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

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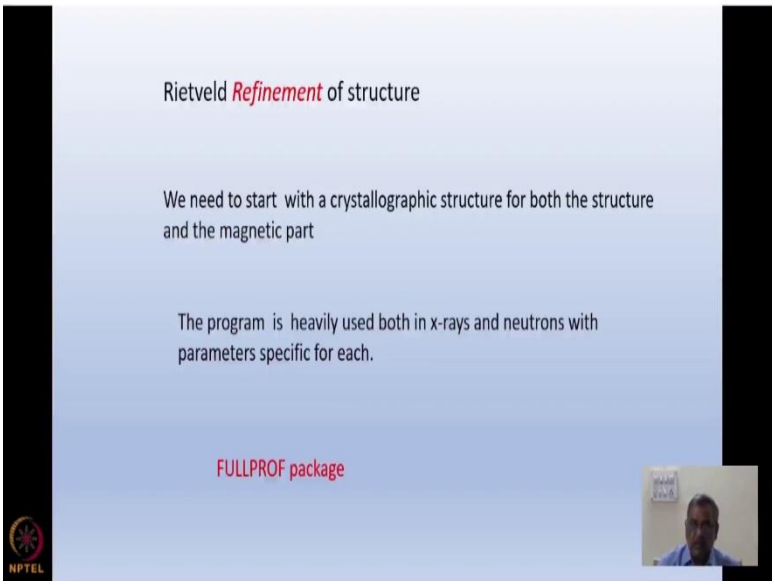

Rietveld Refinement technique is the most widely used technique for magnetic structure refinement. The word refinement means this is not an ab initio solution for crystallographic and magnetic structure, rather you start with a given structure, magnetic and crystallographic, and then you keep refining it.

We need to start with a crystallography structure for both the structure and magnetic part. So, there is a starting point and then we refine that structure. That means, while we are running this fitting program, we must understand that we are undertaking optimization of the given structure. This program is available online and as I told you anybody interested to learn the technique can look into the lectures given in another course [details given].

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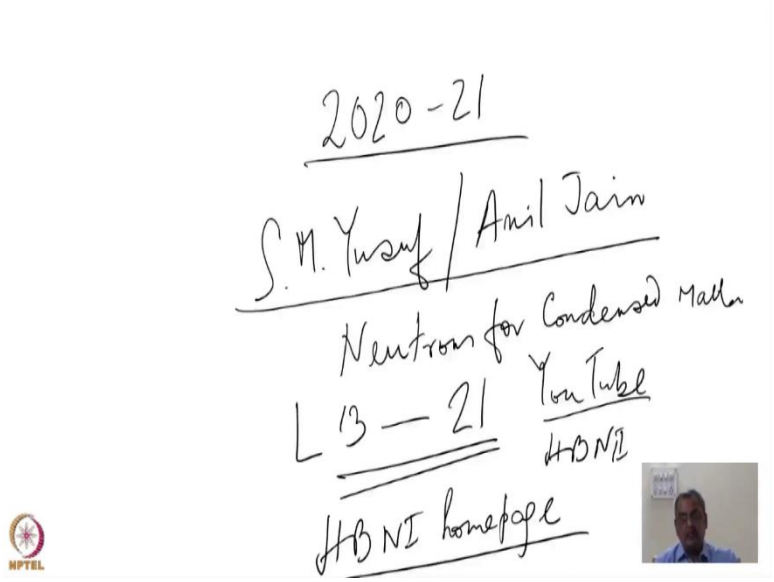

This is used for both x-rays and neutrons all over the world and tutorials are also available online.

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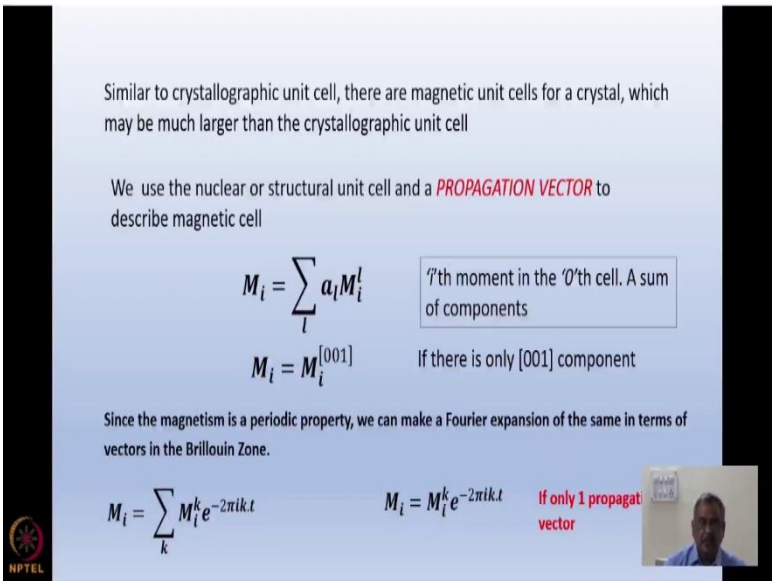

In crystallography by unit cell we understand that it is a repetitive cell that through translation gives me the entire crystal. But the magnetic unit cell can be different from the crystallographic unit cell. For example, if I consider an anti-ferromagnetic sample, then you can see that with the simplest example, a crystallographic linear chain.

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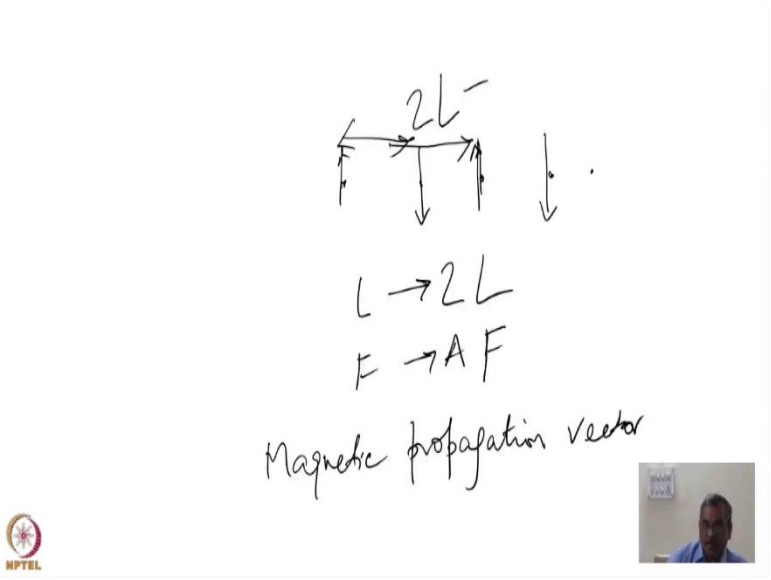

In case of ferromagnetic material, the repeat distance is *L*. Now if it is antiferromagnetic, then nearest neighbor will be antiferromagnetic and the repeat distance has gone to 2*L*, that means the unit cell has doubled when it is going from ferro to anti-ferro. This is a one of the simplest possible examples that I can give. There are other kind of unit cells which are commensurate or incommensurate with respect to the crystallographic cell. I will come to it. There is something called a magnetic propagation vector. If from one crystallographic structural unit cell to the next the magnetism changes slightly, the magnetic unit cell may have thousands of atoms in them and may have a much larger length scale compared to the crystallographic unit cell.

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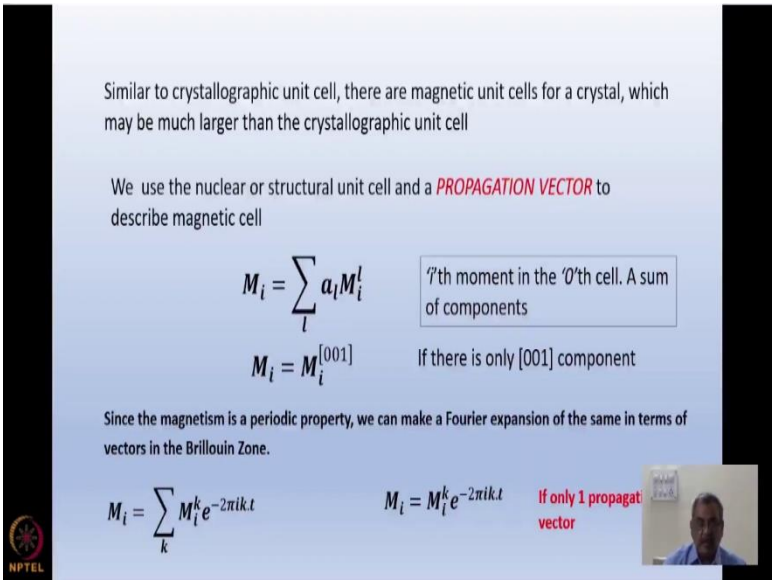

In that case for the fitting of the data we will use the crystallography unit cell and a propagation vector which will use the properties of the crystallographic unit cell and tell me at what distance my magnetic cell is repeating.

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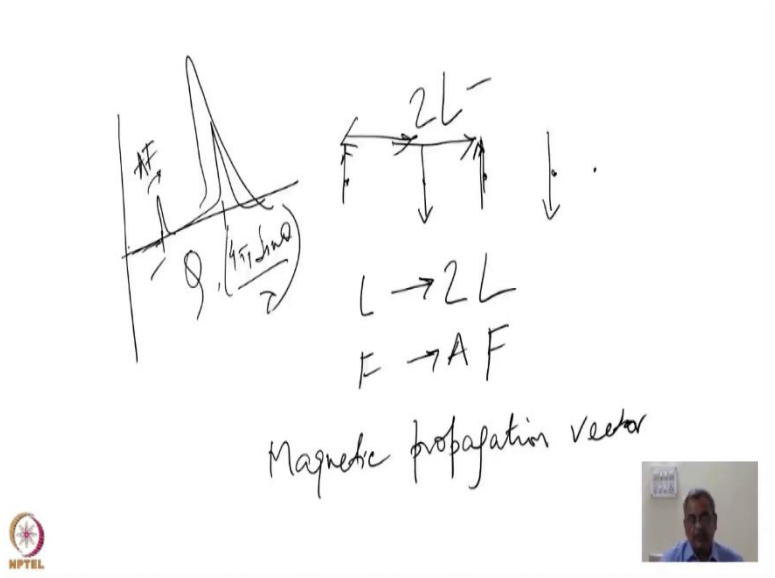

As I showed you in the linear chain, when I go from ferromagnet to anti-ferromagnet, the repeat distance goes from L to $2L$ and actually if you go from ferromagnet to anti-ferromagnet and look at the Bragg intensity vs. Q or $\frac{4\pi \sin\theta}{\lambda}$ plot, you will find that the ferromagnetic peak matches with the crystallographic peak then, at smaller angles, the antiferromagnetic peak will be approximately at half of that angle. So, you do see a new peak appearing when an

antiferromagnetic order takes place. This is because if repeat distance goes from L to $2L$ then the reciprocal lattice vector has gone to 1/2

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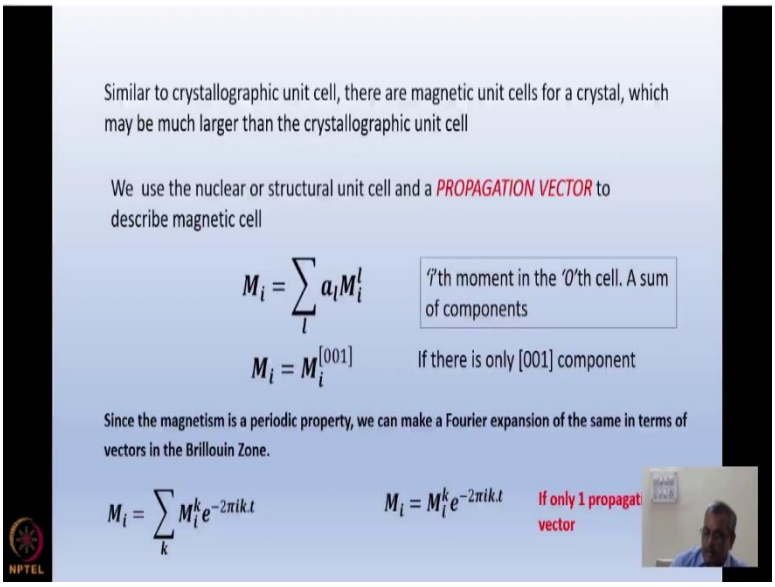

That means I have to find out the magnetic propagation vector for the additional peaks. Here, I have considered a zeroth cell as one of the crystallographic or structural cells, and then the magnetic moment in this cell at any site i can have components in various directions. Now, I have to write down the magnetic moment at a site.

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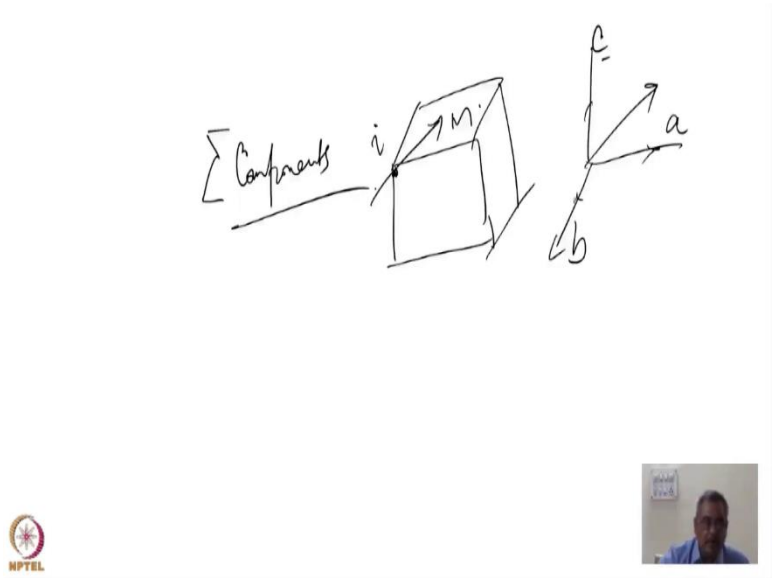

Let me just geometrically show. Suppose this is my unit cell, this is the i^{th} point in my unit cell and this moment is M. Now if I consider crystallographic axes a, b and c, then this M will have

components along *a*, *b*, *c* and basically that means that it is the vector sum of the components in three directions.

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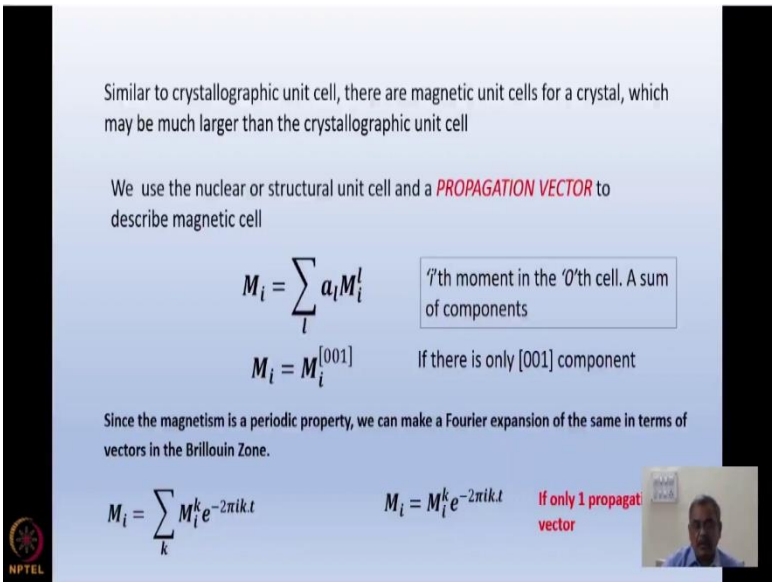

Here, this *l* which is nothing but direction cosine and then *'M'* is the vector sum of the components. *l* can be [0 0 1], [1 0 0], [0 1 0]. Sum of three components in *a*, *b*, *c* directions give you the magnet vector at a certain lattice site. Now, if there is only [0 0 1] component of magnetic moment, say in *'c'* direction, then I can write it as M_i is nothing but $M_i^{[001]}$.

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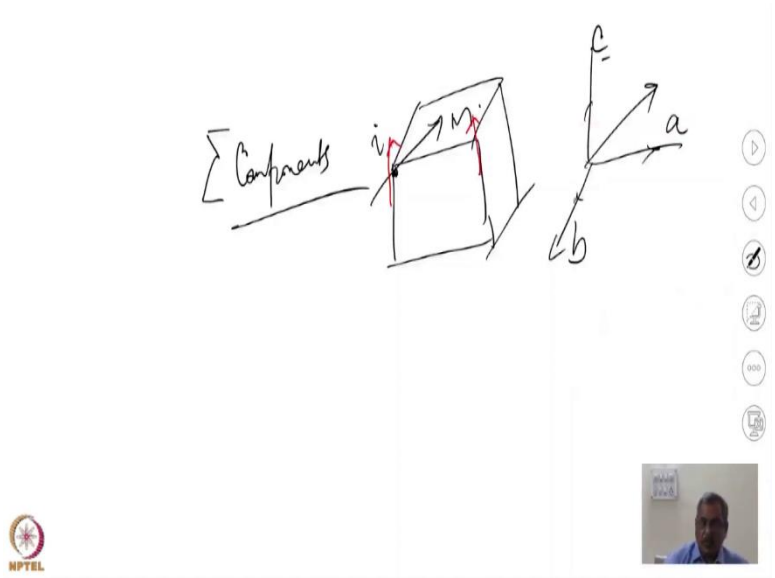

That means in this diagram, moments are in the [0 0 1] direction.

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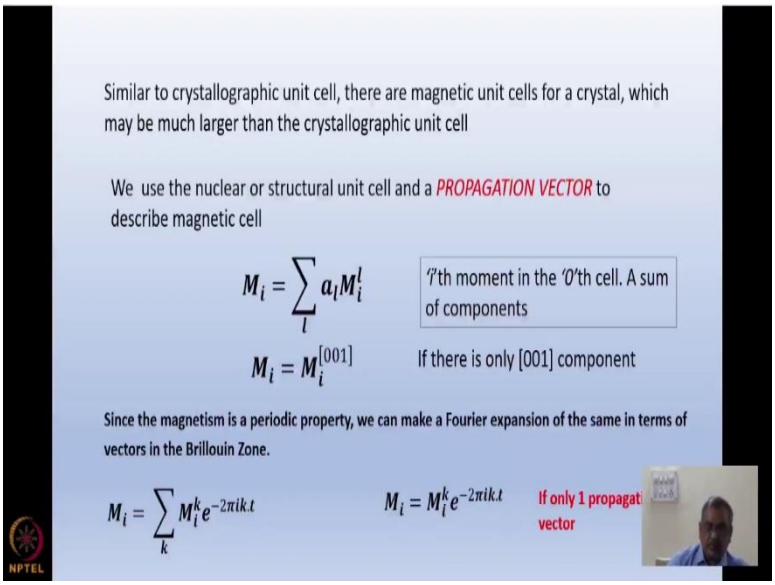

Then I can write magnetic moment as $M_i = M_i^{[001]}$. Since this magnetism is a periodic property, either it is repeating every unit cell, two-unit cells or may be thousand unit cells. From mathematics we know that for any periodic function we can do a Fourier expansion in terms of vectors in the Brillouin Zone. What is a Brillouin Zone?

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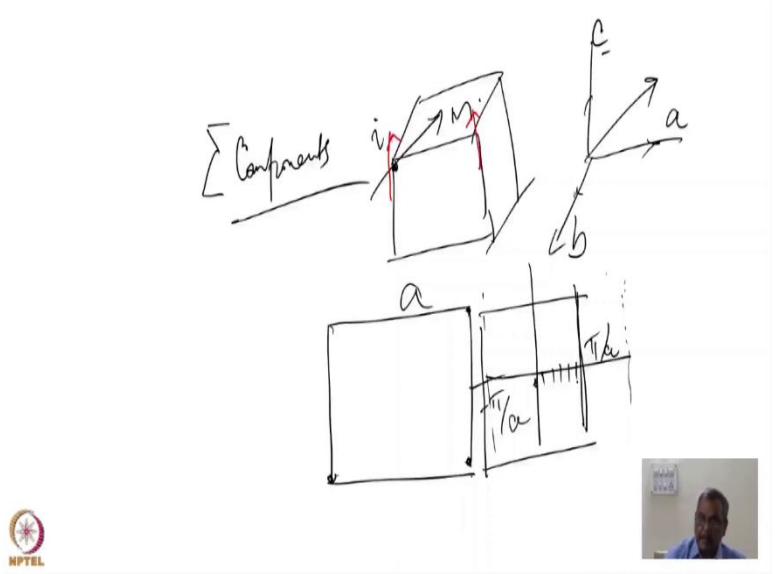

Let me just explain to you. If these are the nearest neighbors at a distance a, then in the k space, I can draw a line to the nearest neighbor in the reciprocal space at $2\pi/a$ and then draw perpendicular vector to that, and that is my first Brillouin Zone and this has boundaries at π/a and $-\pi/a$, if I take the origin here. This is known as a Brillouin Zone in reciprocal lattice space. So now, in this Brillouin Zone there are various values of allowed k vectors in a crystal lattice.

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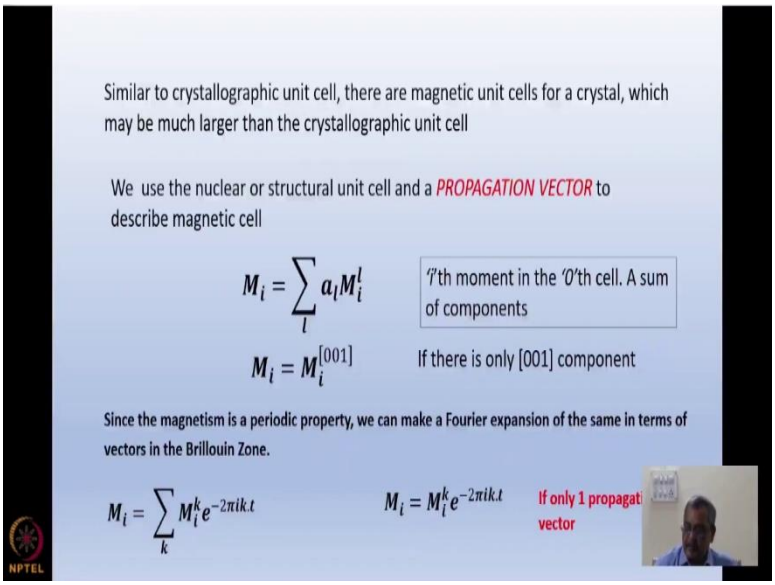

And I can write down the magnetic vector at a site in terms of its Fourier components $M_i^k e^{-2\pi ik.t}$, where k is that propagation vector and t is the translation. If there is only one propagation vector for the system then I can write it as $M_i = M_i^k e^{-2\pi ik.t}$, the summation will have a single component.

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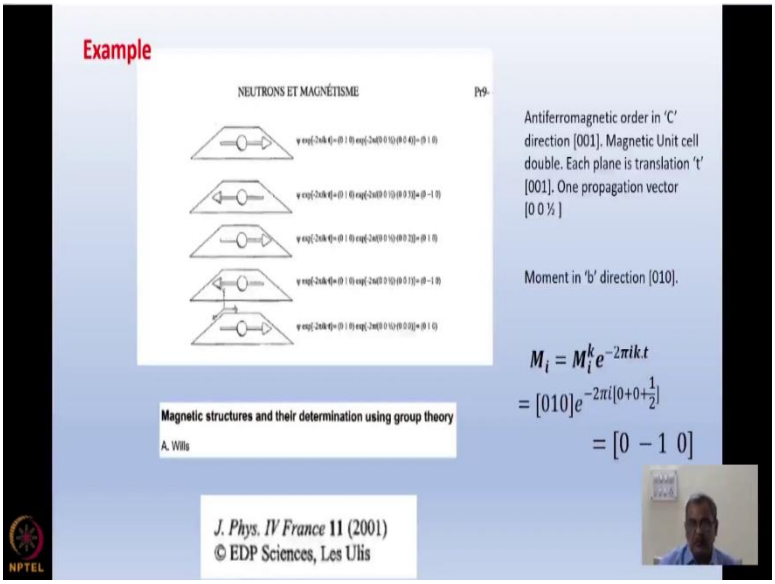

Let me just explain it with an example. I just take an anti-ferromagnetic order in one direction. This is a plane. And the direction of the magnetic moment switches between plus and minus from one plane to another as you go in '*c* ' direction.

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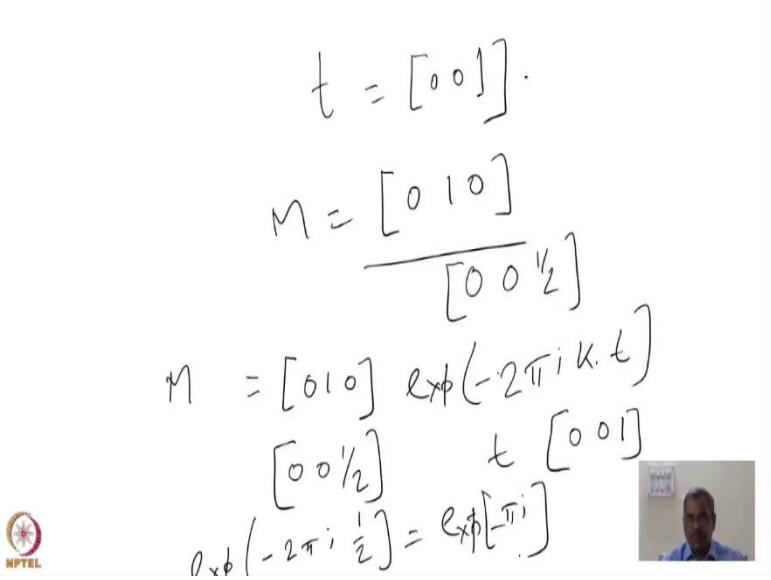

I am going in *c* direction, so, translation *t* is in *c* direction given by [0 0 1]. And moment is along the *b* direction as I showed in the drawing. So, I can write in some units this moment is [0 1 0]. Here, the moment is [0 1 0] and transition is [0 0 1]. Now, let us see, in this case when it is an anti-ferromagnetic alignment, if I take a propagation vector of 0 0 ½ then what happens after one translation? After one translation,

$$M = [010]e^{-2\pi ik.t}$$

With *k* = [0 0 1/2] and *t* = [0 0 1], exponential term becomes $e^{-\pi i}$.

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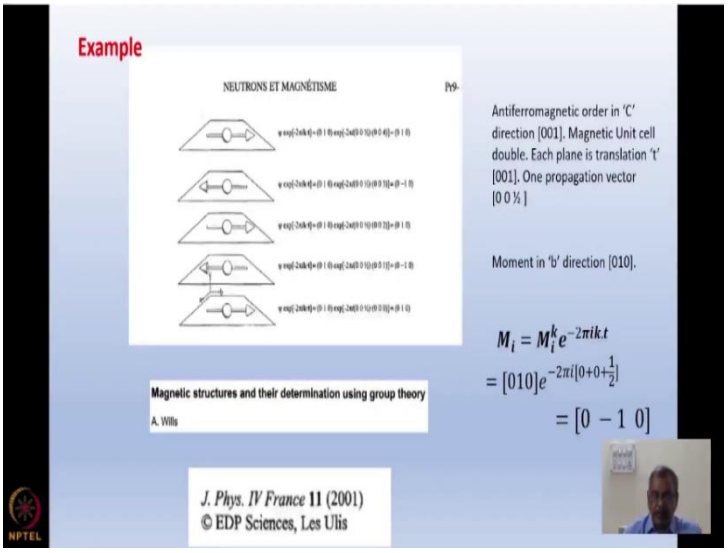

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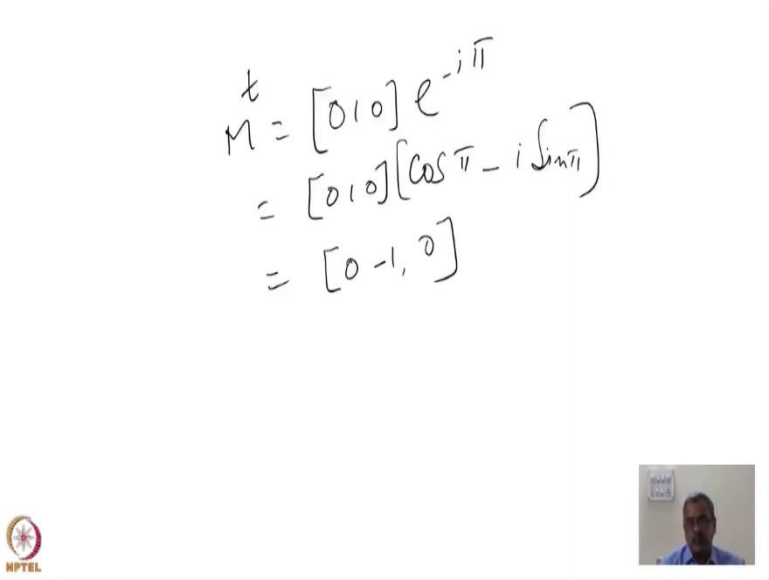

Here *M* becomes,

$$M = [010]e^{-\pi i}$$

$$M = [010][\cos\pi - i\sin\pi]$$

$$M = [0\ -1\ 0]$$

So, after translation of *t*, my magnetic moment has become [0 -1 0] from [0 1 0].

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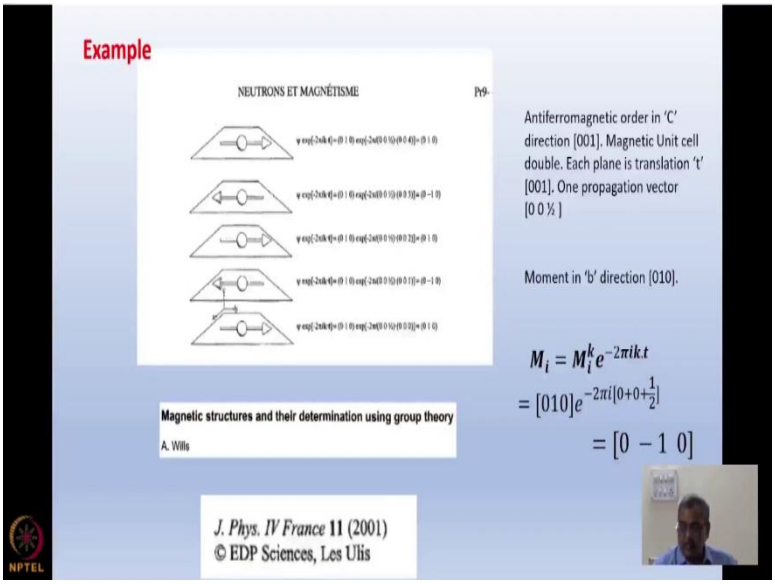

That is exactly what I have shown in the diagram in an anti-ferromagnetic order. So, given this magnetic propagation vector there is only one propagation vector here which is k = [0 0 1/2]. For this I could straight away guess, because it is very clear L became 2L, so k becomes 1/2.

Instead of 't' which is 1 unit translation, it is 2t now, my k is 1/2. Very easy to guess in this case,.I have taken it from this reference [given in transparency]. While you are fitting a magnetic sample data, we need to start with a guess of the propagation vector. I would say physically reasonable guess, which comes from knowledge in magnetic structures.

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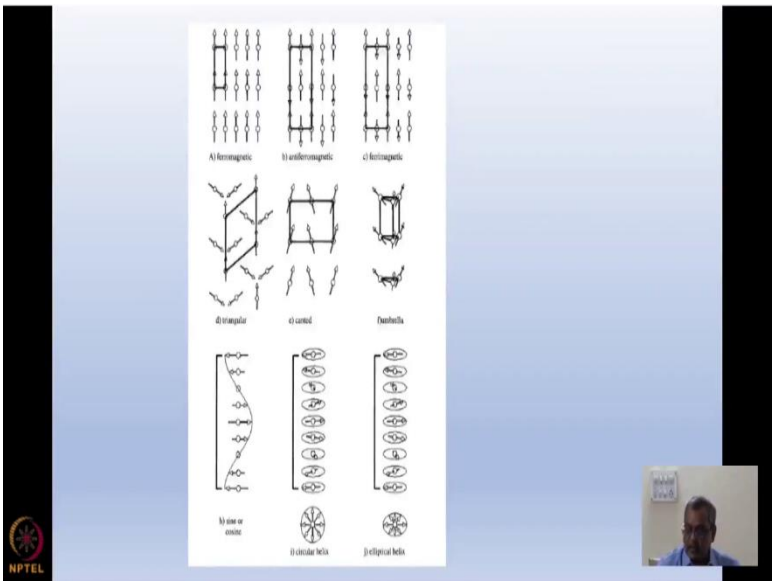

Like, I showed you here, various kinds of alignments. For example, this is a ferromagnetic sample. Here the propagation vector will be [0 0 1]. In the previous diagram what I showed

was for an anti-ferromagnet it is [0 0 1/2]. This is a ferrimagnet. Then with every '*t'*, I also have to add an αtt to account for the length change of the magnetic moment. That means the length of the vectors are also changing. Not just that they are changing in site they are also changing in size. Similarly another one is a triangular kind of lattice, it is a canted lattice. This is an umbrella kind of lattice where all of these vectors we have to represent in terms of *a, b, c* and then the propagation vector in terms of reciprocal lattice in the Brillouin Zone I can choose a set of *k* vectors which can give the values correctly.

I show a sin or cosine kind of variation here. Because this is a ferrimagnet, the length of the moment is changing. Similarly, these are circular helix, where as we go ahead in one direction, for simplicity in [0 0 1] direction, the magnetic moment gets rotating, and finally, comes back to its original direction after a certain number of lattice points and 2π divided by that will be the propagation vector for the magnetic moment,.. Then these are elliptic propagation. So, here the moment, is not only rotating, the size is also changing. There are various possible structures in magnetic crystallography that we can consider and that is the part of the game of solving a magnetic structure.

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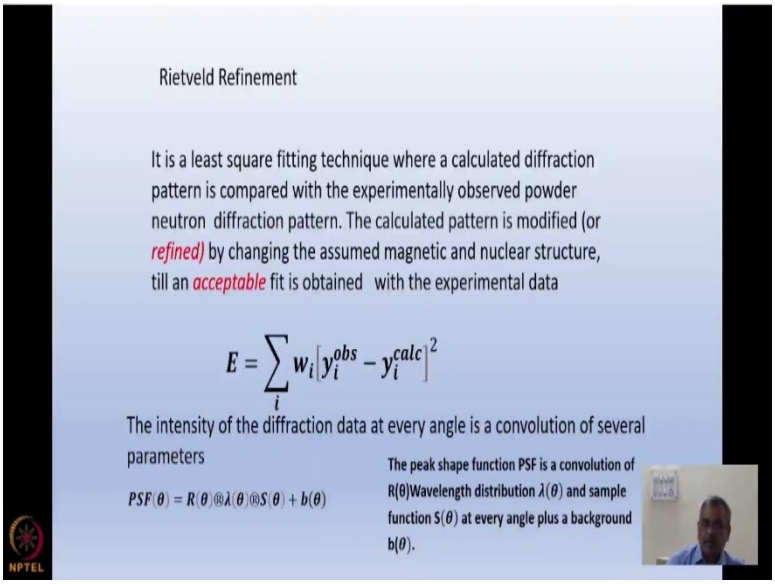

About Rietveld refinement what I want to say is that, it is a least square fitting technique; that means you start with an assumed diffraction pattern in hand.

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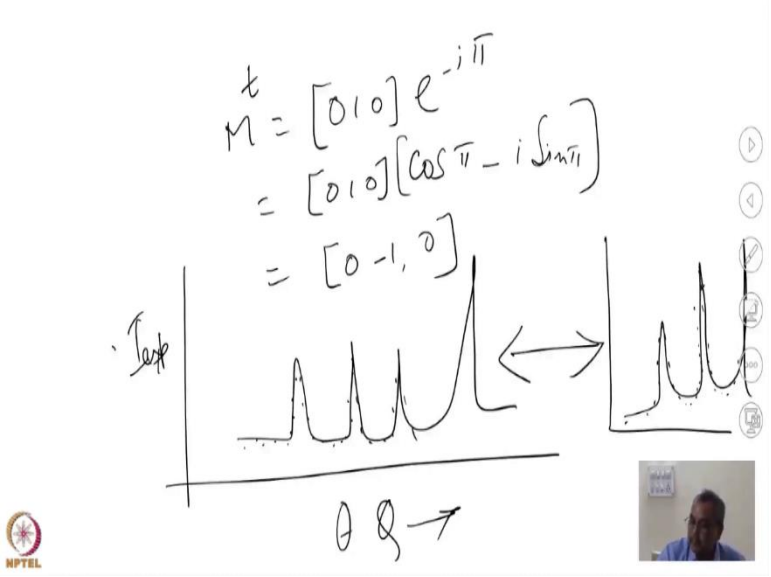

You have got an experimental diffraction pattern which you have measured at a certain temperature (intensity vs 'θ' or 'Q'). And on the other hand, you have got a calculated pattern and I have to compare these two. That means at every point where I have measured the data I also have a model data. I have considered a model and I have generated this and I am comparing these two patterns.

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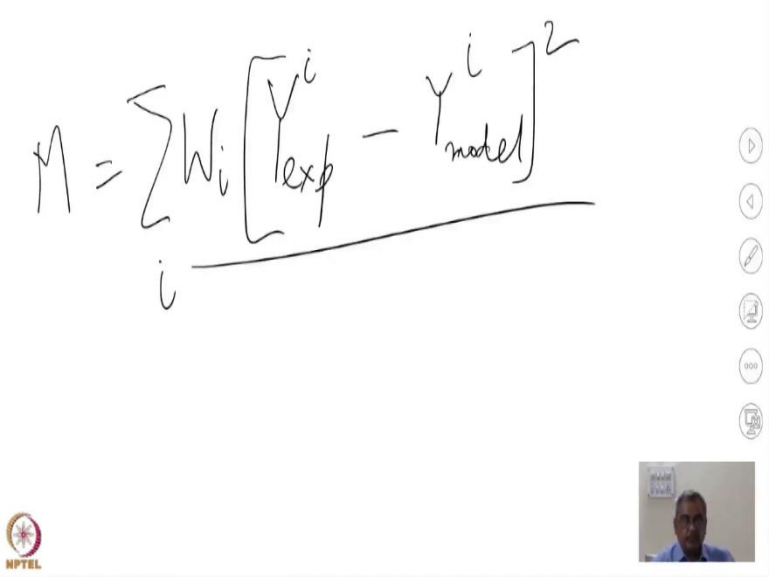

I have got y_{exp} and I have got y_{model}, and I have to minimize the values [y_{exp} - y_{model}] of them. There are many points, so you need to sum over those points *I*, $\sum_i \left[y_{exp}^i - y_{model}^i\right]^2$. If I want, depending on physical reasoning, I can put a weight factor over here $\sum_i W_i \left[y_{exp}^i - y_{model}^i\right]^2$. So, I have to calculate this difference [χ^2] and fundamentally this is the numerical comparison between data that I am using for my fitting.

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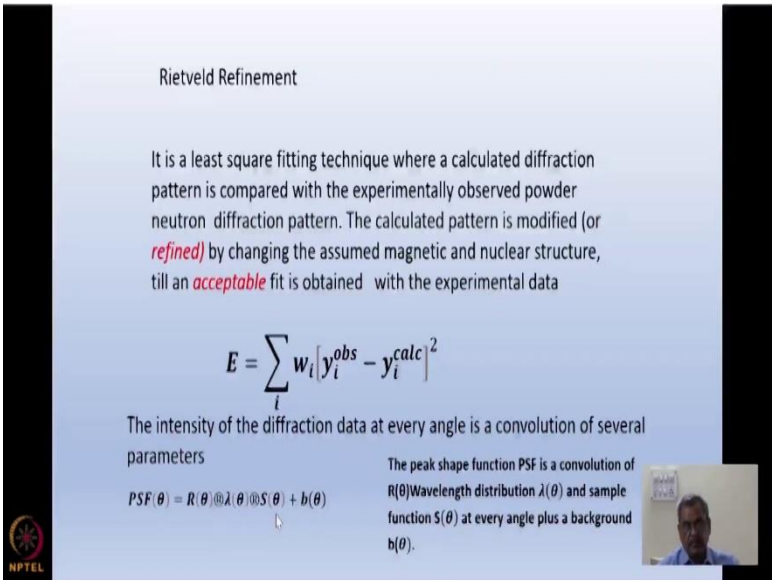

As I said, $E = \sum_i W_i \left[y_{exp}^i - y_{model}^i \right]^2$ it is a weighted sum of the difference between the observed or experimental and the calculated(model) value. The intensity of diffraction at every angle, again is a convolution of several parameters and is given by,

$$PSF(\theta) = R(\theta)\lambda(\theta)S(\theta) + b(\theta)$$

$R(\theta)$ is resolution, $\lambda(\theta)$ wavelength dispersion, $S(\theta)$ sample related part and $b(\theta)$ is the background at the specific angle.

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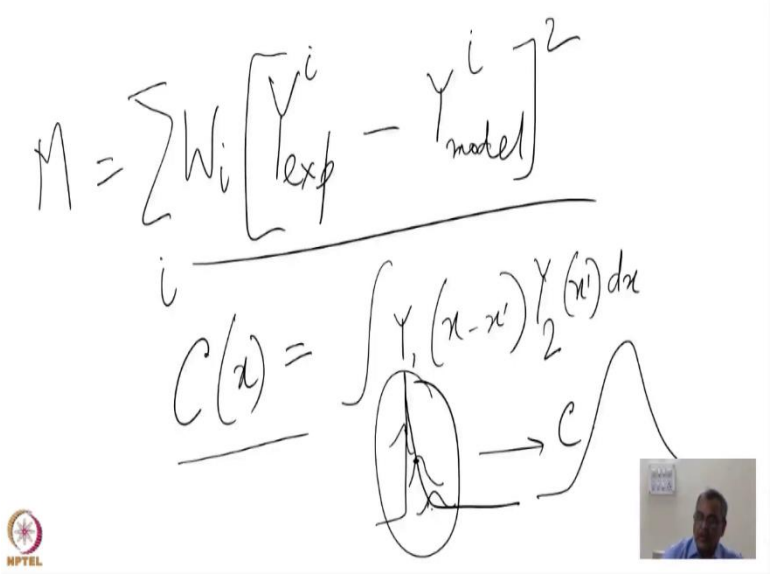

I must mention that convolution of two functions Y_1 and Y_2 at a point x is given by,

$$C(x) = \int Y_1 (x - x')\, Y_2 (x') dx$$

Experimentally suppose, I have got a peak like this. Now if my instrumental resolution is a Gaussian like this, then each and every point will tend to spread out based on that Gaussian and then I will have a broader peak, whereas this is the theoretical peak and this is the convoluted peak.

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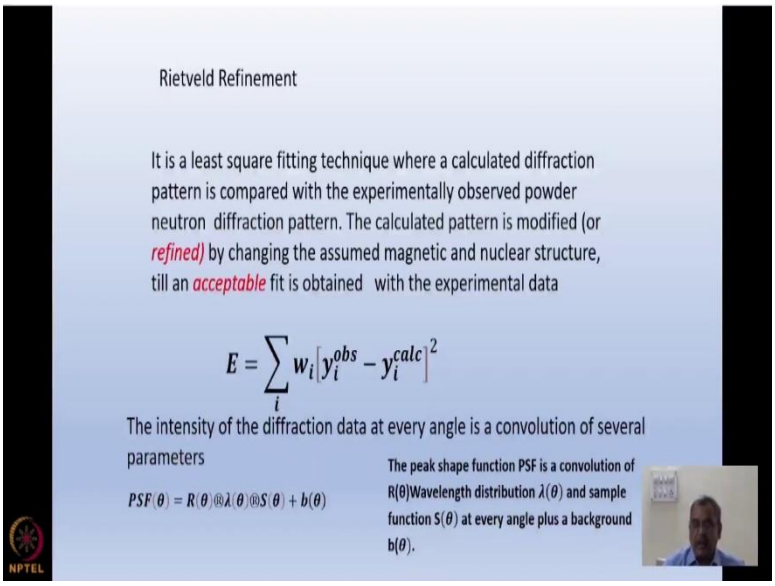

So, apart from these two over there when I wrote I have got resolution function, I have got a wavelength dispersion, because the wavelength of neutrons that I use is not unique. I use a

band of neutrons because I need intensity. If I try to make it monoenergetic then I will have very few neutrons. So, I have got a band off.

Then there is a sample; there can be a preferred orientation in the sample, there can be strain in the sample, if I know them, they also will cause broadening. There is a background, because anywhere I do the experiment there will be background neutrons and at every angle it will have a value.

The calculated value has to be convoluted with all these and then only I can compare the calculated value convoluted with all these with the experimental value. With this I come the end of this lecture. I have given a very general expression for the Rietveld refinement. But now I will tell you specifically what are the inputs in the next lecture,.

There are several tutorials available online which will give you the references and I will also mention, what are the important parameters, that need to be given in Rietveld refinement program. Let me emphasize once again that this is actually making a given model more and more commensurate with the experimentally observed pattern which is known as Rietveld refinement.

It was developed by Hugo Rietveld. The program name is FullProf and it is a very, very important program suit, which is used heavily for the magnetism. This is possibly the most important package in use today for crystallographic/magnetic structure determination. I will come back to Rietveld refinement in the next lecture. I will briefly mention some examples and then we will go ahead.