

Neutron Scattering for Condensed Matter Studies
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Week 5 Lecture 14B

Keywords: Pauli Exclusion Principle, Exchange interaction, Superexchange, Curie-Weiss Law, Magnetic Hysteresis, Paramagnet, Ferromagnet, magnetic Susceptibility, RKKY interaction

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Exchange energy in a magnetic lattice

$$H_{exchange} = - \sum_{ij} J_{ij} \bar{S}_i \cdot \bar{S}_j$$

i, j can be nearest neighbor, next-nearest neighbor, directional etc

The origin of exchange energy are the atomic spins or the magnets at lattice sites

But not magnetic dipole-dipole interaction^X

Magnetic interaction is $\ll KT$, will not give any order at room temperature $e^{-J/KT}$ dictates alignment



Now we have come to the very important part of magnetic interaction known as exchange interaction. Basically, exchange energy in a magnetic lattice usually written like $H_{exchange} = - \sum_{ij} J_{ij} S_i \cdot S_j$ where J_{ij} is an exchange integral, and S_i and S_j are the local atomic spins or magnetic moments that interact through the exchange force in a system.

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$H_{exch} = - \sum J_{ij} \vec{S}_i \cdot \vec{S}_j$

Dipole-Dipole? 30 meV

meV




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In a lattice, the exchange interaction can be between nearest neighbours or it can be between next nearest (or even farther, in principle) neighbours with the exchange energy H_{ij} . This is responsible for the alignment to the ordered state. Later, I will discuss various magnetic interactions briefly that are possible in a solid.

I must say that the nature of interactions is so varied and interesting (in magnetic materials) that magnetic neutron diffraction is possibly the most popular tool to understand magnetic interactions vis-a-vis the structures. Right from the beginning of neutron scattering till date, it is being used extensively to understand these interactions.

As the atomic spins are involved in the interaction so the question comes whether is it a dipole-dipole interaction. One can imagine that in a lattice at a site there is one magnetic dipole and

then at another site there is another dipole and the question is whether is it a dipole dipole interaction? The answer is no.

Magnetic exchange interaction is not a dipole-dipole interaction because the interaction between two magnetic dipoles is very weak, it goes as $1/r^3$ and if it comes to estimating the energy, it is even less than the thermal energy at room temperature (~ 30 meV). This is so much smaller than room temperature that if it is only dipole-dipole interaction, then we will not have any magnetic alignment at room temperature. Whereas in iron the Curie temperature ' T_c ', below which it aligns from paramagnetic to ferromagnetic phase is much higher (than room temperature). Also, cobalt and nickel are magnetically ordered at room temperature. It is because the root of exchange interaction is not in dipole-dipole interaction but it is electronic in nature and much stronger than magnetic dipole-dipole interaction.

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The slide contains the following content:

- Equation:
$$V_{ab} = e^2 \left(\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} \right)$$
- Text: "Typical for a molecule"
- Diagram: Two atoms, 'a' and 'b', each with a nucleus (red dot) and an electron (blue dot). Atom 'a' has electron 1, and atom 'b' has electron 2.
- Text: "This is purely Coulombic in nature"
- Text: "Heitler-London Theory introduces an exchange term apart from Coulomb terms"
- Equation:
$$E = K \pm J$$

K is the coulomb term, but J is the exchange interaction originating from Pauli Exclusion principle
- Equation:
$$J_e = \int \psi_a^*(1)\psi_b^*(2)V_{ab}\psi_a(2)\psi_b(1)dv_1dv_2$$
- Small inset showing a matrix element formula and a video thumbnail of a speaker.

I have just taken the simplest example, a hydrogen like molecule. We have got an atom a with an electron 1 and atom b with an electron 2. The interaction energy between these two which I have written down. It is the interaction between electron-electron, electron-nucleus and nucleus-nucleus.

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$$V_{ab} = e^2 \left[\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right]$$

$$J = \int \psi_a^*(r_1) \psi_b^*(r_2) V_{ab} \psi_a(r_2) \psi_b(r_1) d^3r_1 d^3r_2$$

$$V_{ab} = e^2 \left(\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} \right)$$

Typical for a molecule

Atom a, electron 1 and atom b, electron 2

This is purely Coulombic in nature

Heitler-London Theory introduces an exchange term apart from Coulomb terms

$E = K \pm J$ K is the coulomb term, but J is the exchange interaction originating from Pauli Exclusion principle

$$J_e = \int \psi_a^*(1) \psi_b^*(2) V_{ab} \psi_a(2) \psi_b(1) dv_1 dv_2$$

Exchange energy in a magnetic lattice

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The origin of exchange energy are the atomic spins or the magnets at lattice sites

But not magnetic dipole-dipole interaction^x

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It can be written as,

$$V_{ab} = e^2 \left[\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right]$$

But this is not purely coulombic in nature, J -exchange is due to electron interaction but not purely coulombic, it comes from the exchange of electrons between the two sites. I can say it is Pauli's Exclusion principle, that exchange of electrons between 1 and 2 gives me the exchange energy. So, with the coulomb term, the exchange term is there and I have written down this exchange term as an integral below. Exchange term can be written as,

$$J_e = \int \psi_a^*(1)\psi_b^*(2)V_{ab}\psi_a(2)\psi_b(1)dv_1dv_2$$

Here the integrated is over entire-space. This gives me the exchange energy.

Interestingly, the origin of this lies in Pauli's Exclusion Principle. You can see here all that I have done is actually, I have just put electron a at 1 and electron b at 2 and then I have taken two states where the electrons have been exchanged. This is possible for identical particles and in this case following Fermi direct statistics. A similar expression you might have seen is when you write down the Slater of determinant for a N electron system.

J_{ij} is a calculation of this integral and interestingly there is no typical classical force term that I can bring in to explain the exchange energy. It is simply because of the Pauli's Exclusion principle of two identical electrons at the two atomic sides, I can exchange the two and create a new state and this J is basically the evaluation of the exchange interaction V_{ab} between the two states.

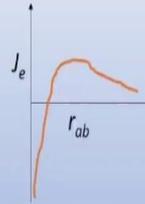
If you remember even in neutron diffraction, I did that earlier when I took a plane wave state with another plane wave state and between the two, I put the interaction potential. It is exactly same only here the state of the system is $\psi_a(2)\psi_b(1)$ after exchange, and $\psi_a(1)\psi_b(2)$ before exchange. I can say it is quantum mechanical in nature and this term is appearing due to pure exchange caused by Pauli's Exclusion Principle.

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In a solid magnetic material the exchange interaction is between spins at two sites and the sign of J dictates the type of order

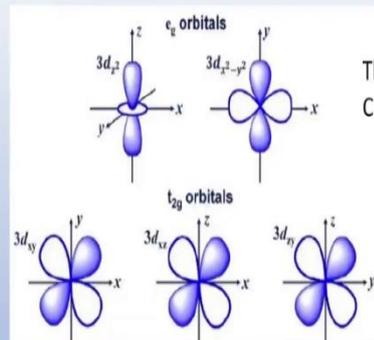
$$H_{\text{exchange}} = - \sum_{ij} J_{ij} \bar{S}_i \cdot \bar{S}_j$$

If $J_{ij} < 0$, it is non-ferromagnetic



When ' r_{ab} ' is large exchange takes over and $J_{ij} > 0$

r_{ab}	Fe (3.26 Å)	Co (3.64 Å)	Ni (3.94 Å)	Cr (2.60 Å)
	F	F	F	x



These are degenerate
Crystal field removes that.

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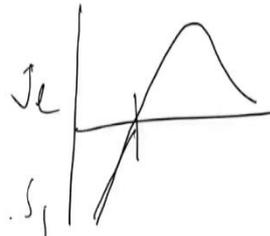


This J_{ij} calculation is an involved task, What I showed you earlier, depends on the actual physical extension of the electronic wave function. From here you can see that J_{ij} can be calculated for any system depending what are the electrons (orbitals) that are responsible for the exchange and then that energy turns out to be much higher than what we can get from a magnetic dipole-dipole interaction. This is the origin of magnetic interaction and can be comparable or higher compared to kT which that dictates the alignment. This is what I showed you and interestingly because this depends on the overlap integral for the electronic wave functions, so this J can change sign depending on whether we push the atoms closer or farther.

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$$J_e < 0$$

$$H = - \sum_{ij} J_{ij} \frac{S_i \cdot S_j}{-|e|}$$

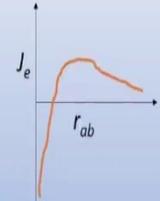
$$J > 0$$




In a solid magnetic material the exchange interaction is between spins at two sites and the sign of J dictates the type of order

$$H_{\text{exchange}} = - \sum_{ij} J_{ij} \bar{S}_i \cdot \bar{S}_j$$

If $J_{ij} < 0$, it is non-ferromagnetic



When ' r_{ab} ' is large exchange takes over and $J_{ij} > 0$

r_{ab}	Fe (3.26 Å)	Co (3.64 Å)	Ni (3.94 Å)	Cr (2.60 Å)
	F	F	F	x



If you are considering the exchange integral J_e for low separation distance, it is negative and then it becomes positive. Now if $J_e < 0$ then $S_i \cdot S_j$ should be negative to lower the energy and anti-ferromagnetic alignment is preferred (with above sign convention). Whereas above a certain distance because the electronic overlap integral changes sign, it becomes positive and when $J > 0$ we get ferromagnetic order. I just mentioned here that r_{ab} in case of Fe is 3.26, for Co is 3.64 and for Ni is 3.94 Å. These are all ferromagnetic because we have gone above negative value of the exchange integral whereas for Cr it is 2.6 Å and it is not a ferromagnetic material because the J is negative in its case.

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Paramagnetic to Ferromagnetic/Ferrimagnetic or antiferromagnetic

$$B = H + 4\pi M = H + 4\pi\chi H = (1 + 4\pi\chi)H = \mu H$$

Curie Weiss law $\chi = \frac{C}{T - T_c}$ T_c is Curie temperature

For antiferromagnets $\chi = \frac{C}{T + T_N}$

Neutron diffraction is done below and above T_c or T_N to distinguish ordered and disordered phase



Now let me quickly introduce you to the bulk properties of the magnetic material that is important to know because the bulk measurements will tell you whether it is a ferromagnet or ferrimagnet or anti-ferromagnet in a macroscopic scale.

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$$\begin{aligned} B &= \vec{H} + 4\pi \vec{M} \\ \chi &= \frac{M}{H} \\ B &= \vec{H} + 4\pi \chi H \\ &= (1 + 4\pi\chi) H \\ &= \mu H \quad - \textcircled{\mu} \end{aligned}$$



Paramagnetic to Ferromagnetic/Ferrimagnetic or antiferromagnetic

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Let me write down relation for the field inside a magnetic material. It is given by the applied magnetic field plus the magnetism induced in the system: $B = H + 4\pi M$. Here, the susceptibility of a material is given by, $\chi = \frac{M}{H}$ that is the magnetic moment induced per applied field. With this, $B = H + 4\pi\chi H = H(1 + 4\pi\chi) = \mu H$. The μ is the permeability of the medium. These are relationships you are well aware of but I just write them for completeness's sake so that when later we discuss there should not be any confusion.

Now coming back to ferromagnets and we know that χ for a ferromagnet follows Curie-Weiss Law, which states that, $\chi = \frac{C}{T - T_C}$ where T_C is Curie temperature. You can see at $T = T_C$ the susceptibility diverges to infinity. For anti-ferromagnetic order $\chi = \frac{C}{T + T_N}$ where T_N is known as Neel temperature. So, neutron diffraction is done below Neel temperature or Curie temperature for the ordered state and we also do neutron diffraction above the ordering temperature (for chemical structure).

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$$\chi = \frac{C}{T - T_C}$$

$$\frac{1}{\chi} = \frac{T - T_C}{C}$$

$$\chi = \frac{C}{T + T_N}$$



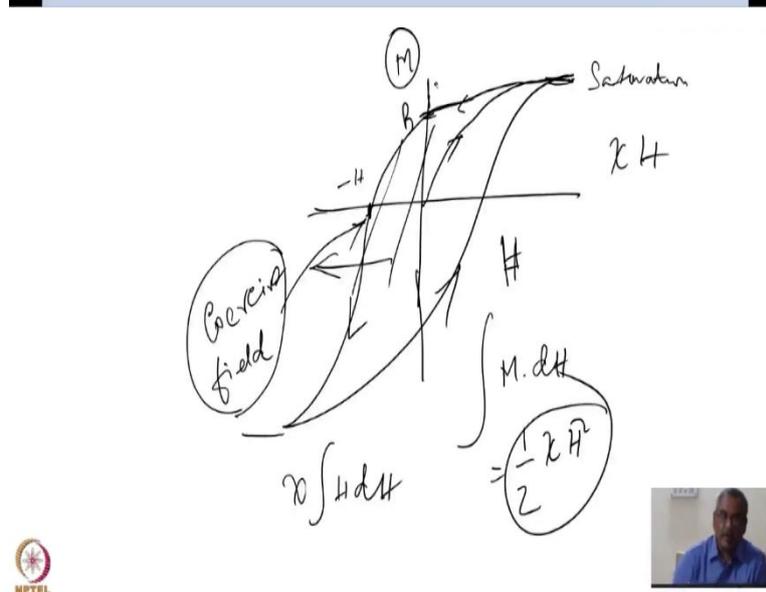
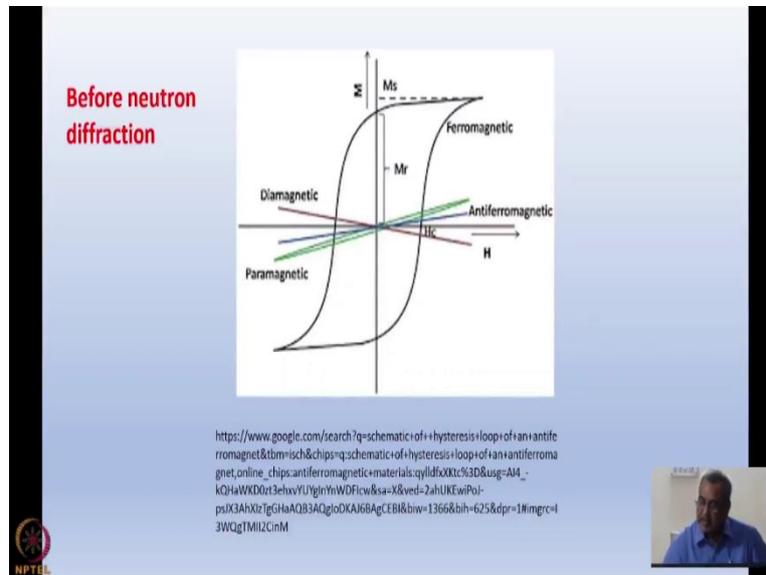
Let me tell you that in case of ferromagnet because $\chi = \frac{C}{T - T_C}$ so if I plot $\frac{1}{\chi}$ vs T then that is a straight line and cuts the temperature axis at $T = T_C$ which dictates the Curie temperature. Similarly for an anti-ferromagnet because $\frac{1}{\chi} = \frac{T + T_N}{C}$ so $\frac{1}{\chi}$ vs T plot cuts temperature axis at some negative value T_N .

In the figure, $\frac{1}{\chi}$ vs T plot for a ferromagnet and the antiferromagnet in the ordered state is shown. So, by measuring the susceptibility we can at least understand whether the ordered state is ferromagnetic or anti-ferromagnetic.

On the other hand, if it is a ferromagnetic state then as we raise temperature the magnetic moment undergoes a second order phase transition. Here M is the order parameter for a magnetic phase transition from ferro to para. In paramagnet it is a 0 for the sample whereas in

the magnetic state, you can see the magnetic moment rises to a high value. Now we do experiments in both magnetic ordered as well as in disordered paramagnetic state.

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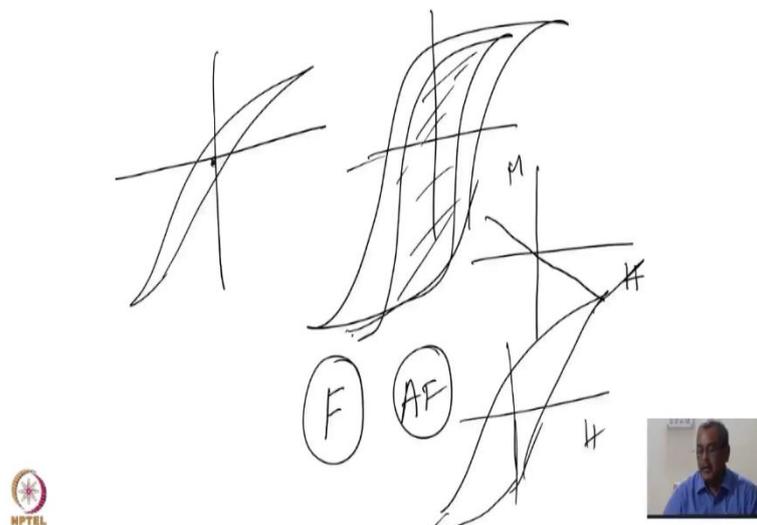
Let me give you the idea about the hysteresis loop because even before we do any kind of diffraction studies, when you make a sample the first thing, we can do is to measure the hysteresis Loop. The hysteresis loop is B versus H curve. Let us take a piece of iron initially in a non-magnetic state because its magnetic domains are all misoriented. With an applied magnetic field, the induced magnetic field also increases till it reaches a saturation but when I reduce the field from saturation the magnetization decreases but does not become 0 at 0 magnetic field. I have already aligned the domains and they will remain (partially) aligned. Now if I start applying a magnetic field in the negative direction, again I can force it to go to 0

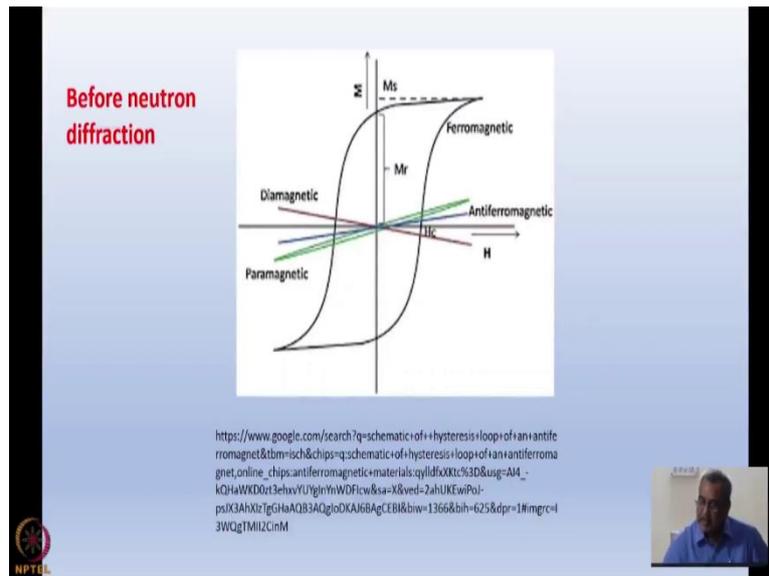
at some negative field H and then the same nature repeats in the other half and this is how the hysteresis loop looks like. We know that the area of the hysteresis $\int M \cdot dH = \chi \int H \cdot dH = \frac{1}{2} \chi H^2$. In one cycle, this is the energy spent in the system in magnetization reorientation. If you take a ferromagnetic material through cyclic magnetic fields, you will find this causes heating of the sample. So, this is the hysteresis loop of a ferromagnet.

If you cycle an applied field the magnetization goes from zero to saturation magnetization then goes back to a value which is known as remnant field where you just bring the applied magnetic field to 0. After that when I go to negative part of the cycle, it goes to zero magnetization at is known as the coercive field. Again, it goes to negative saturation and then this cycle repeats.

This is a whole cycle known as magnetic hysteresis loop. Hysteresis because you lose power every time you go through one cycle of this hysteresis loop. That is why magnetic material inside a transformer gets heated up. But now this hysteresis loop also has several other properties. I have drawn one for a ferromagnet which is a hard magnet. If I consider which is a soft magnetic material then this loop will be much smaller.

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That means the difference between a hard ferromagnet and a soft ferromagnet is that for a hard ferromagnet hysteresis loop will be wider, while it will be narrower for a soft ferromagnet. Reason being, the area is smaller for this soft ferromagnet and so the heat dissipated is smaller than the hard ferromagnet.

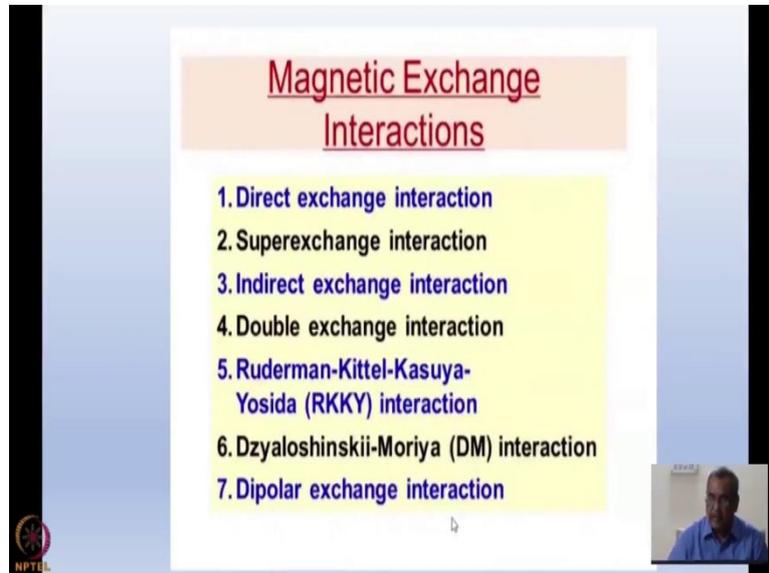
If it is a diamagnetic material then the induced magnetization is small but will be in the negative direction, opposing the applied field. In case of a diamagnetic material, H versus M or B should show a linear, negative slope which means for H positive M is negative and for H negative it will be positive. So, it will oppose the applied magnetic field. For anti-ferromagnets, where the average $\langle S \rangle$ is zero. Again, it should show a very narrow loop narrow loop centred on zero. There are various cases where this loop can shift left and right and you can say there is something called ‘interface exchange interaction’.

Those, we will come to later but the fact is that from the hysteresis loop of a material you can at least make some inferences whether it is ferromagnet, anti-ferromagnet, a soft magnet or a hard magnet. The one shown in picture is the integrated diagram of various kinds of materials. For a paramagnetic material it is almost similar like diamagnetic but the fact is that paramagnetic materials do not oppose the field and as you apply field the magnetization increases and tries to align the magnetic moments in the direction of the applied field. So, you get a loop which looks like the green loop.

I have indicated to you the first experiment that one will be doing when one makes a sample. That is the measurement of the magnetic hysteresis loop and you can see that this is the saturation magnetization. Sometimes, the magnetic moments are difficult to align and in that case your hysteresis loop even if you apply a high field will not reach saturation and before

that you might be coming back to the negative branch in the field direction because the sample is a hard magnet and even large magnetic fields are required to align them compared to what you have available in your experimental facility.

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In next lecture, I will briefly mention the various magnetic exchange interactions which are important for understanding the alignment in our systems. There is direct exchange which I discussed just now but there is also something called super-exchange. There are indirect and double exchange interactions and importantly there is something called RKKY or Ruderman-Kittel-Kasuya-Yosida interaction through conduction electrons. There is also an interesting kind of interaction known as DM or Dzyaloshinskii-Moriya interaction and dipolar exchange interaction.

I will briefly take you through some of these interactions which are important in case of neutron diffraction and in determining, the final magnetic structure. With this introduction, I end this module.