magnetism

Magnetisation distribution measurements from powders using a ^{3}He spin filter

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The measurement of polarised neutron-dependent cross-sections is an extremely powerful technique that provides information on the distribution of magnetisation in materials with unpaired electrons. High quality data can even be used to determine the tensorial nature of the local magnetisation and so provide direct information about the electronic configurations of the valence shells. At present, the employment of the technique only at single crystal diffractometers (e.g. D3 at ILL) means that its application is limited to subjects where the single crystals are available. The development of this technique for the study of powder and polycrystalline samples could open the door to new fields of science. Years ago, measurements on powders demonstrated the great potential of the technique, but they remain isolated studies that did not explore either the technical issues associated with powdered samples or the application to weakly magnetic samples, as would be important to chemistry and biochemistry.

The well-known powder diffractometer D1B has been modified for the collection of polarisation-dependent cross-section data using a ^{3}He spin filter. The standard collimator located in between the monochromator shielding and the sample table has been replaced by the magneto-static cavity Cryopol [1] and a new collimator containing guide-fields ensuring the adiabatic transportation of the polarisation to the sample located in a 5 T cryomagnet (figure 1). Great care was taken over the effects of depolarisation and absorption of the neutron beam by the powder. The first of these effects was explicitly measured in our experiments using a Cu_2MnAl Heusler crystal that was glued to the side of the vanadium sample can. The data collected from the [111] reflection of the Heusler positioned in front and behind the sample characterised the depolarisation. The absorption was measured with a monitor positioned before and after the sample. In order to take into account the effects of ^{3}He polarisation relaxation, data were collected using a repeated (+−−+) neutron polarisation sequence.

Figure 1: The experimental team on D1B. From the left: Francis Tasset, Andrew Wills, Eddy Lelièvre-Berna and Nolwenn Kernavanois.

In the case of powder samples better quality information can be derived from the difference data $I_+ - I_-$ as contamination from the cryomagnet and sample can is then cancelled, within statistics, and only magnetic data are left. The difference spectra are related to M and N according to $I_+ - I_- = 4 K P_i D N M$ where K is a scale factor that contains the Lorentz factor, the multiplicity and the absorption coefficient for each reflection, P_i is the incident polarisation, D is the depolarisation of the beam, N and M are the nuclear and magnetic structure factors respectively (the flipper efficiency of Cryopol is 99.9%).

In order to determine the sensitivity of the technique, we have measured the difference spectra of the weak ferromagnet YNi_3 below T_c = 30 K. Previous workers had already determined the magnetisation density distribution from single crystal data [2]. The successful observation of the small saturation moment (0.04 μ_B per Ni atom) after a 15-hour data collection attests the high sensitivity. Indeed, the flux at the sample position was only $5x10^5$ n cm s^{-1} at 2.52 Å on D1B and a much better statistics could be obtained in one hour on D20.

Prussian Blue, $Fe_4^{III}[Fe^{II}(CN)_6]_3 \bullet xD_2O$, is an archetypal mixed-valent molecular ferromagnet. It displays ferromagnetic ordering of the Fe(III) spins below T_c = 5.5 K. As the magnetic Fe(III) ions are well separated, it is believed that central to the magnetism is a contribution from what would naïvely be expected to be low-spin diamagnetic Fe(II) ions. Arguments based on the charge transfer transition in the optical absorption

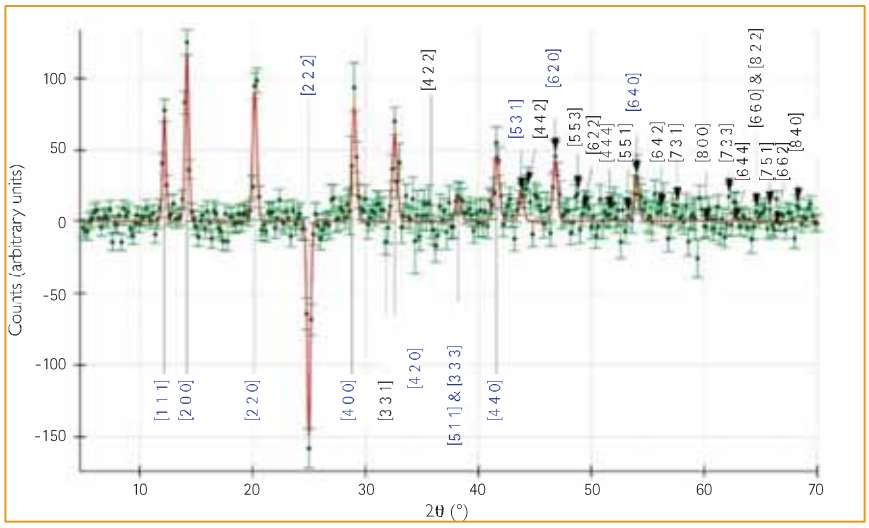


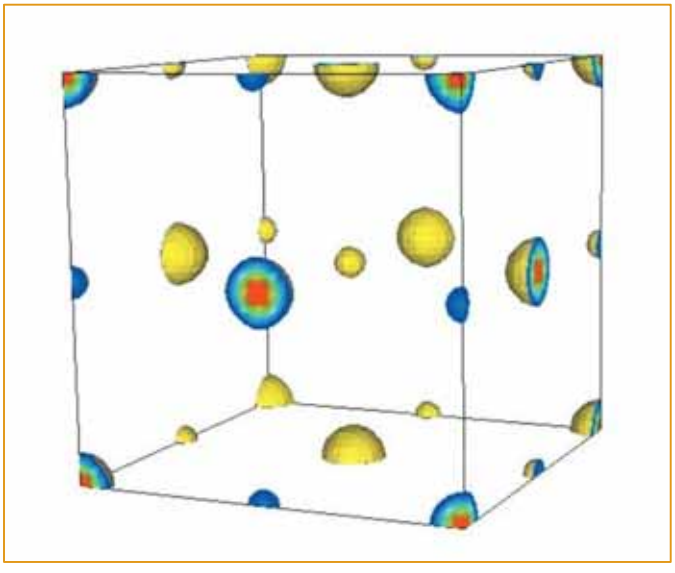
Figure 2: The Prussian Blue difference spectra collected in 10 hours with neutrons of 1.28 Å after correction for the time-dependent relaxation of the ^{3}He spin filter. Fits of Gaussian functions to the individual reflections are shown.

spectrum at 14100 cm^{-1} that leads to its well known intense blue colour, led Day and co-workers [3] to search for spin transfer from the high-spin Fe(III) to the diamagnetic Fe(II) using flipping-ratio measurements. As Prussian Blue is only known in powder form, their measurements on the polarised neutron single-crystal diffractometer D5 at the ILL demonstrated well the restrictions associated with the study of powders. In their study only 3 reflections could be resolved allowing them to deduce a maximum amount of transferred spin as 0.003 ± 0.026 μ_B.

In our measurements a total of 11 reflections were clearly discernible in the difference spectrum collected for 10 hours (figure 2). Nuclear structure factors were taken from data collected in the paramagnetic phase at 20 K in zero applied field, and used to calculate the magnetic structure factors. Determination of the magnetisation distribution was carried out using the Maximum Entropy software MEMSYS 3 and PRIMA. The major features of the magnetisation maps generated by both codes are the same (figure 3): unpaired spin density is largely localised at the Fe(III) position but a significant component at the Fe(II) position is also observed. Initial refinement suggests values for the spontaneous magnetisation of 3.0 ± 0.1 and 0.3 ± 0.1 μ_B per atom respectively.

This experiment demonstrated the ease with which a powder diffractometer may be adapted for use with polarised neutrons with the help of large area neutron polarisers (^{3}He filters). Such devices can be included in the design of any new instruments. The high intrinsic sensitivity of the technique (measurement of NxM instead of $N^2 + M^2$) is evidenced by the observation of magnetic scattering from 0.04 μ_B per Ni in YNi_3. It encourages the study of the magnetisation distributions in chemical, physical and biological powder samples. This technique can apply successfully to relatively weak ferromagnetic systems without strong anisotropy but will not compete with the determination of the magnetisation distribution in single crystals.

Figure 3: MaxEnt reconstruction of the magnetisation map in Prussian Blue. The high density corresponds to Fe(III) and the low density to the ferromagnetic component present at the Fe(II) ion.



References: [1] J. Dreyer, L.P. Regnault et al., Nucl. Instr. and Meth. in Phys. Res. A 449, (2000) 638-648
[2] D. Gignoux, R. Lemaire et al., J. Magn. Magn. Mater. 21 (1980) 307
[3] P. Day, F. Herren, A. Ludi et al., Helvetica Chimica Acta 63 (1980) 148