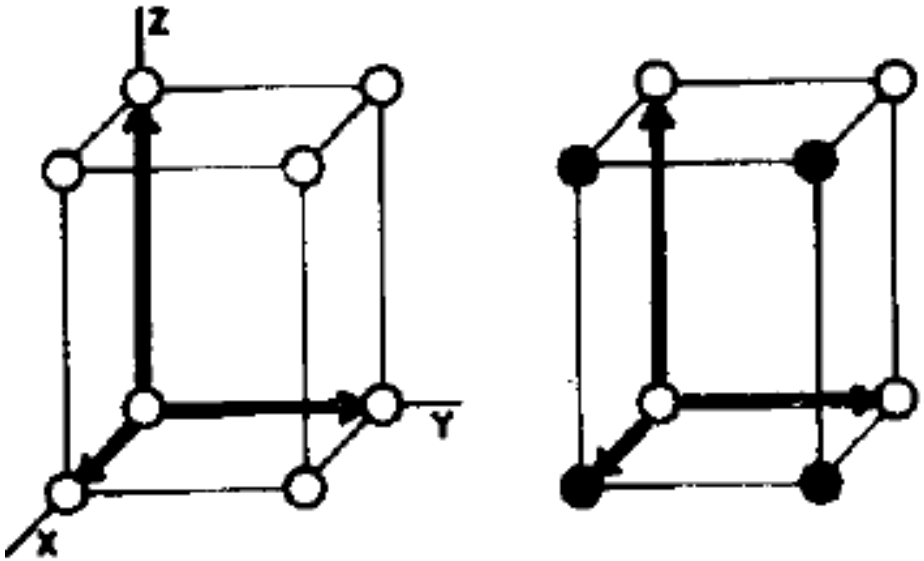
Magnetic ordering, as indicated by the name, refers to the ordering of the magnetic moments (i.e. spins). Since the magnetic moment or the spin comes from the electrons of atoms, therefore obviously the ordering of magnetic moment relies on the atomic arrangement of the system. However the magnetic ordering is not always the same as the atomic arrangement, and the reason is simple since for the magnetic moment, we have not only the position of the magnetic moment, but also the orientation of the spins. Even more, we also have the relative orientation of different magnetic moments sitting on different sites, i.e. the propagation of the magnetic moments. Generally, the magnetic ordering can be divided into two main categories – commensurate and incommensurate ordering, which we can always come across during literature review. Simply speaking, the so-called commensurate magnetic ordering can be built up based on the nucleus structure. In mathematical word, the group of magnetic symmetry for the commensurate ordering can be built up based on the group describing the nucleus ordering symmetry. There are three main classes for the commensurate magnetic ordering. The first one is the most simple one, which is actually just no magnetic ordering. Such a situation is called colorless, and the group of the magnetic symmetry in such cases is exactly the same as the symmetry of the nucleus structure. The second situation is also quite simple, which is the paramagnetic ordering, Where we have all the magnetic moments aligned up in the same direction, and such Situation is called “grey” (the corresponding groups are called “grey” groups). The third situation is a bit complicated where we have the alternating ordering of the direction of the magnetic moments. A typical example is the antiferromagnetic structures, where the neighboring magnetic moments are aligned up in opposite directions.

In such situation, the magnetic lattice is no longer the same as the nucleus structure, since by simply following the symmetry operation corresponding to the nucleus structure, we cannot build up the alternating arrangement of the orientation of the magnetic moments. For example, in the picture shown below, the one on the left-hand side is the nucleus Structure and the one on the right is the magnetic ordering where the white and black colors represents the different orientation of the magnetic moments. Obviously we can see that the repetition unit of the magnetic ordering should not be the same as the nucleus structure. However, in the a-direction, if we double the nucleus lattice then we will get the unit lattice for the magnetic structure. This is actually what we mean by 'commensurate'.



More details about how to build up the space groups corresponding to the magnetic ordering can be found in the lecture on the so-called Schubnikov groups (the terminology for the magnetic space groups) given by Juan Rodriguez-Carvajal: Click Me!

As for the incommensurate magnetic ordering, the magnetic moments will not be aligned up perfectly like that in antiferromagnetic structure. Instead, the changing of magnetic moments between neighboring sites could be small in either magnitude or orientation (or both at the same time). Therefore the repetition unit of the magnetic ordering may not be simply the integer multiplier of the nucleus lattice as the one shown in last slide. A bit more Detailed explanation for the difference between the commensurate and incommensurate Magnetic ordering can be found in the following document (a ResearchGate question-answer): Click Me!

One of the crucial notions for describing the magnetic ordering is the so-called propagation vector. If imaging the variation of the magnitude and the orientation of the magnetic moments as a propagating wave, then the propagation vector is just the corresponding wave vector. Moreover, in real situation, the propagating pattern of the magnetic moments could be quite complicated and we cannot simply describe the pattern with a single propagation vector. This is where the Fourier transform comes to help, since in theory we can build up the real propagation pattern by composing the basic patterns together with each component weighted by the corresponding Fourier coefficient. Mathematically, the *j*th magnetic moment in *l*th unit cell can be given as:

$$\boldsymbol{m}_{lj} = \sum_{\{\boldsymbol{k}\}} \boldsymbol{S}_{\boldsymbol{k}j} \exp\{-2\pi i \mathrm{k} \boldsymbol{R}_l\}$$

Where the complex component is just the Fourier coefficient corresponding to certain propagation vector and specific magnetic moment. is the position of the *l*th unit cell in the nucleus crystal structure.

Since the Fourier coefficient mentioned above is complex and obviously it is also a vector, therefore one single contains 6 parameters. Considering the number of magnetic atoms and the propagation vectors to be considered, the number of parameters is usually quite large. But the problem here is that for the powder neutron diffraction, the number of observed reflections owing to the magnetic contribution is limited. Therefore it is difficult to deal with the large number of parameters corresponding to the formulation mentioned in last slide. Here then comes the representation theory to help, which, simply put, is something like expanding the guess Fourier coefficients with the basis functions corresponding to certain irreducible representation of the propagation vector group. Detailed introduction about the utilization of representation theory in magnetic structure analysis can be found in the following document: Click Me!

Back to the symmetry of the magnetic moments arrangement, it should be mentioned that the symmetry operation for the magnetic moment is a bit different from that for the atoms. First of all, magnetic moment has direction therefore when carrying out the symmetry operation, we have to consider the changing of the magnetic moment orientation. The second thing is that the magnetic moment is a pseudovector (also called axial-vector, see Wikipedia), which means its reflection behavior is different from the normal vectors. For example, when a normal arrow is pointing perpendicularly to a mirror, then the reflected arrow will definitely point out. But for the pseudovectors, the normal reflection mirror does tot change the direction of the vector when reflected, i.e. if we have a magnetic moment pointing perpendicularly to the normal reflection mirror plane, then the reflected magnetic moment is pointing to the same direction of the original magnetic moment. Simply put, the behavior of the magnetic moment when reflected by the normal mirror plane is always counter-intuitive.

However, now that we have the normal mirror plane and 'abnormal' vector, it can be imagined that we should also have the 'abnormal' mirror plane. How the pseudovectors behave when reflected by the 'abnormal' mirror plane is the same as how the normal vectors behave when reflected by the normal mirror plane. In technical language, the normal mirror plane for the magnetic moments reflection is called black mirror plane and the abnormal mirror plane is then called red mirror plane. In the symbol representing the magnetic moments space group, a prime will be used to indicate the red operations (not only reflections, but also including rotations). More detailed illustration for the magnetic moments symmetry operations can be found in the following document: Click Me!

Experimentally, since neutrons holds magnetic moment, it can interact with the atomic magnetic moments therefore can be used to detect the magnetic ordering. For the system with long-range magnetic ordering, especially those with commensurate magnetic structure, tools like GSAS can be used to extract the magnetic ordering information. An introduction tutorial on refining magnetic structure with GSAS can be found in the following link: Click Me! & Click Me! & Click Me! & Click Me! However for systems where only have the local magnetic moments correlation or generally for incommensurate magnetic ordering systems for which the propagation vector is too large, the obtained reflection pattern in reciprocal space may be just a few bumps which makes it impossible to extract useful information about the magnetic ordering. In such situation, the local magnetic ordering analysis in real space then becomes important to discuss the correlation between the magnetic ordering and some physical properties (e.g. the negative thermal expansion behavior of some materials). Tools for the analyzing the magnetic ordering in real space include those based on big box modeling such as SPINVERT, RMCProfile and also those based on small box modeling such as diffpy.mpdf.

From the classic perspective, the magnetic property should originate from the current. To understand the magnetic property in the microscopic world, we can still borrow the same idea. Taking one unpaired electron as the example, the electron can 'rotate' around the nucleus and also at the same time it can have spin (for which we can understand pictorially as the spin of the earth). Due to the rotation of electrons (either the rotation around the nucleus or the spin), it can bring in the current which then will lead to the corresponding magnetic moments. Although the classic picture here is not that appropriate in the quantum world, but actually the magnetic property can indeed be attributed to the angular momentum of the electrons, which includes both the orbital angular moment (in analogue to the electron rotation around the nucleus) and the spin (in analogue to the rotation around the self-axis). According to the Pauli exclusion rule, each orbital can only hold two electrons with spins in different directions. Therefore normally for the filled shells, the angular moment of the paired electron cancels each other out and we are left with no net magnetic moments. Then we know that the existence of the magnetic moments relies on the unparied (or, lone-pair) electrons. However this is still not the full picture since we know that for many elements in the periodic table, they do not show magnetic property. It is the transition metals for which the d- or f-orbital is not filled (either atom or ion) that shows the magnetic property. Why is it the case? The real situation for magnetic materials is complex where we not only need to consider the coupling between the orbital and spin angular moment of the single atom, but also we need to consider the coupling of magnetic moments between different electrons. There we have to introduce the exchange interaction and the corresponding theoretical model based on this is called the Heisenberg model – refer to the book Magnetism in condensed matter by Stephen Blundell. With the effect of exchange interaction, the magnetic moments can then align themselves up in certain pattern. But the left question is why it is the d- or f-orbital electrons but not other orbitals contribute much to the magnetic property.

One of the main reasons is that the exchange integral of electron orbitals relies on the localization of the orbital, and d- or f-orbital is more localized as compared to others. This gives larger exchange integral and the system will favors the lowering of energy due to the aligning up of magnetic moments.
Here one more thing to mention is that although the magnetic moments originate from electron spins, but actually the formation of magnetic moments involve many contributing factors including the coupling between the spin and orbital angular moment and also the coupling between different magnetic moments located on different atoms. Also in the real material, it is the band structure instead of single electron picture that can better describe the system, therefore the magnetic property is already not a single-electron problem. This means that the magnetic property does not only rely on the moments of single electron but also on the band structure of the material, e.g. the density of states around the Fermi level, etc.

More detailed discussion can be found in the following attachments: