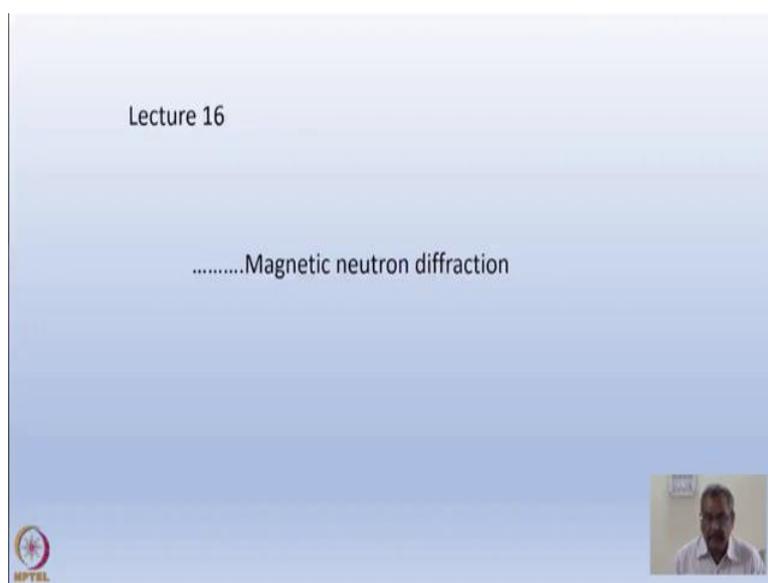**Neutron Scattering for Condensed Matter Studies**
Professor Saibal Basu
Department of Physics
Homi Bhabha National Institute
Week 6: Lecture 16 A

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In this lecture, we will continue with magnetic neutron diffraction. How we carry on magnetic neutral diffraction? Any diffraction, whether it is crystallographic or magnetic, needs pre-knowledge of a little bit of crystal symmetry and the space lattices.

I will introduce you briefly to that because otherwise this is a full-fledged subject in itself. but I will introduce you to the extent that you can use it for neutron diffraction. And then I will introduce you to some results that were obtained using neutron diffraction. With this I start today's lecture.
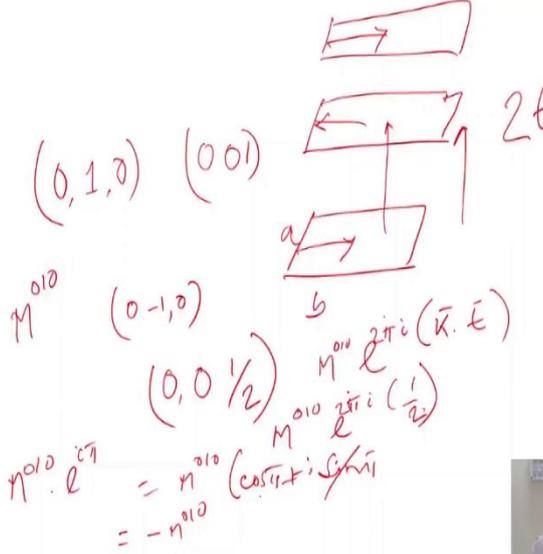
As I told you earlier Rietveld refinement, the technique that I can use for finding out the crystallographic structure, is an optimization tool. It is very important to understand that we are starting with a model structure and then we keep refining it till we get a good fit between the experiment and the model.

Good fit also depends on the error values that we have on the experimental points. That means we have to collect data for sufficiently long time to support one model or other. Running through the parameter space, the starting structure (model) should be good.

First it should be physically reasonable. As an example, and possibly a very bad example, is taking the starting guess for iron to be hexagonal close packing, because then I am too far away from the physical reality as iron has a bcc lattice. So, I should start with an assumption of a

bcc lattice and then I try to figure out the site magnetic moment. One needs to start with a crystallographic structure plus a magnetic structure when I am looking at magnetic neutron diffraction and microscopic magnetic structures like ferromagnets, anti-ferromagnets, ferrimagnets etc. To start with I need a propagation vector. In the last lecture I explained it to you with an example. I will repeat it.

I showed you that if I have a planar moment and if the planes are translated along the Z axis, calling this as a, this is as b, I defined the magnetism in some unit as [0 1 0] and the translation is along [0 0 1] direction. Earlier I said that once I translate it by one lattice plane it is an anti-ferromagnetic order and then in the next translation it comes back to ferromagnetic order.

This is a simple example. In this case, it was very simple to show you that magnetism, which I called $M_i^{[001]}$, goes to (0 -1 0), if I use a magnetic propagation vector, (0 0 1/2). And how I did it? It was $M^{[010]}e^{-2\pi ik.t}$ where t is the translation vector and k is the propagation vector, here 'k' is [0 0 1/2] and 't' is [001]. When I translated magnetic moment vector by [0 0 1] it became $M^{[010]}e^{-\pi i}$ and expanding $-M^{[010]}$. That is how I could choose a propagation vector because here the anti-ferromagnetism means the repeatability is $2t$, double the lattice spacing. So, it is very easy to choose the propagation vector [0 0 1/2], because I know that every time, I go one lattice plane (one d spacing) my magnetic moment reverts. But in reality, there can be more difficult or more complicated magnetic propagation vectors. Sometimes it may even require thousands of lattice planes to repeat and also there are cases where the structure is commensurate with the crystallographic structure.

That means, I start with 1 crystallographic lattice plane with a certain magnetic moment in a certain direction. After an integral number of lattice planes, I will come back to the same moment which will match with another lattice plane, maybe several or thousands of lattice planes away. In case of incommensurate magnetic structure, which is a more complicated problem, this structure, the magnetic structure is not commensurate with the crystallographic lattice structure and there will be some gap. I will discuss those things later.

Rietveld refinement is an optimization tool and one needs to start with a crystallographic structure and a magnetic structure; that means a magnetic structure, a propagation vector, site moments, etc.

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Tutorial on Magnetic Structure Determination and Refinement using Neutron Powder Diffraction and FULLPROF

Juan Rodriguez Carvajal

Now, how the process flows?
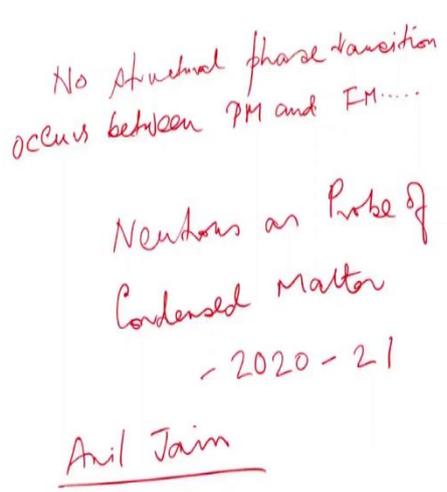
First a neutron powder diffraction above the ordering temperature will give me the crystallographic structure in the paramagnetic phase. This discussion is under the assumption that no structural phase transition occurs between paramagnetic phase and magnetically ordered phase. If that remains true, then I can take the data in the paramagnetic phase by going above the ordering temperature and get all structural parameters using FullProf.

This is equivalent to carrying out an x-ray diffraction on a crystallographic powder sample. Only here the difference is that the scattering amplitudes are different for x-rays and neutrons, otherwise you should get the same pattern and both of them (x-ray and neutron) in this case, the neutron powder diffraction pattern can be solved using the suite of programs called FullProf.

In this regard I must again tell you that in case you are interested in a full-fledged tutorial on FullProf to solve magnetic structures please look for the lectures by professor Anil Jain in a course on Neutrons as Probe of Condensed Matter taken between 2020 and 2021. And I point out that the lectures taken by Anil Jain and Professor S. M Yusuf, where a full-fledged tutorial was done how to fit a magnetic structure using FullProf.

After collecting the data above the magnetic transition, now we cool the sample and collect again neutron powder diffraction data below the ordering temperature, that means, when the sample is magnetically ordered. If the magnetic order is commensurate with the structure, for crystallographic structure like a ferromagnet we will have additional intensity at the ferromagnetic peaks.

So, if there is a crystallographic peak above order temperature, I will show you, there will be added intensities because of the magnetic order. If it is anti-ferromagnetic then new peak will appear in this intensity versus q data. Not only you will have the crystallographic Bragg peak below ordering temperature but also magnetic Bragg peak. This is when your order is anti-ferromagnetic. This happens because for anti-ferromagnetic order, in the simplest picture, the unit cell has doubled causing θ reducing to $\theta/2$. Because from Bragg's relation, $2d \sin\theta = n\lambda$, we also get peak at $\theta/2$(for smaller angles $\sin\theta \sim \theta$.

When you start the program, the first thing is to determine the propagation vectors for the magnetic structure by trial and error, and once the propagation vector has been determined, the program BASIREPS is used in order to get the basis vector of the irreducible representation. There is a lot of technical jargons.

Basically, the symmetry operations of a crystal they form a group. Group means, combination of any two symmetry operation A and B, gives rise to another symmetry operation C, which is also in the group. That is why they form a mathematical group and there is a unit operator which does not make any change in the system.

For an irreducible representation I can always represent the symmetry operations by a matrix. For example, a rotation we know can be denoted by Eulerian matrix, a rotation around an axis by theta. Now if I consider a 90-degree rotation then this will be a matrix representation of that symmetry operation.

The irreducible representation is one which cannot be broken down into further representations. We may say this is the smallest size representation.

This flow I have taken it from a tutorial on Magnetic Structure Determination and Refinement using Neutron Powder Diffraction and FullProf by J.R Carvajal available at this is the site. If some of you are interested you can also take help from this tutorial. This is how the process flows. But now it is important that before I go further even if briefly, I introduce you to the symmetry operations.

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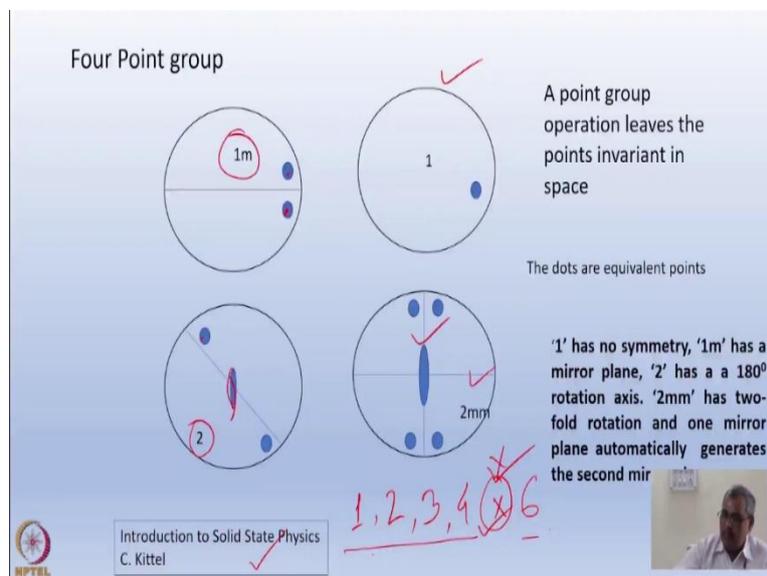
Here, I have taken the example from Introduction to Solid State Physics by Kittel. This figure just indicates 1-fold symmetry. It leaves the point invariant, but imagine now in this same diagram I have got an object here and I have got a mirror plane. When I have a mirror plane perpendicular to this, then this object is reflected onto this side and then I call this symmetry operation as 1m.

Now I can also invoke a rotational symmetry. A point group operation basically means that the operation leaves the points invariant in space. So, here if I have, let us say two oxygen atoms, at these two points inside this circle in some structure then they have got 1m symmetry i.e a reflection symmetry. Similarly, here I show you a rotational symmetry. This is a two-fold rotation because if I rotate around this axis, axis passing through the center of the circle 180 degree, the point goes here. From here it goes there. And if these are the two atoms sitting here, then this system or this structure remains unchanged through a rotation of π or a two-fold rotation.

Next, I have taken one more example. Here there is a two-fold rotational symmetry around this axis. You can see, plus I have used two mirrors; mirror 1, mirrors 2, normal to the plane. Now interestingly you can see if I use one mirror after rotation, we have got these four points and this automatically gives rise to the second mirror. So, this justifies my argument that two symmetry operations in a group invokes a third operation.

Here 2m invokes another mirror plane and mirror plane is represented by m. Rotations are invoked by 1, 2, 3, 4 and 6, because we have learned that we can fill space through translation with these rotational symmetries. A rectangle, a triangle, a square, a hexagon can fill space but a pentagon cannot and that is why we say that the possible rotations are 1, 2, 3, 4 and 6, but 5-fold symmetry in solid is not possible.

The cover page of this book also showed why pentagon cannot fill space. But today we know, here as an information for you that even if we consider pentagons we can fill space though not with transitional symmetry, but still we can fill space. Because that is the target, that using a crystallographic unit cell, by repeating the unit cell we should be able to fill up space.

That is how you can create a crystal which has, which I can see has millions of such unit cells. Today this is also accepted that 5-fold symmetry is possible. This group of crystals are known as Quasicrystals. But in this lecture, I will retain the old rules that 1, 2, 3, 4 and 6 folds symmetries are only allowed.
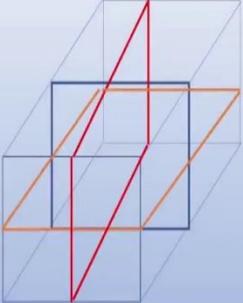
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And then what are the 32 point groups in crystallography? These are combinations of symmetry operations, given the symmetry of a unit cell in a crystal. Let me just do it for a cuboid.

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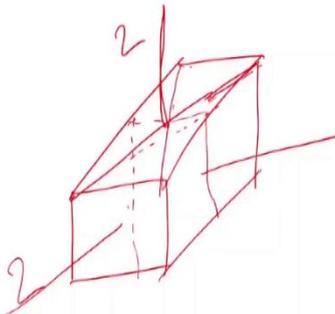
In this cuboid, please note that this is a 2-fold axis, that means I can rotate it by 180-degree around this, passing through the intersection of the diagonals in the plane.

There is a 2-fold axis around this because 180-degree rotation will leave the parallelopiped unchanged. I have one more axis at the intersection of these two diagonals in this plane and one more here. So, there are three 2-fold axes, but interestingly normal to these axes, I also have mirror planes.

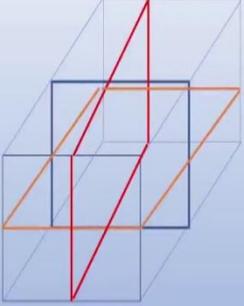You see this is one mirror plane normal to the axis on this face. This one is one mirror plane, which is normal to the vertical axis and this is one more mirror plane normal to this axis. So, there are 3 mirror planes. Tha means I have got three 2-fold axis and 3 mirror planes and the mirror planes are normal to the axes.

This is the international convention and if you are planning to do structural analysis using Rietveld fitting, you should know that. For this it is 2/m 2/m 2/m, so, and also you can see that combination of any 2 of the symmetry operations here will get back us to one more symmetry operation. So, 2/m 2/m 2/m is the international convention to present symmetry operations of a cuboid. There are several conventions one of them is this.