Neutron Scattering for Condensed Matter Studies
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Week 6: Lecture 15 B

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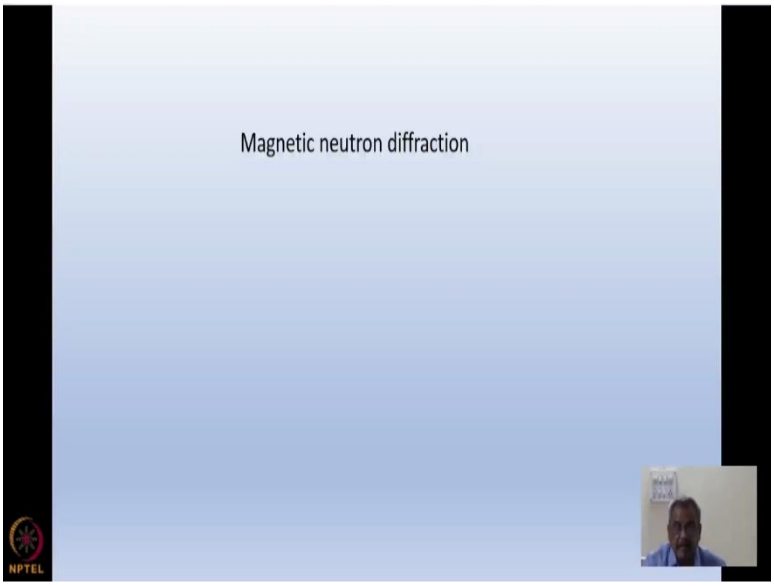

After introducing you to various magnetic interactions, I am back to magnetic neutron diffraction. In many ways magnetic neutron diffraction is similar to x-ray diffraction. Let me state at the onset that often we do these experiments using powdered crystals.

Powder consists of small crystallites oriented in all possible directions and the magnetic neutron diffraction has an additional advantage over x-rays. X-rays can give us structure: physical structure or chemical structure. But magnetic neutron diffraction in addition gives us magnetic structure also. Possibly, this is the only technique with which magnetic crystallographic structures like ferromagnetic, anti-ferromagnetic structures have been determined. I will come to specific examples later.

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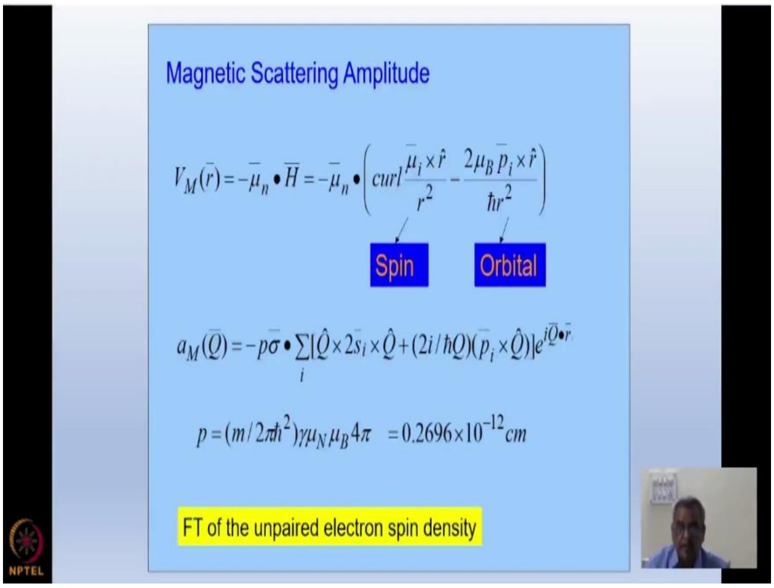

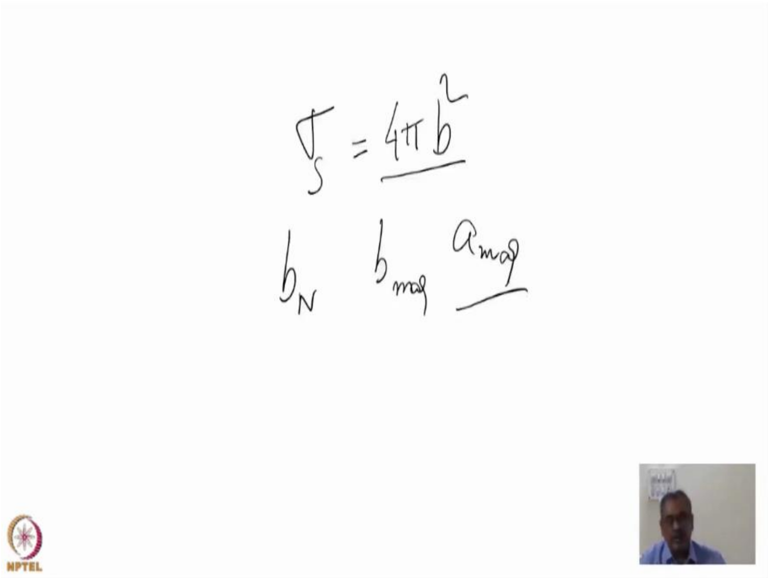

The magnetic diffraction is due to the potential V_M. If you remember, earlier when I was talking about nucleus scattering, I talked about V_N which was a delta function and was nuclear potential. Magnetic potential is due to the unfilled orbitals giving rise to magnetic moment that interacts with the applied magnetic field H on the sample.

It has two parts actually- μ_n is magnetic moment of the neutron and two parts of the potential are spin and orbital in origin. I will just give you the expressions because derivations will be out of scope at the moment. Ultimately, I can define a magnetic scattering length. When I say scattering length, I must tell you that any scattering cross section is given by, $\sigma_S = 4\pi b^2$ where b is the associated scattering length.

This b can be nuclear or magnetic in origin. I can define a scattering length associated with the magnetic scattering. It is given here in units of centimetre: of the order of 10^{-12} cm. So, the corresponding scattering cross-section comes to be of the order of 10^{-24} cm^2 which is one barn. Earlier r, I told you that I was looking at the Fourier transform of the nuclear density in our experiments. Here, I am looking at the Fourier transform of the unpaired electron spin density together with the Fourier transform of the nuclear density. So, I get both of them when I do neutron diffraction for a magnetic sample.

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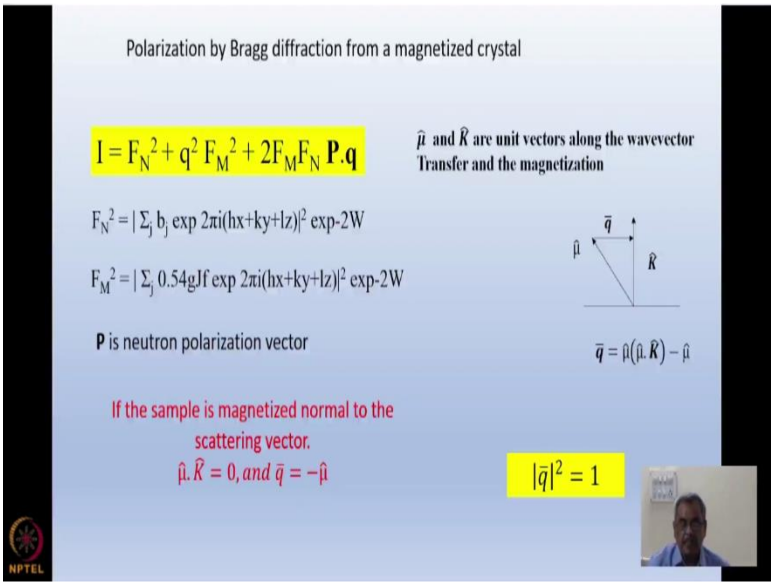

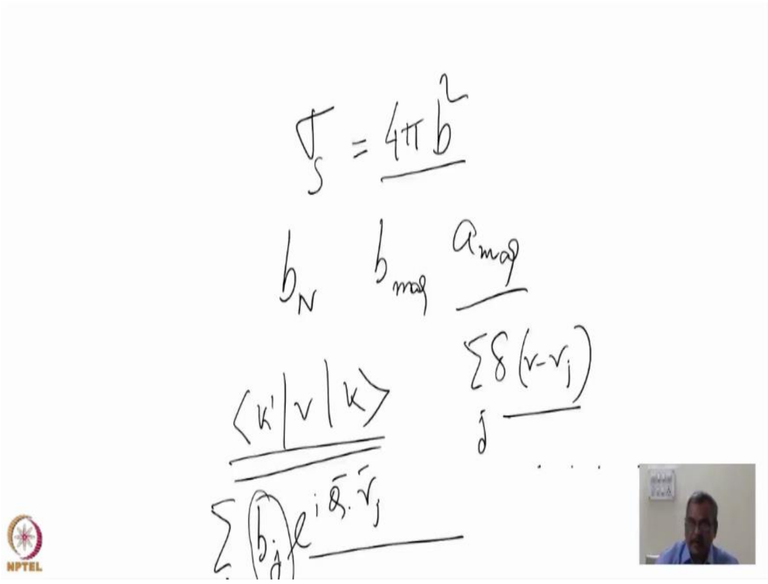

While discussing monochromators, I used this expression and I told you that if I do a vector diagram K is the momentum transfer and μ is the direction of the magnetic field then I can define a vector q which is basically the component of μ along K subtracted out from μ .

If this magnetic moment is in plane or if the K vector is normal to the magnetic moment in the sample, then this angle will become 0. This angle becomes 90 degrees. And in that case, your q is equal to -μ . In summary, if sample is magnetized normal to the scattering vector, then $\hat{\mu}.\widehat{K} = 0$ and $\bar{q} = -\hat{\mu}$ and magnitude of $q^2 = 1$.

This expression has got 2 components which I gave you earlier. It has got a nuclear component and a magnetic component weighted by q^2. Often $q^2 = 1$ because the direction of the magnetic moment or the magnetic field is normal to the *K* vector or the magnetic momentum transfer.

But most importantly, when I talk about these components, F_N^2 is a square of the scattering amplitude which I gave you earlier. It can be written as,

$$F_N^2 = \left|\sum_j b_j e^{-Q.r_j}\right|^2 e^{-2W}$$

This is for nuclear potentials present at the lattice sites.

Along with this I also have F_M^2 term. In its expression apart from other terms there is an '*f*' term. What is this '*f*' term? This is the magnetic form factor. In case of nuclear potential, the form factor is replaced by b_j and I told you earlier also that if I consider this in *q*-space, it is a continuous constant value (in a plot of *q* vs b_j).

Whereas in the second case, I have got magnetic form factor due to the unpaired electrons in the shells. Let us say it is 3*d* electrons in case of nickel, cobalt, iron- the *d*-group magnets which are known to us or *f*-electrons in case of rare earth materials.

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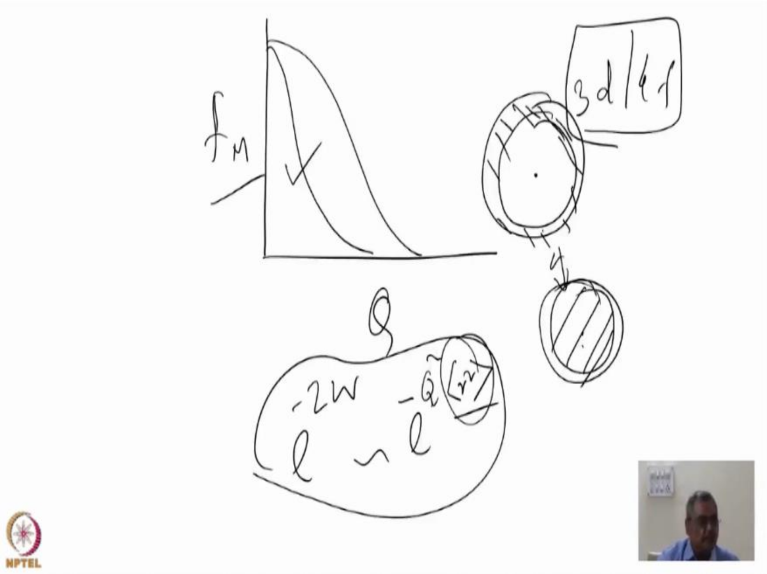

In these cases, my unpaired spin is in a shell which is either 3*d* or 4*f*. Now, the Fourier transform of this shell unlike b_j which is a constant for all *'q'* values this will tend to fall as a function of *'q'* . This we discussed earlier when we talked about x-ray diffraction because in case of x-ray diffraction which is due to the atomic charged cloud, if you take a Fourier transform the form factor decreases as a function of *'q'*.

But the difference between these two is that, here I consider the entire atomic charge cloud at a lattice site for x-ray form factor. Here I am considering only the shell which contains the unpaired electrons for magnetic form factor in neutron diffraction. So, this shell in general has larger average value of average size *'r'* and it will be falling faster with respect to *'q'* values in case of magnetic materials.

Before I go forward, there is also a term e^{-2W}. If you remember that we talked about Debye-Waller factor for thermal vibration. This is the Debye-Waller factor when I consider a crystallographic structure, whether magnetic or nuclear. The entire electronic cloud and the whole object at the lattice site undergoes thermal oscillations. This is the thermal oscillation and I showed you earlier that $2W = Q^2\langle r^2\rangle$, so $e^{-2W} = e^{-Q^2\langle r^2\rangle}$. This thermal factor again, at any q it will reduce the intensity of the Bragg peak and we can also evaluate from the reduced intensity what is the amplitude of the oscillation.. This temperature factor is also a part of the intensity observed.

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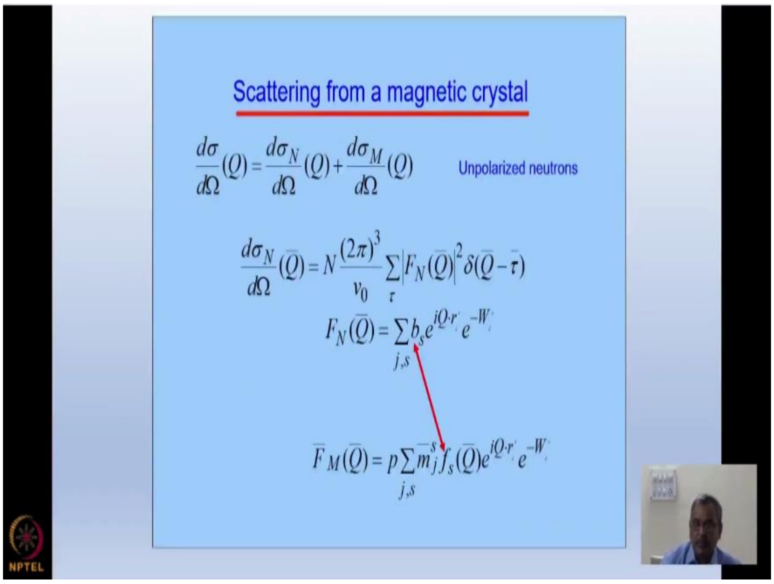

Now the scattering for a magnetic crystal as I told you has got two parts- the nuclear part and the magnetic part. The nuclear part is given by, I repeat $\delta(Q-\tau)$ for Bragg peak position in 'q' space. I discussed with you the Ewald construction and this τ is equal to a reciprocal lattice vector. Every time a diffraction peak appears then

$\bar{K} - \bar{K}' = \bar{\tau}\ or\ \bar{G},$ which is a reciprocal lattice vector.. Excuse my expression, here τ is a reciprocal lattice vector and for the magnetic part, all these remain same. There is a prefactor as well as a structure factor and a form factor for the magnetic part which we have to accommodate.

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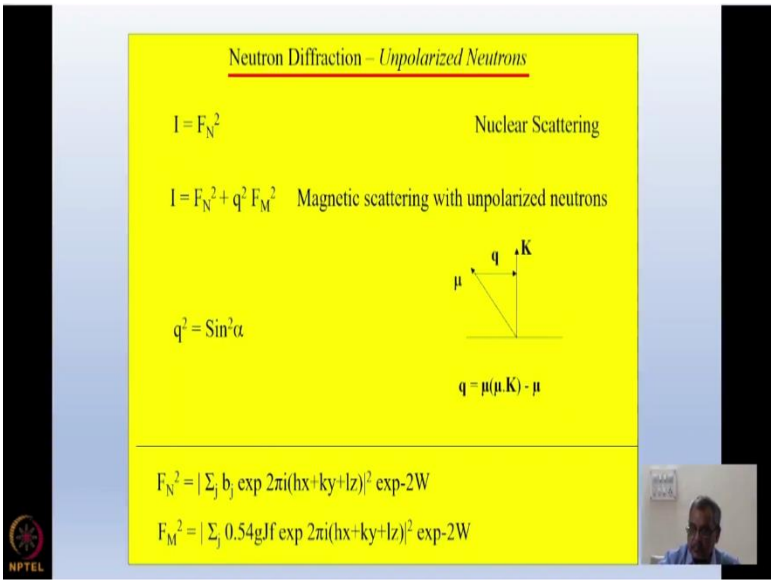

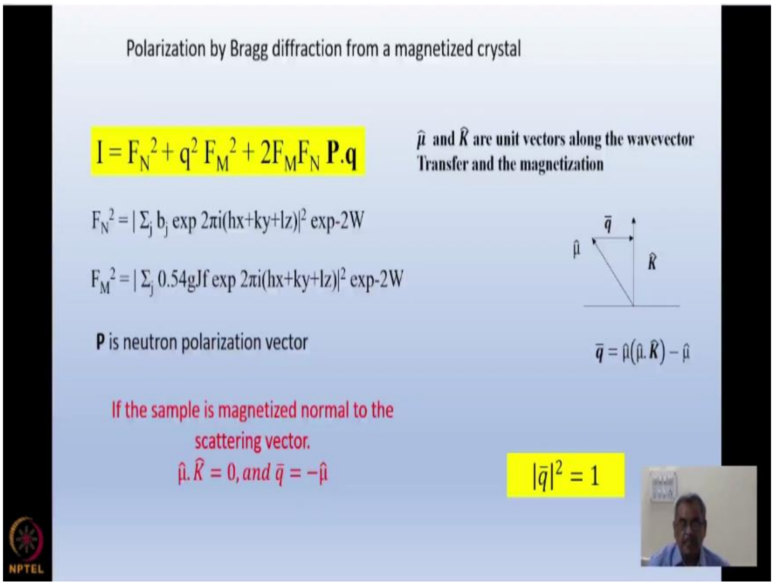

Neutron diffraction for magnetic material, as I showed you in this expression, if the neutron beam is unpolarized then this part will average out to 0 and intensity for an unpolarized beam will be $F_N^2 + q^2 F_M^2$ and for $q^2 = 1$ means it is $F_N^2 + F_M^2$. So, in case of unpolarized neutrons also, we have got two parts in the intensity. One is due to the nuclear part and one is due to the magnetic part. We can determine the magnetic structure by fitting such a pattern. So really speaking, to find out magnetic structure in solids we need not polarize the neutron beam because one might think that since I am talking about spins which are aligned then I should also have a dressed or curtailed neutron beam where I take only one spin with respect to the spin which is there in the lattice. But it is not necessary.

In unpolarized neutron beam diffraction, as you can see from this expression, I have got a nuclear part and also, I have got a magnetic part and both can be fitted or taken out from a measured intensity. Only thing is that the magnetic part has this form factor.

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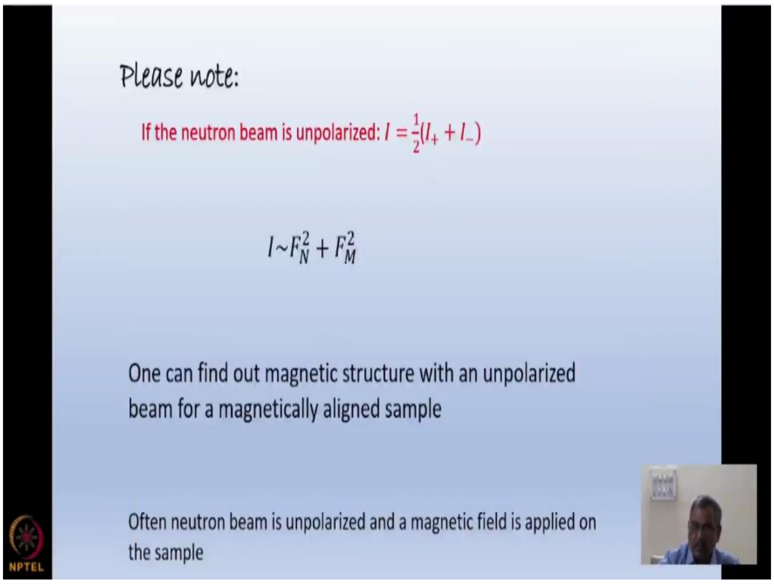

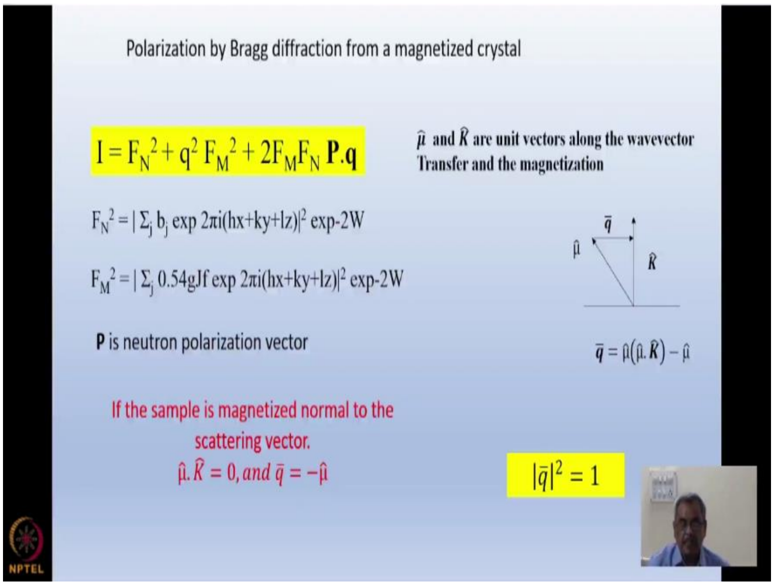

If the neutron beam is unpolarized, the neutron beam intensity for an aligned sample is a sum of I_+ that means neutron beam and the magnetic spin are , parallel and I_- i.e. neutron beam and the magnetic spin are anti-parallel. It is actually, $\frac{1}{2}(I_+ + I_-)$ which gives the unpolarized neutron beam diffraction intensity. It is sum of nuclear scattering amplitude square and magnetic scattering amplitude square. So, we can find out the magnetic structure by fitting the intensity from the data.

Of course, there are instances where we use polarized neutron beam but in general for powder neutron diffraction for magnetic structure, we do not need to polarize the neutron beam. The general expression is,

$$I = F_N^2 + q^2 F_M^2 + 2F_M F_N P.q$$

In this expression $P.q$ average out to 0 for an unpolarized beam and we do have addition of these intensities separately coming from the magnetic part and the nuclear part.

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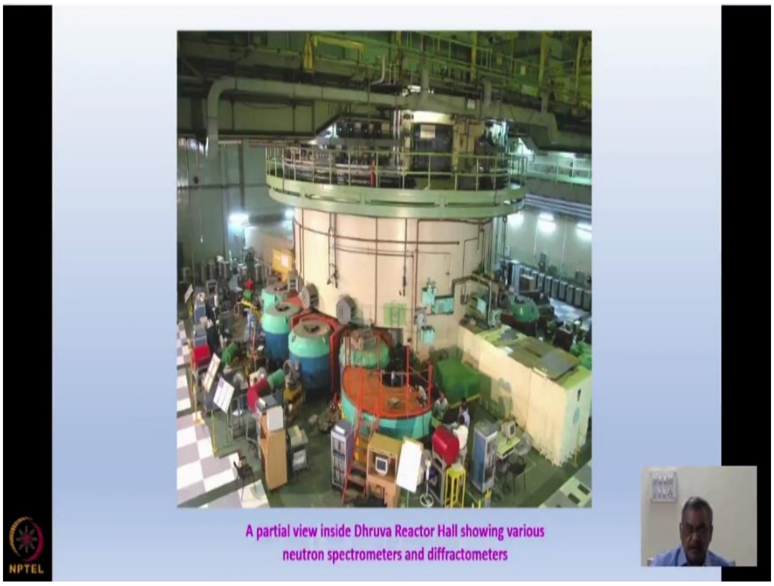

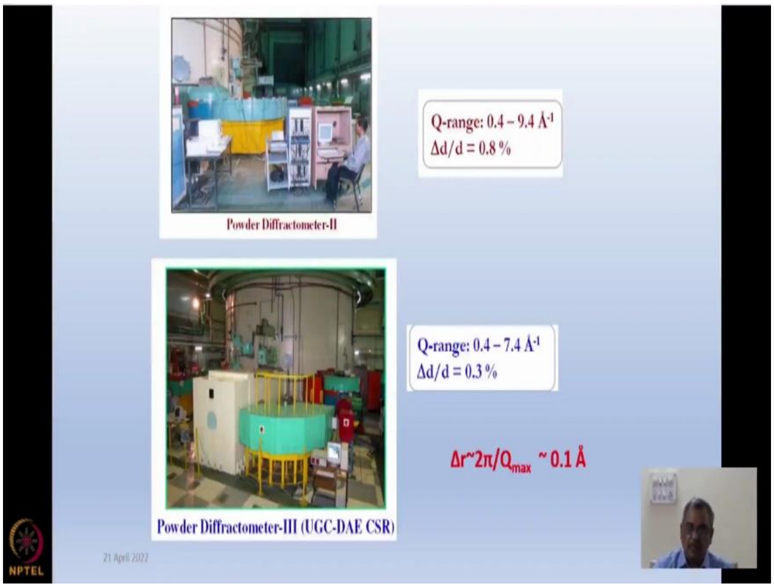

Let me just show you where this experiment can be done. All over the world, possibly neutron magnetic diffraction is one of the major activities in the research reactors. I will show you the two instruments which are available at Bhabha Atomic Research Centre which have been used extensively by my colleagues. Both of them are based on position sensitive detectors. The instrument which is run by solid state physics division of Bhabha Atomic Research Centre. Typical Q-range is around 0.5 to 10 $Å^{-1}$ for such experiments. We do need a reasonable resolution in *'Q'* space to resolve peaks which are close by. This instrument has got a resolution of around 0.8 %.

The other one is run by UGC-DAE CSR which is an UGC center at Bhabha Atomic Research Center that runs this instrument. This is again a powder diffractometer,using position sensitive detectors. The *'Q'* -range is marginally different but has got slightly better resolving capability of nearby peaks because $\Delta d/d$ which dictates the nearby peak is slightly better [0.3%] We can see that the from the Q_{max} values quantum mechanics allows us to study crystallographic structures because Δr dictates the value of these distances, the order of distances that we can measure using these instruments.

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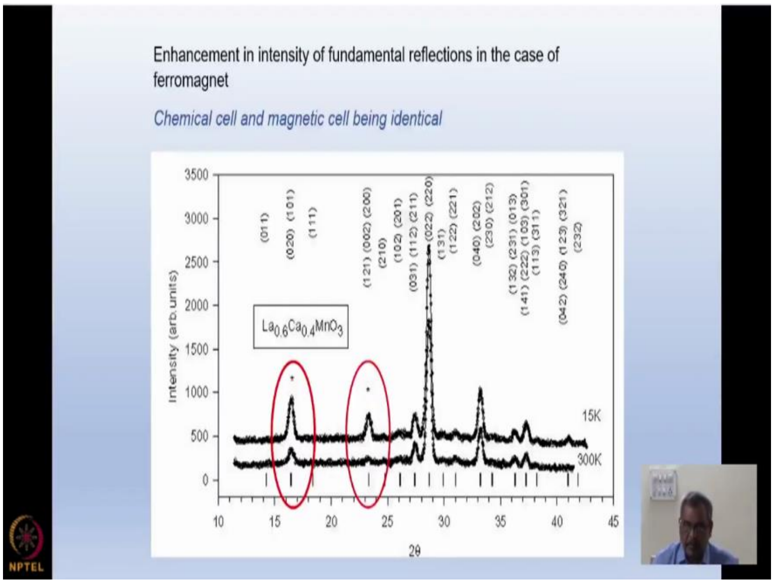

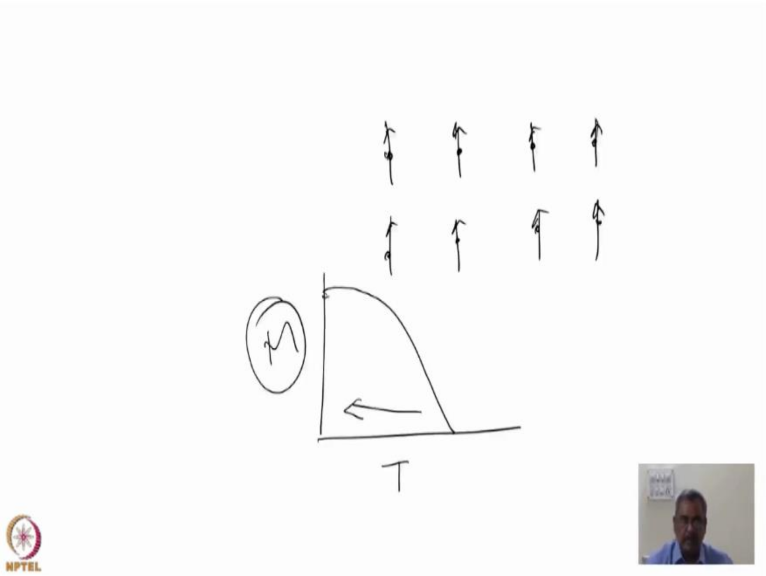

I will discuss some patterns with samples having magnetic properties. Let me just bring to you a diffraction pattern of lanthanum calcium manganese oxide. Please note that the patterns have been taken at 15 K and 300 K. The crystallographic peaks which are possible are listed out here. Not that all of them you can see but many of them you do see here. I just refer to this as a representative diffraction pattern of a ferromagnet. For a ferromagnetic material, crystallographic and magnetic structures are same. They have the same repeatability.

That means here I will find crystallographic peaks and the magnetic peaks coinciding. But please note that at 300 K, you have this crystallographic peak which also has magnetic contribution which is very small. As we go to lower temperature, the magnetization of the sample increases and then the magnetic intensity increases. You can see it from the rise in the peak intensity from 300 K to 15 K.

Reason being, for a magnetic material, if I consider the moment versus temperature, it undergoes a second order phase transition. As we go to lower and lower temperature, the moment increases at lower temperature and that is what is indicated in the patterns here, taken at 15 K and at 300 K.

Another interesting thing I want you to note that the magnetic peaks, they come at lower values of '*Q*'. This is due to the fact that there is a magnetic form factor working as an additional factor with respect to the Bragg peak intensity. If your Bragg peak is a delta function ideally, then there is instrumental resolution which has been convoluted with, causing broadening. Then there is a background which is added on to the diffracted intensity and also one needs to take care of.

The magnetic peaks in magnetic neutron diffraction appears at relatively lower angles, because of the rapid fall of magnetic form factor with *'Q'* (or angle) compared to the higher angle nuclear peaks. At high angle peaks we will not find much contribution of magnetic intensity.

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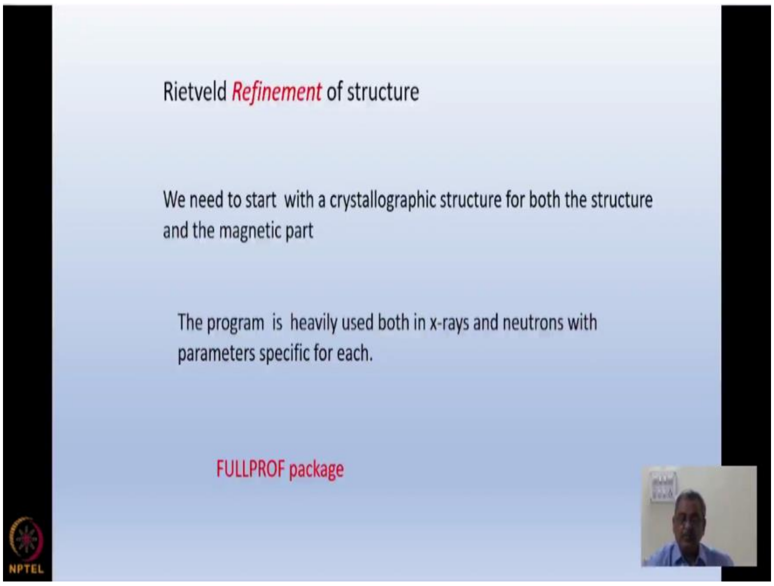

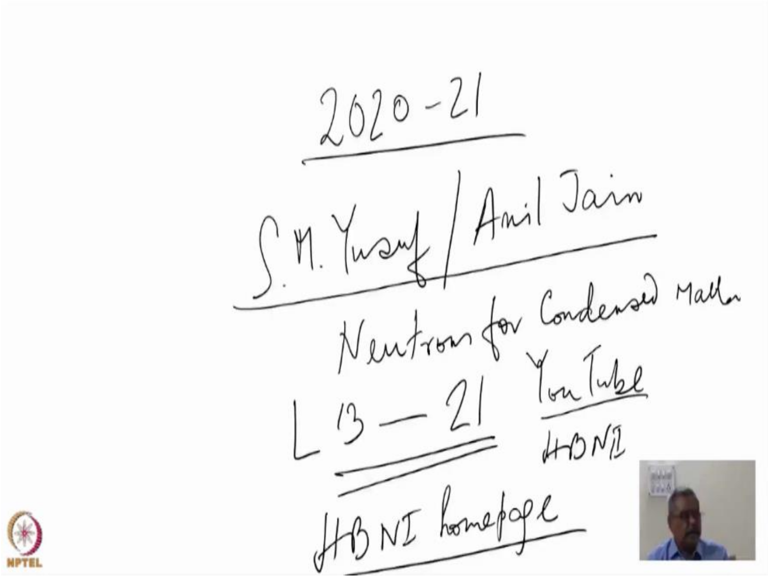

Now I will come to the actually the refinement technique we use for magnetic structures. In this regard, I must tell you that a course was delivered in 2020-21 on neutrons for condensed matter which has been recorded and kept at Homi Bhabha National Institute, India site. Regarding magnetic neutron diffraction, Professor is S.M Yusuf and Professor Anil Jain presented a detailed description of the technique. Especially tutorials taken by Professor Anil Jain on fitting of magnetic structure using Rietveld fitting program was dealt in great details. It needs a large number of tutorials to perfect use of the fitting technique. In this case, in case some of you are keen to learn the technique; follow the lecture 13 to 21, in the course “Neutrons for Condensed Matter”. It deals with magnetic neutron diffraction and there are a large number of tutorials. Any one of you interested to learn this technique in greater details for your samples. I will request you to use this.

These lectures are available in YouTube under the heading HBNI and also can be downloaded from HBNI homepage. Here in this course, I will briefly introduce you to the Fullprof or the fitting refinement techniques for magnetic neutron diffraction.