2. INSTRUMENTATION AND SAMPLE PREPARATION

Mitsui *et al.* (2009) have developed a device that includes a cryo-cooled split-pair NbTi superconducting magnet and a sample furnace, for high fields and temperatures above room temperature, respectively, which can be installed on a laboratory X-ray diffractometer. The magnetic field generated goes up to 5 T at the centre of a 50 mm vertical and 10 mm horizontal bore, with a field homogeneity of 0.1%. The first results of studies on the martensitic phase transition in the shape memory system $Ni_{40}Co_{10}Mn_{34}Al_{16}$ in a field of 5 T and at temperatures up to 473 K have been reported for powders (Mitsui *et al.*, 2009).

Synchrotron radiation can be used to study specific properties such as orbital contributions and their separation from the spin values. Diffraction studies with unpolarized neutrons are common at a constant field to elucidate simple magnetic structures: no confident conclusion about the spin direction can be obtained if the configurational symmetry is cubic, and in the case of uniaxial symmetry (either tetragonal, hexagonal or rhombohedral) only the angle with the unique axis of the magnetic structure can be defined (Shirane, 1959). The sensitivity of non-polarized neutron powder diffraction (the magnetic detection limit) is by a few orders of magnitude less than that of superconducting quantum interference device (SQUID) magnetometry, muon spin rotation or magnetic dichroism spectroscopy. In an antiferromagnetically ordered system the determination of magnetic moments below 0.1 μ_B per magnetic atom presents severe challenges, which become even more pronounced for the localization of weak ferromagnetic components. Less frequent are *in situ* investigations to determine magnetic phase diagrams. The use of powder samples at high magnetic fields is often limited by the redistribution of grains and texture effects.

Experiments with polarized neutrons are normally performed with single crystals. Out of the variety of compounds that have been studied, we have chosen materials with particular properties and report on *in situ* studies of them under magnetic fields.

2.8.3.3.2. *Frustrated magnetic systems*

Multiferroic systems (or more precisely magnetoelectric materials) have gained considerable attention because of their potential applications in devices. In fact, the efficient control of magnetism by an electric field allows magnetic information to be written electrically (with low energy consumption) and read magnetically. A real application, however, requires both phenomena to occur at room temperature. There are very few compounds that fulfil this requirement; examples include $BiFeO_3$ and β-$NaFeO_2$.

Magnetoelectric properties have been observed in many compounds with different structures and chemical compositions. However, they all have a geometrical magnetic frustration in common, which induces competition among multiple magnetic ground states. Furthermore, a magnetic phase transition is thought to be an essential ingredient for realizing a non-linear colossal response in the electric properties. In the colossal effect, the two properties not only coexist but couple strongly in their order parameter. Most novel multiferroic materials exhibit a cycloidal component to the magnetic structure; this has been considered as a guiding principle for tailoring new materials based on the non-collinearity of the spins. Many cycloidal compounds exhibit a small ferromagnetic component in their antiferromagnetic order, giving rise to the Dzyaloshinskii–Moriya interaction. We shall concentrate here on two systems linked by frustration in the magnetic ordering, namely orthovanadates and the manganites of the rare earths.

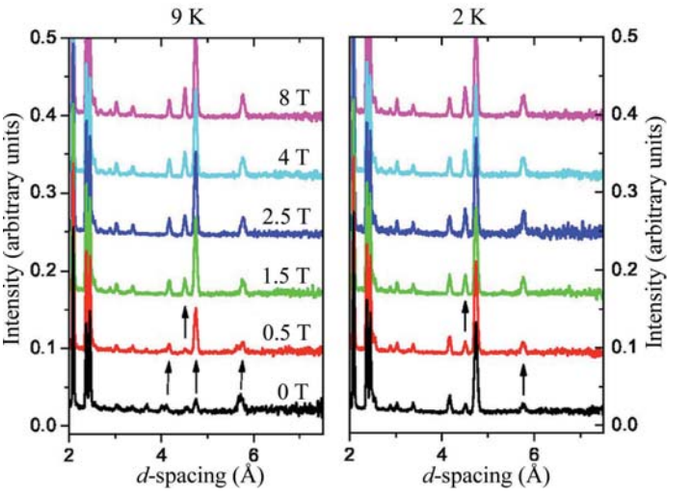

Figure 2.8.14
Neutron powder diffraction data for $Co_3V_2O_8$ at 9 K (left) and 2 K (right) under magnetic fields of 0, 0.5, 1.5, 2.5, 4.0 and 8.0 T. Data from a bank of detectors situated at the scattering angle 35° are shown. The arrows indicate the changes between the data at different fields. Individual curves are offset arbitrarily for display purposes. Reprinted with permission from Wilson *et al.* (2007). Copyright (2007) by the American Physical Society.

2.8.3.3.2.1. *Kagomé staircase systems*

Among the orthovanadates of 3*d* metals, $Co_3V_2O_8$ and $Ni_3V_2O_8$ have been identified as kagomé staircase magnetic structures, which exhibit a considerable number of phase transitions at low temperature. Their crystal structure was determined by Fuess *et al.* (1970) as orthorhombic (space group *Cmca*). Ferromagnetic order was found for the cobalt compound and an indication of antiferromagnetism for the nickel compound at 4.2 K. The crystal structure is characterized by edge-sharing CoO_6 octahedra forming buckled layers of corner-sharing triangles, called kagomé staircases, separated by VO_4 tetrahedra. The magnetic ions (Co or Ni) are situated at the corners of triangles, thus leading to spin frustration. Therefore, if a small amount of energy is supplied by an external magnetic field, a whole sequence of magnetic phase transitions can be introduced. The previously determined ferromagnetic order as the ground state for $Co_3V_2O_8$ was confirmed by Wilson *et al.* (2007). They also reported field-dependent neutron powder diffraction studies under a field of 8 T at 2 and 9 K (Fig. 2.8.14). At 9 K the system has an incommensurate magnetic structure. At a field as low as 0.5 T, new magnetic peaks indexed in a commensurate structure occur, accompanied by a shift in the position of others. The incommensurate ordering disappears completely at a higher field and a purely ferromagnetic behaviour is observed, similar to the low-temperature ground state at zero field. At 2 K and 8 T no additional magnetic reflections are observed but changes in the intensity of several existing ones are seen. The refinement of the magnetic structure based on these data indicated a change of the spin direction in the ferromagnetic arrangement as compared with the zero-field low-temperature structure. Furthermore, the magnetic moments on the two different Co sites in the structure are aligned under the field and reach the same value of 3.15 μ_B on both sites, which is similar to the spin-only moment of cobalt.

The reorientation of spins and the complete magnetic field *versus* temperature (*H*–*T*) phase diagram of the multiferroic $Ni_3V_2O_8$ has been reported (Kenzelmann *et al.*, 2006). The inversion symmetry of space group *Cmca* is broken at low temperature and a commensurate phase is observed. Thus, over a

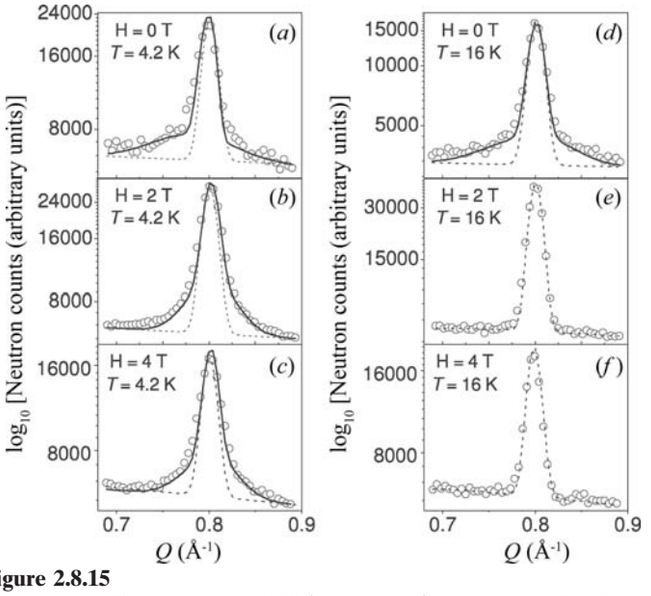

Figure 2.8.15
The observed Bragg reflection 100 (open circles) under an applied field of (*a*) 0 T, (*b*) 2 T and (*c*) 4 T at 4.2 K and (*d*) 0 T, (*e*) 2 T and (*f*) 4 T at 16 K (taken from Yusuf *et al.*, 2013). Copyright IOP Publishing. Reproduced with permission. All rights reserved.

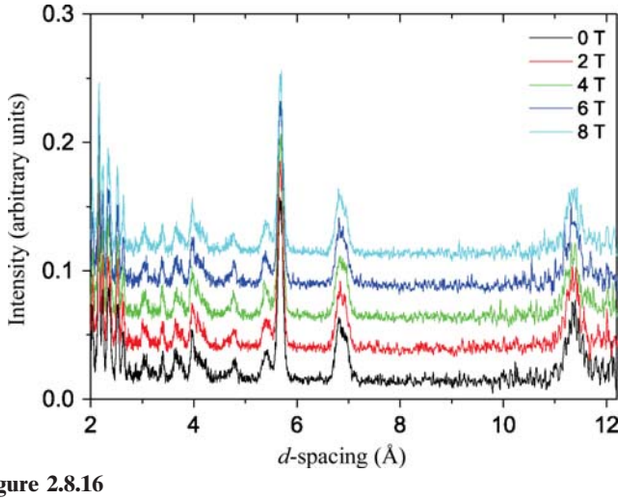

Figure 2.8.16
Time-of-flight diffraction patterns of YMn_2O_5 at 1.6 K under magnetic fields between 0 and 8 T (taken from Radaelli & Chapon, 2008). Copyright IOP Publishing. Reproduced with permission. All rights reserved.

narrow temperature range a macroscopic polar vector leads to a multiferroic behaviour. As this study was based on single-crystal neutron measurements, no further details are given here. Frustrated triangular-lattice Ising antiferromagnets have degenerate magnetic ground states, which give rise to very complex magnetic structures. As there are only small differences in the competing exchange interaction in such frustrated triangular-lattice compounds, a sequence of phase transitions is introduced by changes in temperature or magnetic field. The compound $Ca_3Co_2O_6$ is another example of a frustrated system. Field-dependent powder diffraction patterns were reported for the doped system $Ca_3Co_{1.8}Fe_{0.2}O_6$ by Yusuf *et al.* (2013). They distinguished the short-range magnetic order (SRO), reflected in the half-width of the Bragg reflections (Fig. 2.8.15), from the long-range order as given by the Bragg positions. They stated that even under magnetic fields up to 4 T the broadening of Bragg reflections indicates the persistence of SRO. In a field of 2 T, the observed change in the structure from incommensurate to commensurate indicates a reduction of spin frustration. In fields of 4 T, a ferrimagnetic system is introduced, followed by a ferromagnetic one above 5 T.

2.8.3.3.2.2. Manganite systems

Like the vanadates, in the class of rare-earth manganites of the type RMn_2O_5 successive magnetic phase transitions between commensurate (CO) and incommensurate phases (ICP) can occur. Intensive investigations have been undertaken to understand the relationship between their magnetic and dielectric properties. The spontaneous electric polarization is induced by a magnetic transition. Thus the primary order parameter is magnetic rather than structural. Among the rare-earth compounds, those containing Nd or an element lighter than Nd do not exhibit ferroelectricity. In all these materials a broken magnetic symmetry at lower temperatures leads to a polar symmetry group. In addition, a cycloidal component indicates a common underlying mechanism. The Mn^{3+} and Mn^{4+} ions are fully charge-ordered. Neutron diffraction studies of these phases have been performed by Radaelli & Chapon (2008), who also analysed the possible exchange pathways. In $TbMn_2O_5$ the *H*–*T* phase diagram of the commensurate–low-temperature–incommensurate (CO–LT–ICP) magnetic transitions shows an upward jump in the transition temperature from ∼25 K at zero field to 27 K at 9 T. The low-temperature ICP phase is stabilized under an external field for $TbMn_2O_5$ and the dielectric constant is enhanced. It was concluded that Tb and Mn order independently, implying the absence of coupling terms between them. Strong support for this suggestion was provided by an in-field neutron study on the analogue YMn_2O_5. Neither the positions nor the intensities of the magnetic Bragg reflections were affected by the magnetic field (Fig. 2.8.16). The magnetic low-temperature ICP phase in the Tb compound was stabilized under a magnetic field. This is in contrast to observations on $HoMn_2O_5$ by Kimura *et al.* (2007), using single crystals. In both cases, however, the neutron data correlate directly with the results obtained by dielectric measurements under a magnetic field. The difference in the behaviours is thus confirmed. The two studies also reveal different magnetic order at low temperatures. The same magnetic sequence at low temperatures as for Tb was observed in YMn_2O_5, which does not contain a magnetic rare-earth element. Under fields up to 8 T the positions and the intensities of the magnetic Bragg reflections remained unchanged, showing that the antiferromagnetic structure of the manganese sublattice is extremely stable. As in the vanadates, the main reason for the sequence of magnetic structures is frustration of the manganese spins. Without going too deeply into the details of the different exchange pathways and orbital occupancies, one factor behind this behaviour is the Jahn–Teller effect of the Mn^{3+} ion, which is also relevant in the multiferroic $TbMnO_3$ as part of the $RMnO_3$ family (Kimura *et al.*, 2003). Another feature often found in multiferroic systems is the small ferromagnetic component caused by small spin canting due to Dzyaloshinskii–Moriya interactions. This property strongly influences the low-temperature magnetism in RMn_2O_5 (Kimura *et al.*, 2009).

2.8.3.3.3. *Additional systems and scattering techniques*

Information about the anisotropy of the local magnetic susceptibility at different magnetic sites has been extracted from diffraction patterns for a $Tb_2Sn_2O_7$ powder measured using polarized neutrons under magnetic fields of 1 and 5 T (Gukasov