Keywords: Bravais lattice, Crystal class, Point groups, Screw Axis, Glide plane, Shubnikov group, Primitive Unit Cell, Non-primitive Unit Cell, Neutron Depolarization

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Let us consider a cubic crystal. Note that this figure is from Introduction to solid state physics by Kittel. To form a crystal, we need to have a lattice with basis atoms or molecules at each lattice point.

The most symmetric structure in crystallography is a cubic structure. Please see that there is one plane here. Now, the thing is that there are also other planes which I can draw like this. But I can also create those other planes by a symmetry operation. So, I consider those which are inequivalent. There is one more mirror plane along the body diagonal. There are three 4-fold rotation axes. Then there are four 3-fold rotation axes which are along the body diagonals.

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This is the figure of a cube. There are three 4-fold axis. Then when I add the body diagonals, because there are eight corners, four diagonals and the rotational symmetry around the diagonals are 3-fold. Also, if you join center point of opposite edges then I will get 2-fold axes and there are six of them (because there are 12 edges). These are the rotations that I have shown here. In summary, there are three 4-fold rotations, four 3-fold rotations and six 2-fold axes. But all of these are actually connected by symmetry operations with each other.

I can generate another symmetry axis from one axis by some symmetry operation. Also, there is a center of inversion where all the diagonals meet. I can do an inversion operation.

An inversion operation means x, y, z will be going to -x, -y, -z or in crystallography they are written as $\bar{x}, \bar{y}, \bar{z}$. In inversion operation there is a point of inversion at the center, so, there is an inversion symmetry, for a cube.

For cube, it is given as 4-fold axes perpendicular to mirror m, a roto-inversion axis is a rotation as well as inversion operation which is there and 2-fold axes which cannot be created from this 4-fold axis by a symmetry operation. That is why we write it separately along with a perpendicular mirror that you can see.

So, the international representation is $\frac{4}{m} \bar{3} \frac{2}{m}$, for a cubic crystal. This is important to know. But actually, when we do the fitting, we do not go through it, we simply use the published tables.

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Introduction to Solid State Physics
C. Kittel, 5th Edition

These are the 14 Bravis lattices which gives all possible crystallographic structures in known world of one-, two-, three-, four- and six-fold symmetry.

There are triclinic, monoclinic, orthorhombic, trigonal, tetragonal, cubic and hexagonal unit cells. And for example, that most symmetric one is cubic and then cubic crystal has also got either simple cubic or bcc cubic or fcc cubic non-primitive unit cells.

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Here, I have introduced one more fact with respect to lattice and basis, known as primitive and non-primitive crystal lattices. In a primitive crystal lattice, if you take one unit cell, there is one *equivalent* lattice point. If you take a simple cubic structure, there will be one equivalent unit/atom in every unit cell. How it comes?

If you consider a cube, there are eight corners and each corner is shared by eight of these unit cells. So, $\frac{1}{8} \times 8 = 1$, it gives me one unit of atom (or molecule, whatever forms the basis). Now, if put an atom at the body center also which is often the case then I have got one coming from the corners atoms and one coming from the central atom and there are two equivalent atoms in a bcc lattice.

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When I come to fcc lattice, then this cube has the corner atoms as well as one atom at the center of each face. Now, you can clearly see from the geometry that the one which is at the center of each face is shared by two of those unit cells. So, each unit cell one has got 1/2 atom. And there are six faces. Then you get three atoms coming from the face-centered positions and one atom coming from the corner positions. So, there are four atoms in an FCC unit cell. Not only I have got primitive cubic unit cell but I also have face centered (fcc) or body centered (bcc) lattices.

The way we define a cubic cell is $a = b = c$ and all of the angles are 90 degrees. When it goes slightly off, so that $a = b \neq c$ with all the three angles 90 degree, it is a tetragonal unit cell. Now, in case of cubic, point symmetry and the translational symmetry allows me to have simply cubic, body centered cubic or face centered cubic lattices.

In case of tetragonal cell, it is only body center that is allowed for non-primitive cell. Accordingly, I have shown the table, which actually has been derived from point group symmetry, on the requirement of translational symmetry and worked out by the mathematicians and the crystallographers These are the possible unit cells which are known as Bravais lattices. There are 14 Bravais lattices in condensed matter.

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Along with that you have got 32-point group symmetries. I have explained to you what are the point groups and here I have given the table, I do not have time to explain all of this, but let me just consider one, let us say, cubic, which is easy to see. The symmetry operations are given here.

Symmetry elements are given here according to the elements on the left. This table is used heavily by us while refining data using Fullprof.

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14 Bravais lattices and with -point groups give us total 230 space groups in crystallography. There are two more symmetry operations I need to tell you. With translational symmetry, we have something called screw axis and glide planes. So, it is not just point groups, together with 14 Bravais lattices we also have to consider screw axis and glide planes. What are they?

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I will quickly tell you. Let us see along with translation, if a rotation is there, for example, here you see. Take this atom 'a'. Actually, these are all atoms or units. It can be a molecule also which I am putting at this point. So, you see, there is a translation of c/4 and a rotation of 90 degree.

Another translation of c/4, with another rotation of 90 degree, gives position 3, another rotation of c/4 and the rotation of 90 degree, takes me from 1 to 4 identical positions in the unit cell or in the repetitive unit cell. Here, not only I translate the unit but I also rotated like a screw that is why it is known as a screw axis. Translation associated with rotation is known as a screw axis.

Similarly, I have taken a simple example of a glide plane, the sources are indicated in the transparency. You can see, instead of rotation, if I move in a certain direction and I reflect. And I reflect then you see it is a half a translation reflection the unit is shown as a I can say as a small engine. So, the engine reflected below the plane. It can be a molecule. Actually, it is available in case of molecule. Then again, another half translation and another reflection in the glide plane. The glide plane is shown here. So, that means you translate and rotate, you get a screw axis. You translate and reflect you get a glide plane.

There is an inherent difference between these two. In case of screw axis, if you put a molecule then it maintains the handedness of the molecule. But in case of glide plane, the translation and reflection do not maintain the handedness. And there are cases, where in crystallographic structures such operations happen.

Screw axis and glide planes are the last two symmetry operations that give us the all 230 space groups we know. But ultimately, after talking about all these things, all we need to give as an input is a space group classification, when we try to solve the crystallographic structure.

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Now, in addition to the crystallography space group, there are magnetic space groups, that have an extra dimension. Because we also add another axis: *'time'* and there is a time inversion symmetry operation and reflection around the time axis is allowed. This is because I know that in the simplest explanation, current gives you magnetic field. But current is dq/dt which goes to -dq/dt, if I do a time inversion. So magnetic field does not have *'time-inversion symmetry'*.

Like all other Newtonian motions, the magnetic field does not have time inversion symmetry and that has to be accounted for when I input my data for solution of a magnetic structure. So, in a magnetic space group, each site has a spin, colored black or white say and time inversion or time reversal will interchange them in a magnetic space group.

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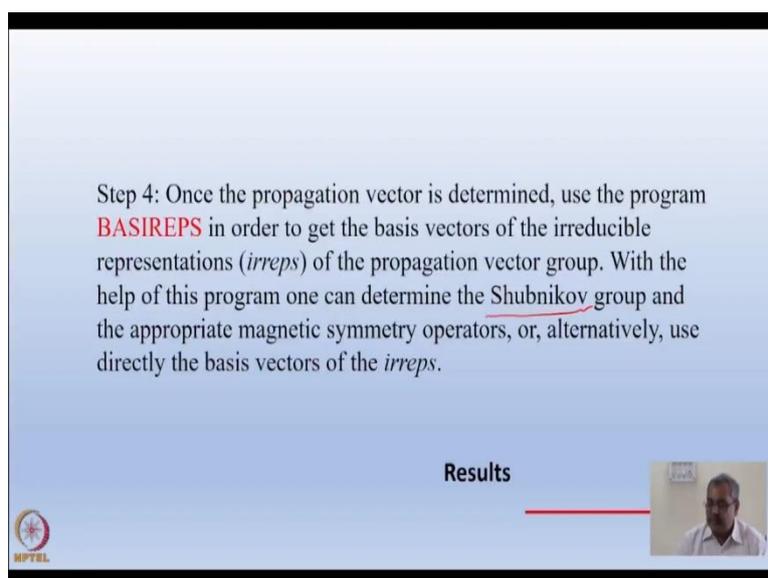
Now, I come to the fourth step in the process of obtaining magnetic structure. But this you need to actually learn through a tutorial. Once the propagation vectors is determined, crystallography structure is determined, the program BASIREPS gives us the basis vectors of the irreducible representation. These are the basis vectors with which we can generate any translation along with the propagation vector.

With the help of this program, we can determine the Shubnikov or the magnetic symmetry operators. Shubnikov, a Russian scientist, who first introduced the magnetic symmetry operators and used them directly as the basis vectors in the irreducible representation of the crystallographic group.

After talking to you about the procedure, how you input the magnetic structure as well as the crystallography structure for determination of magnetic structure, I will come to some of the results, very interesting result, unique to neutron diffraction.

We have discussed the genesis of symmetry operations, the space groups coming from the point group operations and the 14 Bravais lattices, in case of condensed matter crystallography. Now, I will share with you some of the very interesting results, so that you understand the importance of the technique and the capability of it to probe actual magnetic structures.
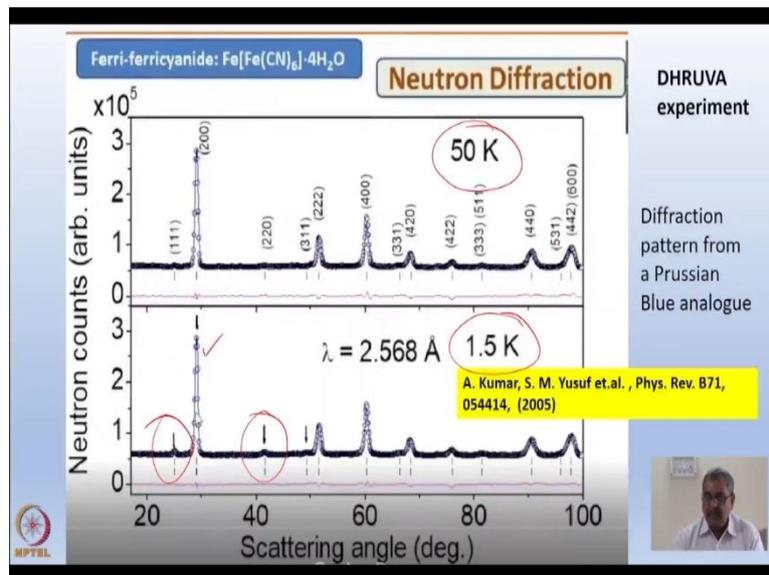
First, I will talk about a compound which is known as a Prussian blue analog, experiment done in our group in neutron diffraction. Now, why I choose this example? I have chosen iron compound because, iron is a ferromagnetic material as an element. It is well known. But look at the structure that you obtain in neutron diffraction, when you use a compound of iron and iron cyanide. For this compound, $Fe[Fe(CN)_6].4H_2O$, this is the diffraction pattern. Here the data is taken at 50 K, above the ordering temperature and then below the ordering temperature at 1.5 K.

Interestingly you see extra peak intensity appearing in these places. This is a diffraction pattern which immediately tells you that certainly, it is not just a ferromagnetic material. Because in case of ferromagnetic material, the intensities only boost the already existing Bragg peaks. But you have got extra peaks here and this has been fitted by using the Fullprof suite by the authors. I have mentioned the reference in the transparency.
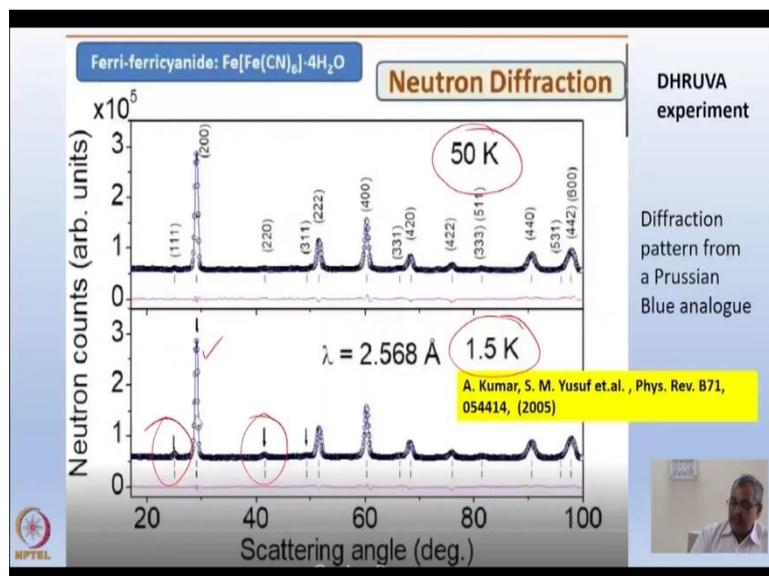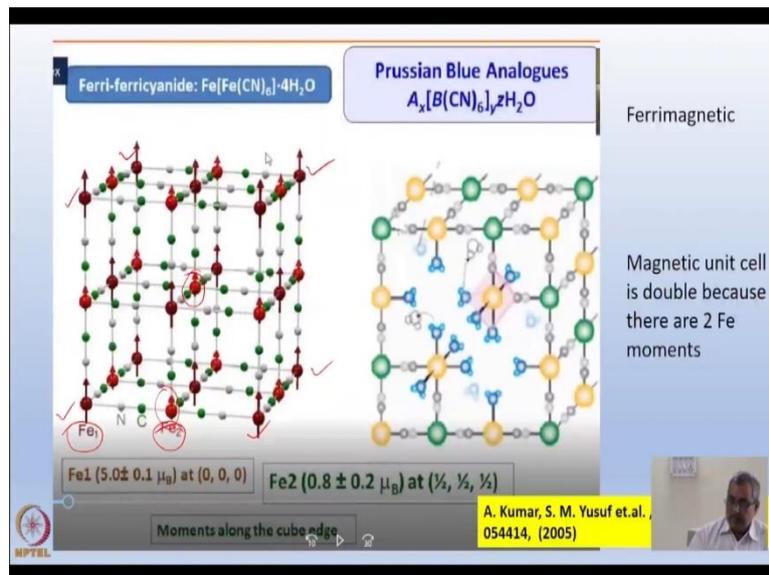
And note the structure that you obtain, the microscopic structure, from the fit. Here in this structure, the magnetic unit cell is double of the normal crystallographic unit cell. Because, here in this compound, there are two irons Fe1 and Fe2 and their magnetic moments are absolutely different.

One Fe has got a magnetic moment of 5 μ_B Bohr magneton which is located at (0 0 0) but the other one at (½ ½ ½) has got a magnetic moment of 0.8 ±0.2 μ_B. It is very much lower but they are aligned ferromagnetically or I should rather say that they are aligned parallelly with each other. But the magnetic moments are different from one site to another and that is why the magnetic unit cells are doubled.

At the edge of this magnetic unit cells, you can see, these are the irons which have got high moment and this is the iron moment which is lower. These two together comprise the iron lattice. And this is a unique result and this you cannot obtain by any other technique.

I started with an iron lattice. I do not know their starting point of the calculation or the optimization but ultimately at the end, the results that fits best this diffraction pattern gives me two magnetic moments at two iron sites aligned parallel. So, magnetic unit cell has doubled and they have got a parallel structure similar to antiferromagnetic structure because the local moments are different.

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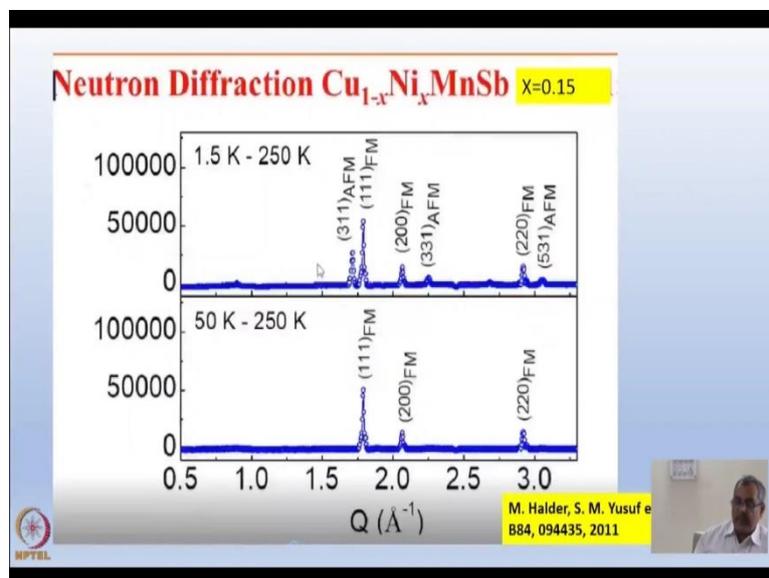
I will take another example for you. This is the neutron diffraction pattern of $Cu_{1-x}Ni_xMnSb$. This is a pattern which gives us ferromagnetic as well as antiferromagnetic peaks. So, this compound again starts with simple magnetic moment of nickel. Nickel metal we know is again a ferromagnet, , with 0.54 μ_B for a nickel atom., But here, the ordering of Ni, in this compound is different. Here, we have got coexistence of ferromagnetic and antiferromagnetic order.
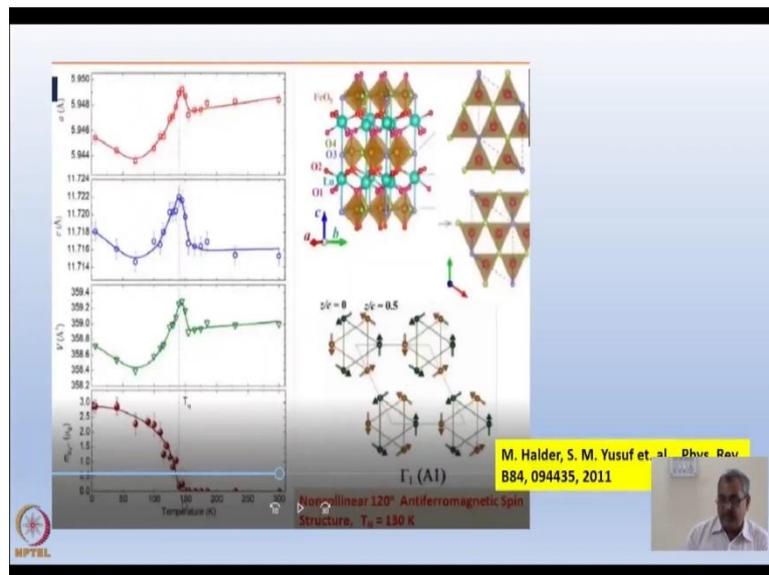
I just show you the fitted results. Here the antiferromagnetic spin structure comes from the orientation of spins here. You can see that the crystal structure here and there are octahedra in the structure. If you form an octahedra here and at the center you have the atoms. You can see the spin alignment which have been fitted and there is a 120-degree relative orientation spin structure.

When relative orientation is 120^0, you always have a component which is antiferromagnetic and a component which is ferromagnetic with respect to spin alignment. And in this case, interestingly, when we fit the crystal structure then we find that there is also a distortion from a cubic structure. You can see this is the magnetic moment versus temperature. So, this is the phase transition point where it goes from order to disordered structure. This matches with the change in a and c parameters of the crystal lattice.

This magnetic phase transition is associated with the change in the volume of the unit cell. That means, if you remember, when I was calculating J_{ij} which is the exchange integral, it changes with inter-moment distance. It changes in such a manner here that you get an antiferromagnetic order together with a change in the volume, a and c parameter of the unit cell. So, basically, the cell expands with temperature. You can see that at this point it suddenly expands. Also a and c both shows a tendency to expand. This is a very interesting result. We have got a Neel temperature of 130 degree for this compound.
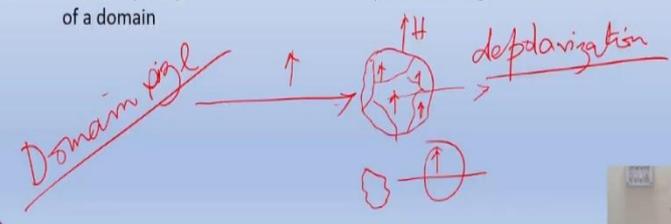
I just discussed with you two examples to elucidate results of magnetic neutron diffraction. If one goes through the literature, there will be thousands of papers on this sybject. All the major

neutron sources like ILL Grenoble or Oakrigdge SNS and also our own reactor Dhruva have a very large number of research programs, going on magnetic materials. Not only because, our interest in the fundamentals of microscopic magnetic structure but also because of their macroscopic physical properties are of interest for magnetic memories and many other applications.
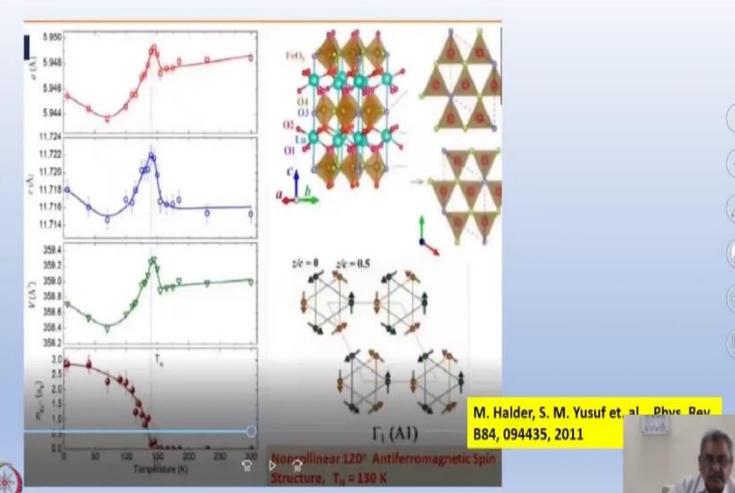
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Neutron Diffraction $Cu_{1-x}Ni_xMnSb$ X=0.15
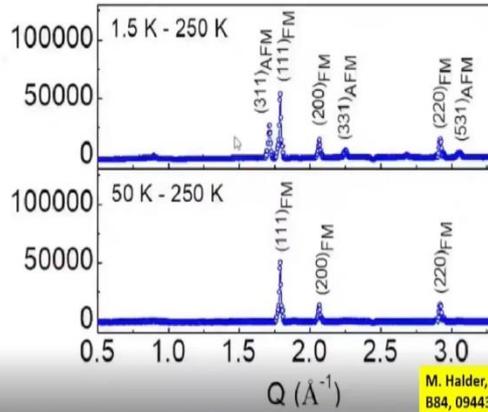
M. Halder, S. M. Yusuf e
B84, 094435, 2011

Ferri-ferricyanide: $Fe[Fe(CN)_6]\cdot4H_2O$

Prussian Blue Analogues
$A_x[B(CN)_6]_y zH_2O$
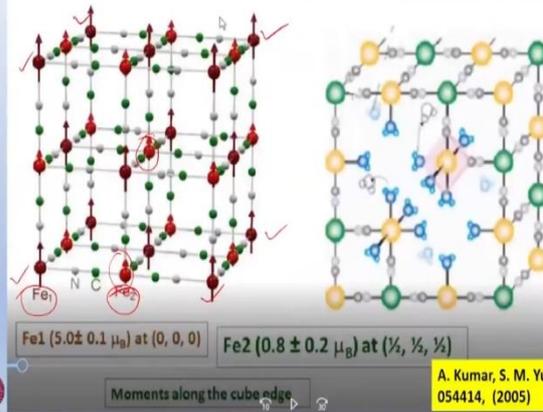
Ferrimagnetic

Magnetic unit cell is double because there are 2 Fe moments

Fe1 (5.0± 0.1 μ_B) at (0, 0, 0)   Fe2 (0.8 ± 0.2 μ_B) at (½, ½, ½)

Moments along the cube edge

A. Kumar, S. M. Yusuf et.al.
054414, (2005)

Ferri-ferricyanide: $Fe[Fe(CN)_6]\cdot4H_2O$ Neutron Diffraction
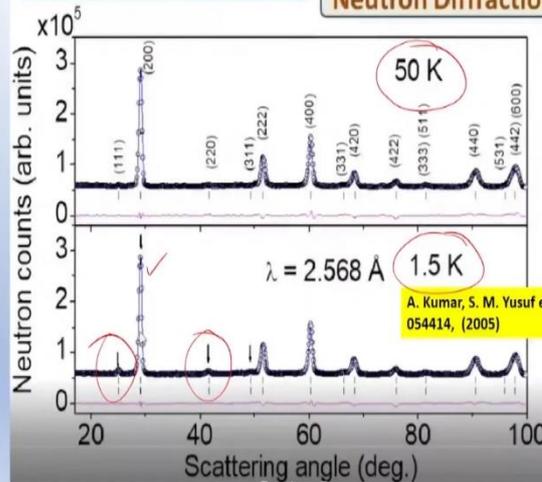
DHRUVA experiment

Diffraction pattern from a Prussian Blue analogue

$\lambda = 2.568$ Å   1.5 K

A. Kumar, S. M. Yusuf et.al. , Phys. Rev. B71, 054414, (2005)

I will just briefly mention one more technique here to complete the magnetization measurements using neutrons. There is one more tool known as neutron depolarization technique. Neutron depolarization technique depends on precession of a polarized neutron beam around the field in the sample or rather the field in a magnetic domain. I will try to explain this. It is a transmission measurement.

 Here, I do use a polarized neutron beam. Let me that all these experiments that I presented to you, we used unpolarized neutron beam. But for depolarization experiments, we need a polarized neutron beam. We apply magnetic field on a sample. There are domains inside the sample, magnetic domains. And they are aligned with an external applied field H and lie in the path of the neutron; the domains force the neutron moment to undergo precision. And this precision causes depolarization of the neutron beam. A loss of polarization of the neutron beam we measure in this experiment. This is an excellent technique to get an estimate of the domain size. This was introduced by Theo Retvelt at Delft reactor, Netherlands to find out the domain size in, '70s and this has also been used very successfully in Dhruva. If time permits, I will try to show you some of the results done at Dhruva. With this I come to an end for the lectures on magnetic neutron studies for understanding condensed matter structure.