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Unlocking the **mysteries of magnetism**

The advantages of neutron diffraction for the determination of magnetic structures

In previous articles we have discussed the importance of knowing where atoms substitute in the complex crystal structures typical of modern magnetic materials,[1] and how density functional theory (DFT) calculations validated using direct measurement by neutron diffraction are set to revolutionize the design of new magnetic materials.[2] Here we discuss the next most obvious problem in the development of a new magnetic material: determining and understanding how the magnetic atoms behave and how their behavior leads to the observed properties.

Neutron diffraction plays a key role in these investigations as it uniquely provides access not only to information about the crystal structure (where the atoms 'are') but can also be used to determine the magnetic structure (what the moments on the atoms are 'doing').[3] This is possible because, unlike an x-ray, the neutron carries a magnetic moment that can interact with the moments on the atoms in our magnetic material and can therefore be used to learn about and analyze those moments. More remarkably, the interaction between the neutron moment and those in the material turns out to be about the same strength as that between the neutron and the nuclei in the material. This means that observing the magnetic contribution to the diffraction pattern is not especially challenging: the signals from the magnetic and crystal structure are comparable in magnitude.

While neutron and x-ray diffraction are very similar, there are two important differences. First, neutrons interact more weakly with materials and are therefore far more penetrating than x-rays. One downside of this weaker interaction is that we generally require larger samples for neutron diffraction, but the advantage is that the neutron beam penetrates through, and thus scatters from, the entire sample, not just a thin layer on the surface. It is a true 'bulk' measurement. If there are other phases present (e.g. an impurity or surface oxidation) the neutron diffraction signal provides a quantitative measure of the amounts present, without being surface biased by limited penetration.

Figure 1: **Looking down on the DUALSPEC neutron diffractometers at the Canadian Neutron Beam Centre (CNBC) Chalk River, Ontario. The large blue cylinder at the center-left is the common monochromator for the C2 powder diffractometer and the C5 polarized inelastic instrument. The blue wedge-shaped unit above the monochromator drum is the 800-wire, 80° detector for the C2 powder diffractometer. The detector (blue) and sample stage (gray) for the C5 instrument are at the lower right. The orange pump on top of the monochromator and the red toolbox on top of the detector provide a sense of scale. The square-foot floor tiles may also be used to establish the size of the instruments**

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Second, the scattering strengths for the elements do not follow the simple increasing progression with atomic number seen with x-rays, but rather they vary almost randomly from element to element while remaining about the same magnitude. This means that neutrons can be as sensitive to some light elements (such as carbon, nitrogen and oxygen) as they are to much heavier elements (such as tungsten, gold and lead). In some cases, elements that are quite close in atomic number (such as titanium and iron) and cannot be distinguished by x-ray diffraction, have very different scattering strengths for neutrons and are readily separated. As x-ray and neutron diffraction have complementary strengths, they are often used together to obtain a complete structural refinement for a given material.

The instruments used for neutron diffraction measurements are essentially the same as those used for x-ray diffraction, only building-sized rather

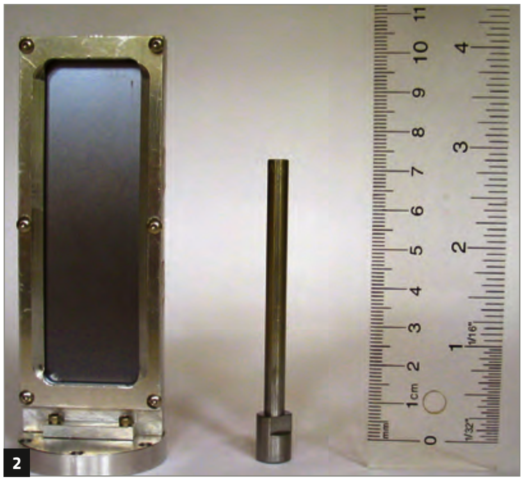
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Figure 2: **Two typical sample mounts for neutron diffraction. The large-area flat plate mount at the left is used for highly absorbing materials, while the cylindrical can is a standard mount used for almost all diffraction measurements**

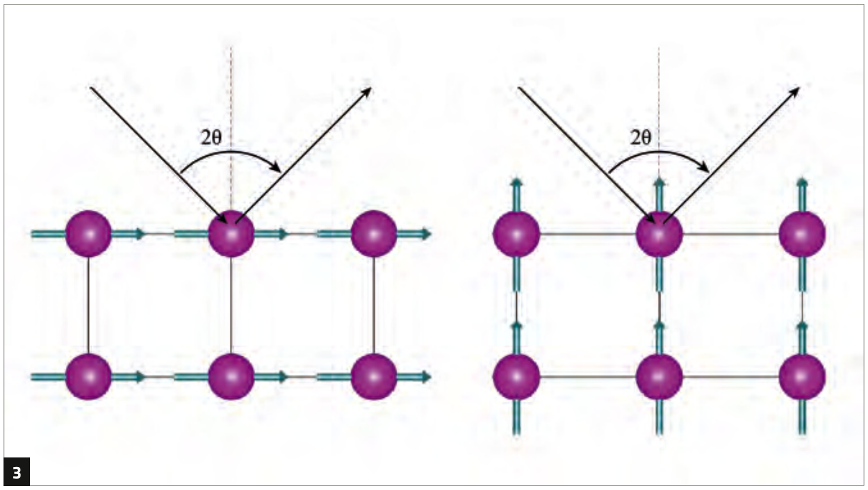

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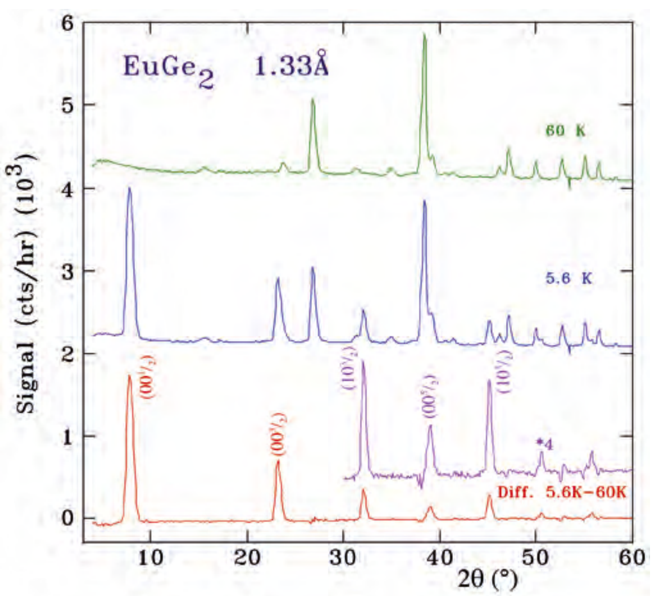
Figure 3: **Impact of the moment direction on the magnetic scattering from two simple magnetic structures. In both cases the neutron momentum in the vertical direction changes from ‘down’ to ‘up’. For the magnetic structure at the left, the momentum change is perpendicular to the moments and a magnetic contribution to the scattering is allowed. For the magnetic structure at the right, the momentum change and moments are parallel, and no magnetic scattering is allowed**

than desktop (Figure 1). This much larger size is the result of neutrons being far more penetrating than x-rays, and the beams of neutrons being far lower in intensity. Being more penetrating, more shielding is required to protect the users. The biological shield around the core of the 100MW NRU reactor at Chalk River, Ontario, is 3m thick, and that around the monochromator on the C2 powder diffractometer shown in Figure 1 is 1m thick. To compensate for the low intensity of most neutron sources, large-area beams are often used (many square centimeters rather than the few square millimeters typical of laboratory x-ray sources), leading to physically larger beamline components (monochromators, collimators, etc). Further intensity compensation is provided by large-area detectors that collect the entire diffraction pattern in one go. C2 at Chalk River covers 80° of 2θ with a resolution of 0.1°, recording 800 data points at once, while D20 at the Institut Laue-Langevin (ILL) in Grenoble covers 135° of 2θ at the same resolution.

Large-area beams of relatively low intensity lead inevitably to the need for large samples. A laboratory x-ray system will produce useful data with a few milligrams of material. Neutron diffraction typically demands grams. Modern instruments with focusing monochromators and high-efficiency detectors can work with tens of milligrams, but grams is still the norm. Figure 2 shows two standard sample mounts. The 5mm diameter thin-walled vanadium can is the workhorse mount for almost every sample and variations of this basic design can be found at every neutron beam facility. It will hold several grams of powder and the vanadium (due to a quirk of its nuclear properties) yields essentially no diffraction signal. On the left is a large-area silicon plate mount used for highly absorbing materials such as many of the rare earths. It exploits the large area neutron beam to great advantage by spreading a thin layer of material over the full beam, minimizing the thickness of the absorbing sample while maximizing the total sample mass placed in the beam.[4]

The diffraction signal from a magnetic sample derives from the same basic physics as that used for diffraction of x-rays or neutrons from a non-magnetic sample. The incident radiation is scattered by the regular three-dimensional array of atoms (or more properly nuclei in the case of neutron diffraction) and where this scattering leads to constructive interference we observe a Bragg peak (named for the Nobel prize-winning team that



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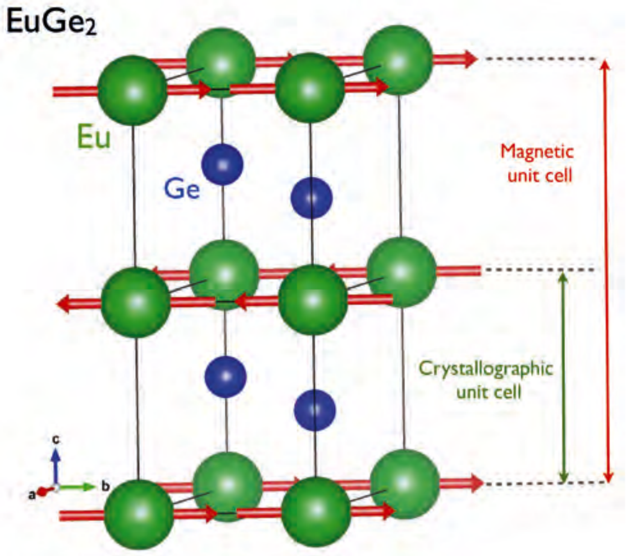

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Figure 4: **Neutron diffraction patterns for EuGe$_2$ taken above (60K, green) and below (5.6K, blue) the magnetic ordering temperature. At 60K only nuclear scattering from the crystal structure is present. At 5.6K many new (magnetic) peaks have appeared. The different patterns shown at the bottom (red and magenta) emphasize the magnetic scattering. The new peaks can be indexed by assuming that the magnetic cell is twice as large as the underlying crystal cell (Figure 5)**

Figure 5: **Comparison of the crystallographic and magnetic unit cells for EuGe$_2$. The europium moments are ordered in the *a-b* plane and alternate between pointing right and left as we move up the *c*-axis. As a result, the magnetic cell is twice the size of the crystallographic cell**

first observed these peaks). The magnetic neutron scattering contribution appears in addition to the structural nuclear scattering, so the observed diffraction pattern contains both kinds of peaks. Often the magnetic and nuclear peaks coincide, in which case they simply add. However, as commonly happens, if the magnetic structure is more complex than the crystal structure, new, magnetic-only peaks are observed.

There is one key physical difference between magnetic neutron scattering and both x-ray scattering and nuclear neutron scattering. The atoms and nuclei involved in x-ray and nuclear scattering can be approximated as points, but the moments (both on the neutron and the moment-carrying atom) are vectors, with a direction that matters. Only moments that have a component perpendicular to the scattering direction of the neutrons can yield a magnetic signal. This greatly affects the observed magnetic neutron diffraction pattern and increases the amount of information about the magnetic structure that can be obtained from it. When we set out to determine a magnetic structure we want to know not only how big the moments are, but also which way they are pointing. Figure 3 shows how the relative orientations of the scattering moments and the change in direction of the neutron flight affect the observed signal. In both cases the scattered neutron continues to travel to the right, so this component of its motion is unchanged, however the vertical motion changes from 'down' to 'up', so this component does change. In the left-hand panel the moments point to the right, perpendicular to the down-to-up change in the neutron motion. These moments can generate a magnetic peak for this scattering geometry. In contrast, the moments in the right-hand panel point 'up' and so are parallel to the change in the neutron motion. These moments do not yield a magnetic scattering signal. Thus the presence or absence of magnetic scattering in a particular direction can immediately tell you which way the moments are pointing (at least in simple cases).

EuGe$_2$ provides an example that can mostly be solved simply by looking at the pattern in Figure 4. Magnetic ordering occurs at about 50K. Above this temperature the material is paramagnetic and the diffraction pattern (shown in green) contains only nuclear contributions. This can be analyzed to determine the crystal structure, however we are concerned with magnetism here so we will

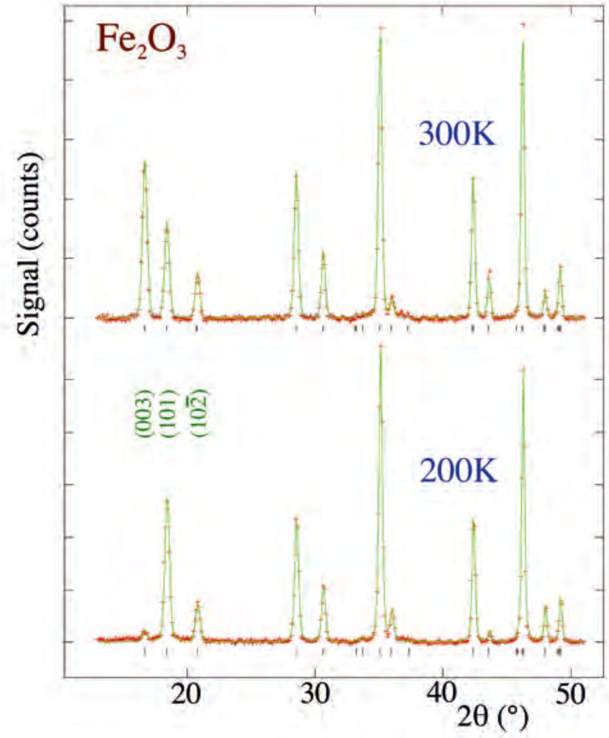

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Figure 6: **Neutron diffraction patterns for hematite (Fe_2O_3) taken above (300K) and below (200K) the Morin transition, where the moments rotate from perpendicular to the *c*-axis (at 300K) to parallel to it by 200K. The very large change in the intensity of the (003) peak, which almost vanishes on cooling, is a clear visual indication of the change in moment direction**

assume that we already know the structure. (It is shown in Figure 5.)

At 5.6K the sample has ordered and many new peaks are apparent. Several are quite strong, indeed one rivals the strongest nuclear peak (magnetic neutron scattering is not a weak phenomenon) but none of them lines up with any pre-existing nuclear peak. Since we already 'know' the crystal structure we can use it to identify the magnetic peaks, and we find that while they can be described in terms of the underlying crystal structure, we first need to double the size of the cell in one direction (as shown in Figure 5).

Looking at the strongest magnetic peak (00½), we see that it corresponds to a change in neutron direction parallel to the newly elongated axis, and this means that the moments must be perpendicular to this direction. The deduced magnetic structure consists of sheets of moments pointing left, then right then left, as we move up the crystal cell. The magnetic cell is twice the size of the crystal cell because while all the europium atoms are chemically equivalent, a left-pointing moment is not the same as a right-pointing moment. So while one vertical step will get you from one europium atom to the next, one has to make two vertical steps in the crystal to get from one left-pointing moment to the next left-pointing moment. The magnetic cell is therefore twice as big as the crystal cell. The magnetic and chemical structures are shown in Figure 5.

Fe_2O_3 (hematite) provides an example of a simple change in magnetic structure and its impact on the magnetic diffraction pattern. At room temperature, the moments in hematite are ordered perpendicular to the crystal *c*-axis. However, on cooling through about 260K (the Morin transition) the moments rotate to be parallel to the *c*-axis. This has a very clear impact on the diffraction pattern as the (003) peak almost completely vanishes on cooling from 300K to 200K. With the moments now parallel to the *c*-axis, the (003) reflection, which involves scattering purely parallel to the *c*-axis (and therefore the moments), is no longer permitted. A weak residual contribution arises because the *c*-axis alignment is not quite perfect.

Neutron diffraction is without doubt the ideal method for determining magnetic structures. It can be used to obtain a complete description of a magnetic structure (direction and magnitude of all the moments in the system) and to solve far more complex structures than have been used as examples here (spirals, cones and even 'magnetic waves' are possible). Armed with an understanding of the magnetic structure derived from neutron diffraction, and combining this with an ability to predict (using density functional theory, DFT),[2] and measure (using neutron diffraction) where dopant atoms will substitute, it is straightforward, in principle, to enhance the magnetic properties of a starting material by judicial use of atomic substitutions or simply by varying its composition. ■

References

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