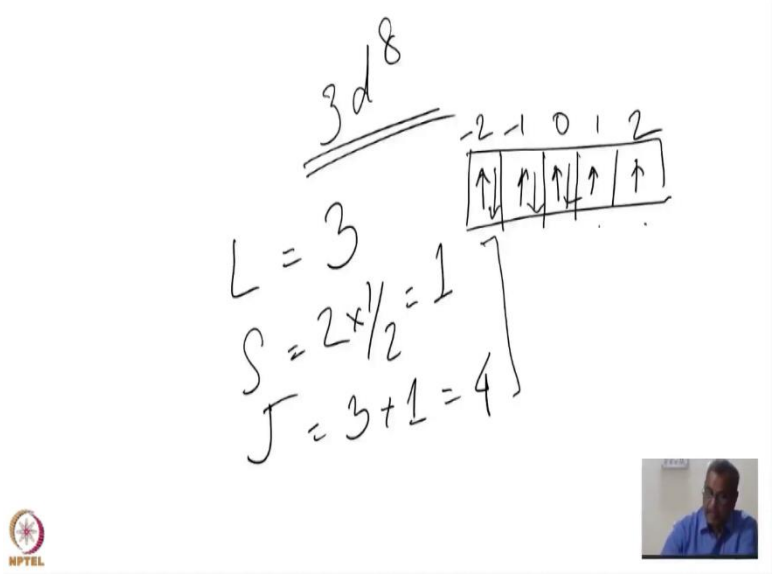

Again for Ni $3d^8$, L = 3, S = 1 and J = 4.

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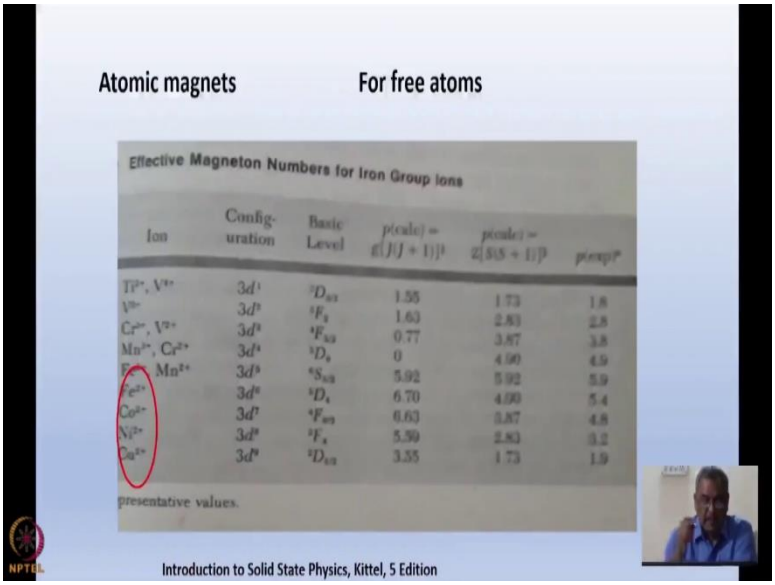

This way you can write down the ground state. In the screenshot, the magneton number for iron groups ions, Fe^{2+}, Co^{2+}, Ni^{2+} is shown. They are the most well-known magnetic materials towards there is $3d^6$, $3d^7$, $3d^8$. Just now I calculated for nickel and its ground state $^3F_4$.

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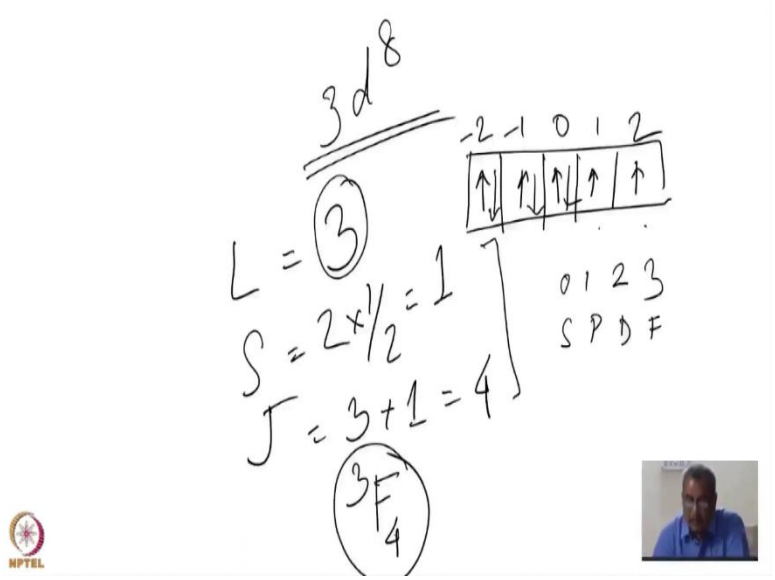

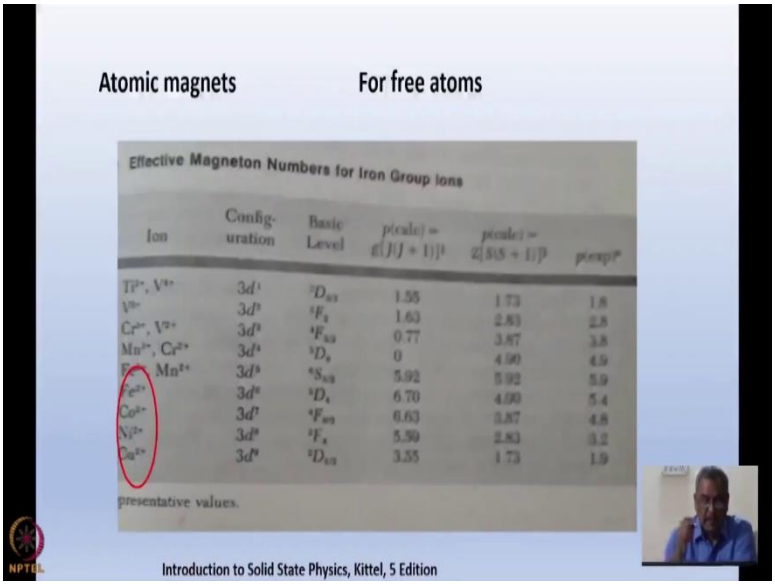

Here, as $L = 3$ so it is a F state and 2S+1 = 3, and J value is 4. This is how we write the ground state for an atom especially for a magnetic atom using Hund's rule and this is used for Ferromagnetic materials and also for the rare earth group materials.

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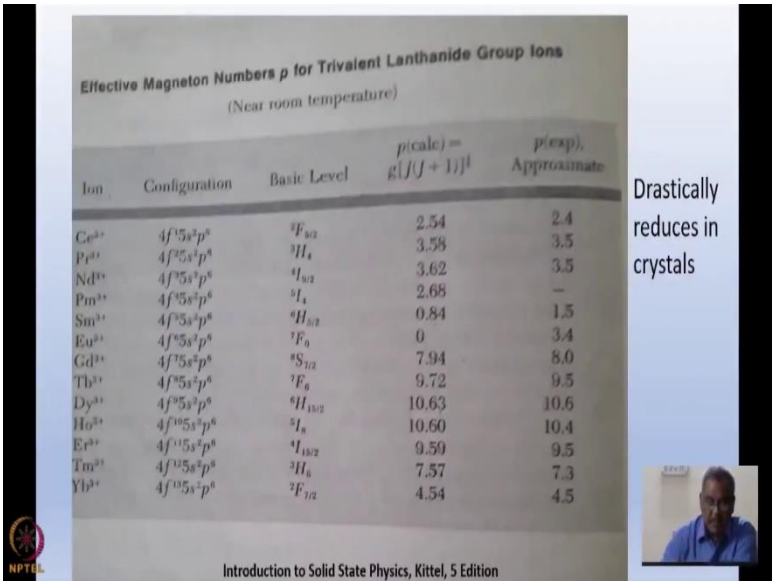

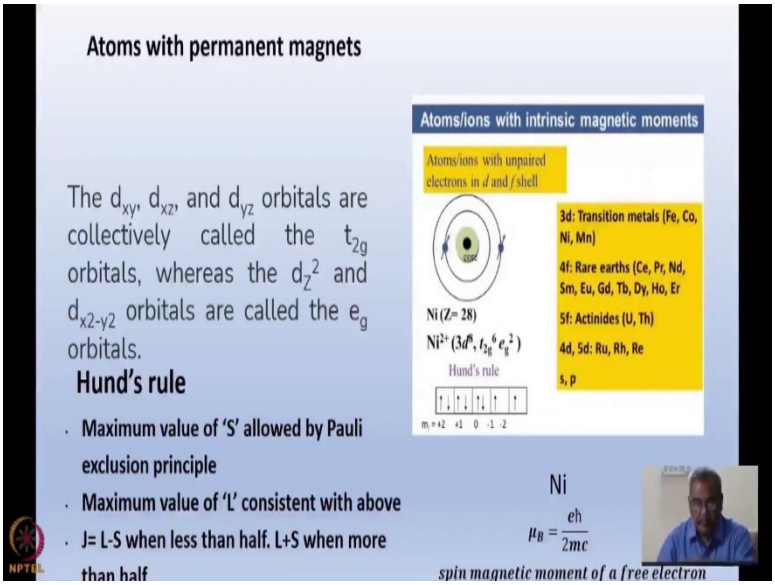

The rare earth group is here. The same technique can be used to calculate out the ground state for all of them. It is just for your knowledge but the thing is that you get a calculated value of the magnetic moment and that is normally written in terms of Bohr magneton, $\mu_B = \frac{e\hbar}{2mc}$.

Let me just mention here that you can also write a magnetic moment for a nuclear particle like neutron which we will be using later. But because this mass is almost 2000 times higher (compared to electron), the magnetic moment is almost 2000 times lower compared to an electron. We can evaluate the ground states and the magneton number in the ground states.

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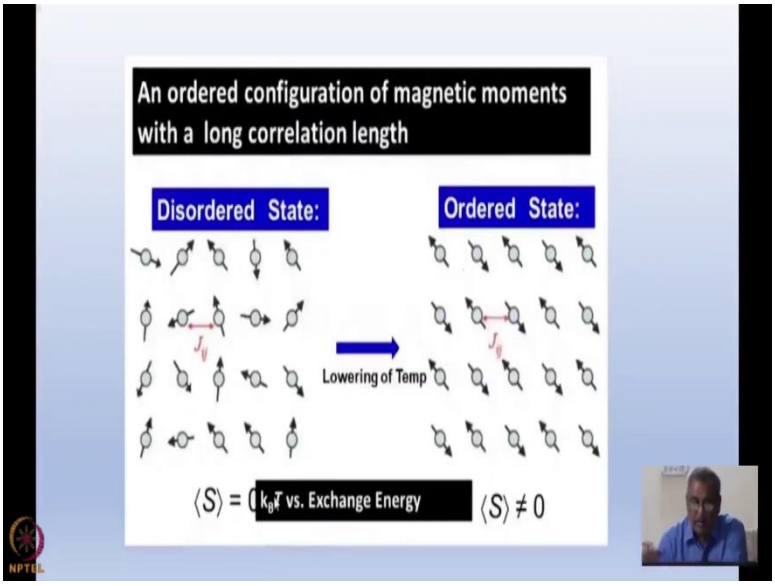

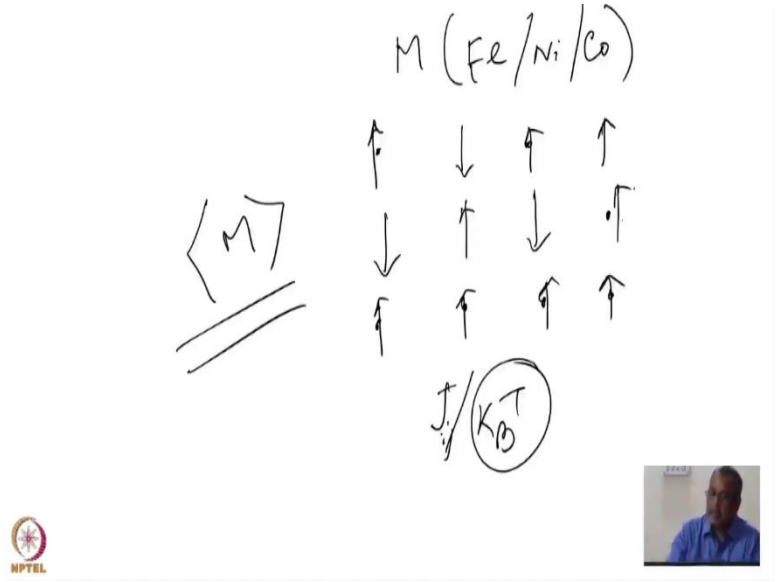

Now, we will be talking about materials which have got inherent magnetic moment.

This is a crystallographic structure which you are familiar and we can find out the crystallographic structure using diffraction experiments such as x-ray diffraction experiments. These are regular structures. But now consider this is a magnetic material, let me consider Fe, Ni, Co, the 3d transition elements. Then each and every site also has a magnetic spin which I calculated out just now using Hund's rule, they are the magnetic spin associated with the site. But please note that I am showing all of them parallel because you are familiar with the fact that these are inherently ferromagnetic. But this is not true for all temperatures because if I raise the temperature then there is something called an exchange energy competing with temperature. The exchange energy's role is to align them (spins). This is the exchange energy operating between the two magnetic moments at two sites and the temperature's role is to misalign them. So, if I raise the temperature then it will be a disordered spin structure like what you see on the left-hand side.

J/k_BT is the thermal energy, it will always try to dynamically disorder the spins and J_{ij} is the exchange energy between two sites which tries to align (or order). When I say align, I must mention that though I have taken examples from only ferromagnets but there are other structures like antiferromagnets, ferrimagnets that are all ordered structures. Though antiferromagnet does not have a bulk value of magnetism but it is ordered if I consider that spins are oppositely aligned. You must understand that this is also an ordered magnetic structure.

So, nearest sites are not aligned to each other but these are ordered moment. Here you see this is an ordered (and aligned) moment where the overall S value that means S averaged over the

enter in system of spins, is non-zero and this you achieve when you come down in temperature. Above a certain temperature which is known as Curie temperature for ferromagnet the spins are disordered.

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Now I have introduced you to sites with local moments but one is a paramagnet which is disordered and as you lower the temperature you go to ferromagnet, antiferromagnet, ferrimagnet depending on the material and their J_{ij}. They are all ordered. There is a phase transition with temperature, from disordered to ordered state and I must mention here, I will get back to it later, that whenever we do neutron diffraction, we may do experiments above the transition temperature when magnetic order is lost but crystallographic order is present. So, you can get the physical crystallographic structure. After that you come down in temperature below the (magnetic) ordering temperature and then I have ordered magnetic moments and they will add to the diffraction pattern and then add up the intensities what you find from in the disordered magnetic state. So, you add up intensities due to chemical and magnetic order in those Bragg peaks.

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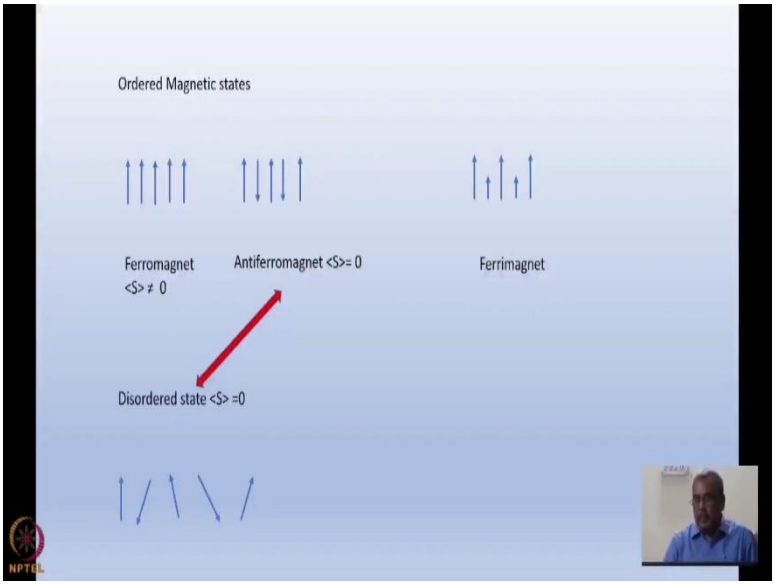

There are ordered magnetic states as I showed you just now. This is a ferromagnet where is average 'S', <S> is not equal to 0. This is antiferromagnet where $< S >=0$ but this is also an ordered state and there are also ferrimagnets where often local sites have different magnetic moments one large moment and other small and it is an ordered state of these moments. These order states are different from the disordered state when $< S >= 0$ again but this is what I call dynamically disordered because of higher temperature 'T'. So, these are the ordered magnetic states which you will be studying using neutron. But for that you also seek information for the chemical order above the Curie temperature. I will stop now before I go to the next module.