Bull. Mater. Sci., Vol. 7, Nos 3 & 4, October 1985, pp. 321–326. © Printed in India.

Studies of materials using polarised neutrons

P RADHAKRISHNA

Laboratoire Léon Brillouin CEN Saclay, 91191 Gif-sur-Yvette, France

Abstract. The scattering cross-sections of a polarised neutron beam, incident on a magnetic sample, are a function of the polarisation of the beam, and of the nuclear and magnetic structure of the sample. An analysis of the polarisation of the scattered neutrons is valuable in isolating magnetic contributions.

The spin distribution, obtained by Fourier inversion of the magnetic structure factors calculated from the cross-sections, has been studied in ferromagnetic metals, intermetallic compounds and alloys. Applications of the method to the study of anti-ferromagnets and canted ferromagnets are outlined. Paramagnetic metals, solid organic radicals and trans-uranium elements have spin distributions in which orbital and other effects can be compared with theory.

The value of polarisation analysis and some of the new technical developments which have made it possible are described. Applications to inelastic phenomena are mentioned.

Keywords. Polarized neutrons; spin distribution; Fourier inversion; magnetic structure factor; ferromagnetic metal; intermetallic compound.

Neutrons are uncharged particles of spin 1/2 and the scattering cross-section from a target with a preferred magnetic axis depends on the relative orientation of this axis and the spin. In the case of an incident polarised beam, the measurement of the cross-section as a function of the initial polarisation can give information concerning the scatterer with a preferred axis system.

In the simplest application, in which no spin analysis after scattering is performed, the incident beam is usually polarised alternately parallel and antiparallel to a magnetic field, and is thus in one of the two possible spin eigenstates. The cross-sections, for a target in which the magnetic moments are aligned in an external field, are measured, and scaled to the nuclear Bragg intensities. The magnetic structure factors can then be calculated, after a certain number of corrections, for extinction, depolarisation etc.

The earliest application of the technique was the determination of magnetic structure factors in the ferromagnetic metals, such as iron, cobalt and nickel by Shull and Yamada, Shull and Mook, Moon and Mook. The magnetisation distribution in real space, obtained by Fourier inversion was analysed in two ways. In one case, the structure factors were fitted to a model in which the contributions included spin, orbital and diffuse parts. In the other, contour maps, showing the variation of the spin density throughout the unit cell, were built up. These contours showed that the distribution was aspherical and that there were regions of negative magnetization in the region between the atoms.

In ferromagnetic intermetallic compounds in which several crystallographic sites are occupied, polarised neutron measurements can often be used to determine the individual moments, and thus clarify the role of the atomic environment in inducing them. In the Heusler alloys, for example in Cu_2MnAl, there are four sites, labelled A, B, C, and D in the superlattice structure. When perfectly ordered, the equivalent A and C sites are occupied by copper, the B sites by Al and the D sites by manganese. The structure factors for the different reflections can be analysed to give the individual moments. In the copper Heusler, for instance, all the magnetization is due to the D sites.

No 4d- or 5d- transition metals order, but some of their alloys like $MnPt_3$ do, and contour maps of the spin density in the unit cell, obtained from polarised neutron diffraction, can be interpreted in terms of the magnetic contributions of the 4d- and 5d- electrons.

In dilute alloys, the interest centers around the effect of the matrix on the moment of the impurity atom and the effect of the latter on long range order in the matrix. The magnetic contributions to the diffuse background for spin-up and spin-down, in such alloys can be separated, without polarisation analysis in the case of ferromagnetism. In other cases, as shown by Hicks, Cable and others, analysis of the spin state of the scattered beam is necessary. Fourier inversion of the diffuse intensity gives the spatial distribution of the magnetic disturbance, expressed as a deviation from the moment density of the unperturbed matrix. Remarkable effects can occur. Cobalt (1–2 %) in iron reduces its moment from 2·2 μB to 2·1 μB but Ti and Cr give oppositely directed moments of $-0{\cdot}7$ μB. Significant redistribution of the moments can occur out to the fourth or fifth nearest neighbours.

Very useful permanent magnets with high saturation magnetization and high coercivity have recently been developed on the basis of the rare earth intermetallics such as $SmCo_5$. A detailed study of a prototype, containing yttrium, was undertaken by Tasset using polarised and unpolarised neutron diffraction. In these compounds there are two sites for the cobalt in the hexagonal structure, and one of them is in a layer containing yttrium atoms as well. These sites for the cobalt have much larger moments and a large orbital moment. They are responsible for the large magnetocrystalline anisotropy of Y_2Co_5. Such studies, in which the orbital contributions are referred to the environment, can lead to a better understanding of these materials for technological purposes.

The importance of garnets in optical and microwave techniques is well known. Bonnet *et al* studied yttrium iron garnet in which there are two sites, one with an octahedral, and the other with a tetrahedral, environment. After extinction corrections, due to the perfection of these crystals, they found a moment of 3·76 μB on the octahedral, and about 3·49 μB on the tetrahedral sites. In addition, a moment of 0·036 μB was found on the oxygen ligands. Calculations on the reasons for this difference are in progress.

The importance of the study of antiferromagnetic ionic compounds, lies in the fact that it is apt to give information concerning orbital magnetic moments. These moments are directionally coupled to the crystal lattice by the ligand field and by covalency. The spin direction is thus linked to the lattice through the spin-orbit coupling. Such effects are responsible for magnetocrystalline anisotropy, which has great importance in technology.

The separation of such effects depends on the different form factors of the orbital and the spin contributions. The measurements of the spin density in MnF_2 in which orbital effects are absent, by Nathans *et al*, showed that the population of antiferromagnetic 180° domains could be evaluated by polarised neutron diffraction. The flipping ratios of a selected reflection (210) were related reciprocally for the two domains. Later studies by the author on cobalt difluoride, in which orbital effects exist, concentrated on the enhancement of the domain populations by using the piezomagnetic effect and their detection with polarised neutrons.

These domains may eventually have technical applications as memory elements. Their direct visualisation has been demonstrated by Schlenker and Baruchel, by detection of polarised neutrons diffracted by the (210) reflection, on photographic plates. The effects of thermal treatment, stresses, external magnetic fields and impurities in MnF_2 were studied.

The phenomenon of weak ferromagnetism lends itself to a study by polarised neutrons, and carbonates of manganese and cobalt, haematite, nickel fluoride have been studied. In these compounds, certain reflections mirror the distribution of the ferromagnetic moment while others depend on the antiferromagnetic distribution. Often the magnetic moments are weakly canted, and mechanisms due to Moriya and Dzyaloshinsky invoke spin-orbit and crystalline field effects.

Extensive measurements on rare earth compounds such as RAl_2 have been carried out at Grenoble, using polarised beams. Hot neutrons are specially suitable on account of the large domain of reciprocal space which is significant, as well as a reduction of extinction and absorption. The graphite sources thermalize the neutrons emerging from the reactor to wavelengths of about 0·5 Å, at the ILL, and at the LLB, where the author has built a spectrometer of this kind.

The direct observation of the magnetisation density in rare earth compounds is related to the state of the 4*f* ion, which results from an interaction between crystal field effects and exchange interactions. Interesting effects connected with the orbital contribution have been demonstrated. The unusual temperature dependence of the samarium moment is due to such effects. In certain cases, specially in the RAl_2 (*e.g.* $NdAl_2$) compounds, the accurate determination of the ground state is possible. The existence of an additional contribution to the magnetisation density due to the conduction electrons has been shown in several cases.

In recent years, the application of band structure calculations in understanding physical properties is on the increase. The paramagnetic form factors of pure metals provide a test of the accuracy of models based on solid state wave functions, which are not directly accessible, as a rule. The availability of superconducting magnets has made it possible to measure the induced moment form factor in several metals. The induced moments are of the order of milli-Bohr magnetons. Long counting times are involved and several side effects have to be corrected for. Measurements on Sc, Ti, V, Cr, Zr, Pd, etc have been made, but the number is limited by the susceptibility.

The APW calculations for some of the metals are in such good agreement with the spin-only form-factor, that the role of the orbital contribution requires clarification. Technetium and rhodium have been recently studied by the author and a comparison with theory is in progress.

The importance of free organic radicals in biological effects and other fields is well-known. Solid free radicals, which can be crystallized, lend themselves to a study by polarised neutrons. Very often, however, a complete set of structure factors, enough for a full Fourier analysis, are not available, and the data can be analyzed in terms of a multipole expansion around the atomic centres, leading to an analytical expression for spin density. F Brown, A Capiomont, B Gillon and J Schweizer applied this method to a nitroxide radical containing a suberate and showed that the unpaired electron in the nitroxide is equally shared between the oxygen and the nitrogen, in contradiction with the theory based on simple model calculations. A similar study on DDPH, a free radical well known as a frequency standard in ESR, is due to B Gillion. She has shown that the polarised neutron technique can in certain cases be applied to non-centrosymmetric structures and the spin density is represented by a multipole expansion in real spherical harmonics and the fit to experimental data defines the parameters in this representation. The measurements of the flipping ratios carried out in a 4·65 Tesla field at 4·2 K showed that the spin density is mostly shared between the two nitrogen atoms, but a part is also delocalised on the two phenyl and picryl groups.

The magnetic form factor of transuranium elements and their compounds has attracted attention recently, although the well known difficulties of handling them have delayed much work. The $5f$ electrons which characterize these elements have a larger spatial extent and are more chemically active than the $4f$ electrons of the lanthanides. They also possess large orbital moments. Polarised neutron measurements on uranium and neptunium oxides, arsenides have been made.

Polarisation analysis and its applications

The analysis of the spin state of the neutrons after scattering from a target often contains valuable information concerning the system. The possibilities of this technique were first pointed out in a classical paper by Moon, Riste and others, in 1968. The neutrons incident on the sample are usually polarised and their spin state can be flipped before and after scattering. Defining the Z-axis along the polarisation direction, four spin-dependent amplitudes are considered. Using the properties of the Pauli spin operators, it can be shown that a certain number of consequences occur for systems in which no nuclear spin order is present. Isotopic incoherent scattering for nonmagnetic samples, with zero nuclear spin, is entirely non spin-flip. Nuclear spin incoherent scattering is one-third spin flip, and the rest is non spin-flip. Examples are vanadium and water. Coherent nuclear scattering or Bragg scattering is, on the other hand, entirely non-spin-flip. In the case of elastic magnetic, paramagnetic or magnetic defect scattering, only the spin component perpendicular to the scattering vector is involved. When the neutron polarisation is parallel to this vector, this component is zero and all magnetic scattering is spin-flip, while it is one half spin flip when the polarisation is orthogonal to it. A valuable general method of separating paramagnetic scattering from other processes is thus available. The paramagnetic scattering from ^{160}Gd, copper-manganese spin glasses, and amorphous erbium-cobalt compounds has given valuable information on the spin arrangement in these materials.

Polarisation analysis has recently enjoyed a measure of popularity on account of several technical developments which have alleviated the difficulties of adequate intensity. Some of these will be mentioned before citing further applications of the technique.

The replacement of crystal polarisers, such as copper Heuslers, for long wavelengths, by reflecting devices which operate over a wide wavelength range has been very significant. Schaerpf described the construction of supermirror polarisers which are small, short, only about 30 cm long, and very efficient. They have a polarising efficiency of about 97 % and a transmission of 60 to 80 % of the correct spin above 4·4 Å. A typical unit consists of mirrors deposited on 0·1 mm thick pyrex glass sheets. Eighty layers of titanium and cobalt are deposited on them, with a gradient of lattice constant, such that the angle of reflection of the cobalt increases by a factor of two. An anti-reflecting layer of gadolinium and titanium between the cobalt and the glass removes the total reflection of the unwanted spin by the glass substrate. These mirrors, curved to a radius of 10 metres, are arranged in a Soller collimator, and magnetised by ferrite magnets. Banks of such supermirrors have been installed on a spectrometer for diffuse scattering at the ILL. The Brookhaven group has developed a programme of polarised neutron inelastic studies for which two types of polariser were found necessary. They have extended the use of selected Heusler crystals and also of iron-germanium multilayers of 40 Å thickness with lattice spacings of about 40 Å. For a triple axis, good Heusler crystals are almost as advantageous as multilayer devices.

Among the more significant studies using this technique, the measurements of the scattering due to spin correlations above the critical temperature in iron, nickel, manganese and chromium by K Ziebeck and J Brown are of great interest. Shirane and his collaborators have also studied nickel, iron and iron-4 % Si using a triple axis and a Heusler analyzer, and have found no spin waves above T_c, disagreeing with earlier conclusions due to Lynn and Mook.

In amorphous erbium-cobalt, which is a magnetic glass, polarisation analysis has been used to separate the nuclear and magnetic scattering, revealing magnetic correlations between the erbium and the cobalt moments with an angular dependence. Studies on intermediate valency compounds, like SmS, have thrown light on the possibility of distinguishing between the valence states.

In an isotropic Heisenberg ferromagnet, spin wave creation peaks occur only in the $(+\ -)$ spin wave cross-section. A study of ferromagnetic chains in caesium nickel fluoride due to Kakurai, Steiner and others, using a polarising supermirror and a Heusler analyser, showed that a spin wave peak also occurs unexpectedly in the $(-\ +)$ spectrum as well, and this fact was attributed to the anisotropy of the spin Hamiltonian. An example of the use of polarisation analysis in the separation of phonons and magnons is due to Stirling *et al*, in palladium-iron, in which they have similar frequencies near the zone-boundary. A clean separation of the phonons and magnons is obtained using incident polarised neutrons and an analyser of copper or graphite. Other examples of the use of polarised neutrons in magnetism are afforded by the demonstration of the magnetic nature of the central peak in Pr by spin-flip scattering, and the absence of a roton-like minimum in amorphous ferromagnets of iron-boron. The latter could only be studied with a polarising analyser, on account of interfering phonons.

In this context, the spin echo method for high resolution inelastic measurements developed by Mezei deserves special mention. In this method, an initially polarised, poorly monochromatic, beam performs Larmor precessions while traversing a region of uniform magnetic field. After scattering, the neutrons trasverse another field region in which they precess in the opposite sense, and the final polarisation depends on the energy change. Extremely high resolutions of the order of nanovolts is available and the applications of the technique to studies in critical phenomena, to liquid helium, to spin glasses like CuMn etc, and in colloids and micelle movements are already too numerous to describe in detail.

New developments like extensions of the supermirror technique to shorter wavelengths, the further development of time of flight using pulsed flippers, and transmission filters using samarium salts at low temperatures can be expected to add to the interest of polarised neutrons for quite some time.

Acknowledgements

The author wishes to acknowledge useful discussions with F Mezei, Otto Schaerpf, R Pynn, J Brown, G Parette and many others.

References

The standard textbooks on neutron scattering provide a detailed and indispensable background. We have chosen to cite, in addition, a few recent reviews, which give further details of the examples mentioned.

Textbooks

Bacon G E 1975 Neutron diffraction (Oxford: University Press)
Kostorz G (ed) 1979 *Treatise on materials science and technology* (New York: Academic Press)
Marshall W and Lovesey S W 1971 *Theory of thermal neutron scattering* (Oxford: Clarendon Press)
Squires G L 1978 *Thermal neutron scattering* (Cambridge: University Press)

Reviews and Symposia

Mezei F (ed) 1979 *Neutron spin echo, Lecture notes in physics*, No. 128 (Berlin: Springer-Verlag)
Int. Conf. on Impact of Polarized Neutrons on Solid State Chemistry and Physics 1982 *J. de Physique*, Colloque C-7, Vol. 43
Other sources of information include the ILL reports and reports from Harwell