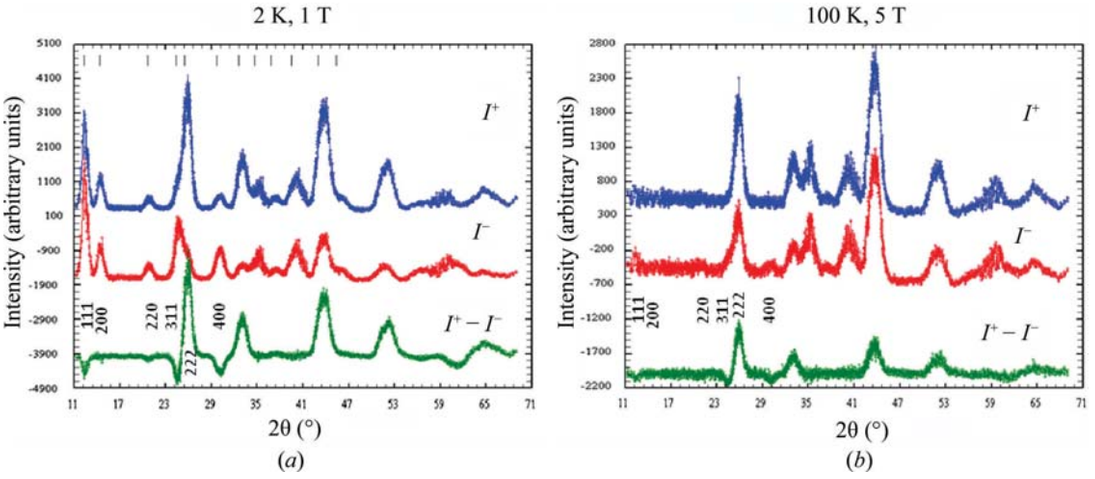

Figure 2.8.17
Polarized neutron diffraction patterns for $Tb_2Sn_2O_7$ at 2 K and 1 T (*a*) and 100 K and 5 T (*b*). I^+ and I^- are the intensities for spin-up and spin-down neutrons, respectively. Taken from Gukasov & Brown (2010).

& Brown, 2010). No magnetic contribution to the diffracted intensities was observed at 2 K in the absence of an external field. However, applying a field led to considerable changes in the diffraction pattern (Fig. 2.8.17). At 100 K and 5 T, the intensities of the reflections that are allowed for the cubic space group $Fd\bar{3}m$ increase considerably. Furthermore, they were found to depend strongly on the polarization of the incoming neutrons, as shown by the difference pattern in Fig. 2.8.17. At a field of 1 T, new reflections appear (Fig. 2.8.17*a*) that are forbidden for the occupied sites in $Fd\bar{3}m$ symmetry, such as 200, 222 and 240. The intensities of these new reflections do not change with the polarization of the neutrons, as demonstrated in the difference plot, hence they are purely magnetic. In conclusion, information on local anisotropic magnetic susceptibility at different sites can be obtained by using a combination of unpolarized and polarized neutron powder patterns. This demonstrates the usefulness of polarized neutron scattering, even for polycrystalline samples.

We now return to X-ray investigations of magnetic materials. A laboratory device for fields up to 5 T and temperatures above room temperature was mentioned in Section 2.8.3.3.1. The corresponding low-temperature apparatus (Koyama *et al.*, 2013) has produced results on magneto-caloric compounds of MnFeP-type materials. Substitution of P in $MnFeP_{1-x}Z_x$ with Z = As or Ge produces materials that exhibit a large magneto-caloric effect and thus allows control of the Curie temperature by chemical composition. Studies under magnetic fields are mandatory, as the refrigerants are working under a field. For two different compositions of the As compound the lattice parameters change drastically and the cell volume decreases with increasing magnetic field strength. In $MnFeP_{0.78}Ge_{0.22}$ a field-induced ferromagnetic phase was observed near the Curie temperature at 280 K. This phase is, however, not identical to the low-temperature ferromagnetic one (Koyama *et al.*, 2013).

2.8.3.3.4. *Concluding remarks*

Despite some shortcomings, powder diffraction studies as a function of magnetic fields are valuable for the qualitative and sometimes even quantitative interpretation of magnetic materials. Unpolarized neutrons are used in most experiments, but the additional information from polarized neutrons has also been exploited. X-rays do not interact directly with the magnetic moments, but structural changes as a consequence of magnetic phase transitions have been observed in several cases. *In situ* powder diffraction under magnetic fields reaching 4 T on an X-ray diffractometer with a rotating anode revealed details of lattice parameters and atomic positions in rare-earth alloys with a higher precision than that accessible by neutron diffraction (Pecharsky *et al.*, 2007). Furthermore, the two test-case compounds studied, Gd_5Ge_4 and $DyCo_2$, contain the rare-earth elements Gd and Dy with the highest absorption cross sections for neutrons in their natural isotope abundance. The data were used to refine the underlying structure models by Rietveld analysis. Advances in X-ray and neutron sources and optics delivered higher resolution and flux to the samples, which in combination with rapid computing made real-time experiments feasible.

2.8.4. Summary

We have shown here that *in situ* studies under electric and magnetic fields are in a well advanced state. Laboratory equipment can be used for diverse experiments where changes occur on a timescale that can be followed with an exposure time of minutes. Real progress is, however, achieved by using high-energy synchrotron radiation and by using neutrons, which can penetrate larger volumes. Thus *in operando* studies of real devices are feasible. In addition to such diffraction experiments, which provide average information on a macroscopic length scale, complementary experiments like electron microscopy are vital for revealing local structural information. Only the combination of several methods can give sufficient insight into structure–property relationships and the functionality of materials.

References

Adam, R., Wadewitz, D., Gruner, W., Klemm, V., Ehrenberg, H. & Rafaja, D. (2013). *Phase and microstructure development in the conversion type electrodes for Li-ion batteries based on the Cu-Fe-O system. J. Electrochem. Soc.* **160**, A1594–A1603.

Anastasopoulos, M., Bebb, R., Berry, K., Birch, J., Bryś, T., Buffet, J.-C., Clergeau, J.-F., Deen, P. P., Ehlers, G., van Esch, P., Everett, S. M., Guerard, B., Hall-Wilton, R., Herwig, K., Hultman, L., Höglund, C., Iruretagoiena, I., Issa, F., Jensen, J., Khaplanov, A., Kirstein, O., Higuera, I. L., Piscitelli, F., Robinson, L., Schmidt, S. & Stefanescu, I. (2017). *Multi-grid detector for neutron spectroscopy: results obtained on time-of-flight spectrometer CNCS. J. Instrum.* **12**, P04030.

Anton, E.-M., Schmitt, L. A., Hinterstein, M., Trodahl, J., Kowalski, B., Jo, W., Kleebe, H.-J., Rödel, J. & Jones, J. L. (2012). *Structure and temperature-dependent phase transitions of lead-free $Bi_{1/2}Na_{1/2}TiO_3$–$Bi_{1/2}K_{1/2}TiO_3$–$K_{0.5}Na_{0.5}NbO_3$ piezoceramics. J. Mater. Res.* **27**, 2466–2478.