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POLARISED NEUTRON DIFFRACTION STUDIES ON WEAK FERROMAGNETISM - A SURVEY

by

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POLARIZED NEUTRON DIFFRACTION STUDIES ON WEAK FERROMAGNETISM - A SURVEY

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Résumé.- On discute brièvement des bases physiques du phénomène de ferromagnétisme faible dans des isolants antiferromagnétiques. Une revue des contributions de la diffraction de neutrons polarisés à la compréhension des différents aspects de ce phénomène est présentée.

Abstract.- The physical basis of the phenomenon of weak ferromagnetism in certain antiferromagnetic insulators is briefly discussed. A survey of the contributions of polarised neutron diffraction towards the elucidation of different aspects of this field is presented.

A weak ferromagnetic moment was first observed to occur along certain crystallographic directions in a few simple antiferromagnets. A spontaneous magnetization of this kind was observed in α-Fe_2O_3 by Néel and Pauthenet [1] and in $MnCO_3$ and $CoCO_3$ by Borovik-Romanov and Orlova. In a plane perpendicular to the trigonal axis, the field dependence of the magnetization $M_\perp$ was expressed by

$$M_\perp = M_f + \chi_\perp H$$

The spontaneous moment M_f was a small fraction, 0.1 % to 10 %, of the nominal moment $Ng\mu_B S$. Only the high temperature phase of α-Fe_2O_3 above ~10°C showed this behaviour. Among the crystallographic isomorphic carbonates of Mn, Ni, Co and iron, the last was found to possess no weak ferromagnetic moment.

A thermodynamic theory of weak ferromagnetism has been given by Dzyaloshinsky [2], based on a model in which the antiparallel spins are slightly canted towards each other. A simple treatment of his theory is sketched below, in order to illustrate the role of the different types of spin interactions involved.

In the case of an antiferromagnet with an elementary cell containing two magnetic ions bearing moments $\underline{s}_1$ and $\underline{s}_2$, an antiferromagnetic vector $\underline{\ell}$ and a ferromagnetic vector $\underline{m}$ are defined such that

$$\underline{\ell} = \underline{s}_1 - \underline{s}_2$$

$$\underline{m} = \underline{s}_1 + \underline{s}_2$$

and for one gram-atom

$$\underline{M} = (N/2)\underline{m} \text{ and } \underline{L} = (N/2)\underline{\ell}$$

where N magnetic ions are involved.

The thermodynamic potential is expressed as follows

$$\Phi = \Phi_o + (\tfrac{A}{2})\underline{L}^2 + (\tfrac{B}{2})\underline{M}^2 + (\tfrac{a}{2})L_z^2 + (\tfrac{b}{2})M_z^2 + \tfrac{1}{2}(L_x M_y - L_y M_x) + (\tfrac{c}{4})\underline{L}^4 - \underline{M}.\underline{H}$$

In this expression, the terms which do not depend on the orientation of $\underline{L}$ and $\underline{M}$ with respect to the crystal axis represent exchange interactions. The much smaller

anisotropic terms are due to the magnetocrystalline anisotropy and arise from spin-orbit and dipole-dipole interactions. An exchange term of the fourth order and the energy of the antiferromagnet in the magnetic field complete the expression. The equilibrium values of $\underline{M}$ and $\underline{L}$ correspond to a minimum of the potential and we thus have six equations as follows :

$$B M_x - \mathcal{E} L_y - H_x = 0$$

$$B M_y - \mathcal{E} L_x - H_y = 0$$

$$(B+b) M_z - H_z = 0$$

$$A L_x + \mathcal{E} M_y + c L^2 L_x = 0$$

$$A L_y - \mathcal{E} M_x + c L^2 L_y = 0$$

$$(A+a) L_z + c L^2 L_z = 0$$

When $\underline{H}=0$, the system has three solutions. The first one, corresponds to paramagnetism and is given by $\underline{M}=\underline{L}=0$. The second solution is

$$L_y = L_z = M_x = M_z = 0 \; ; \; M_y = -(\mathcal{E}/B)\, L_x, \; L_x^2 = -[A-(\mathcal{E}^2/B)]/c$$

or

$$L_x = L_z = M_y = M_z = 0 \; ; \; M_x = +(\mathcal{E}/B)\, L_y, \; L_y^2 = -[A-(\mathcal{E}^2/B)]/c$$

The directions of the vectors L and M in the plane normal to the trigonal axis are not defined since both solutions yield the same value of the potential. In this state, L and M are both non-zero and L is always perpendicular to M. The ferromagnetic moment M is smaller than the antiferromagnetic one in the ratio $\mathcal{E}/B$. The vectors of the two magnetic ions are not exactly antiparallel but are canted through a small angle $\phi \sim \mathcal{E}/B$. In such cases, the magnetic symmetry allows a term in the free energy of the form $\underline{D}.(\underline{S}_i \times \underline{S}_j)$ where S_i and S_j are the spin vectors on pairs of atoms which are nearly antiparallel, and $\underline{D}$ is a constant vector perpendicular to the spin direction. The vector $\underline{D}$ favours an angle of 90° between the spins.

A systematic study of the symmetry in the case of weak ferromagnetism is due to Birss[3] and to Turov [4], who introduced the concept of the parity of an antiferromagnetic spin configuration with respect to the symmetry operations of the crystal lattice. The parity is odd if the transformation interchanges magnetic moments belonging to different magnetic sublattices and even if they come from the same one. It was shown that weak ferromagnetism is possible only in antiferromagnetic structures that are even with respect to all lattice transformations and an inversion centre, if it exists. As a consequence, the magnetic and chemical cells are identical and the moments of all sublattices related by a translation or inversion must remain parallel. Considerations on the detailed application of these rules to the different systems by Turov show that the phenomenon should be far from rare.

The microscopic origin of this canting has been discussed by Moriya [5] who has suggested two mechanisms. In the first, the magnetic ions occupy two non-equivalent sites in the crystal, and the crystalline field acting on them is different. The difference in their energies acting together with the spin-coupling leads to non-parallel easy directions of spin orientation and hence to a canting. An example of this mechanism is NiF_2. In the second case, anisotropic superexchange interaction which is due to the combined effect of the spin-orbit coupling and the superexchange interaction, can produce an antisymmetrical spin coupling term of the form suggested by Dzyaloshinsky, which tends to cant the spins. Some of the orthoferrites and α-Fe_2O_3 are examples.

Polarised neutrons have proved a particularly fruitful technique in the study of canted ferromagnetism. Accurate neutron diffraction measurements of magnetic scattering from ordered magnetic materials provide direct access to the distribution of magnetic moment density in the unit cell, which is, in general, due to the spin and orbital moments of the magnetic electrons, modified by covalency, in the case of the

transition elements.

In principle, the method is based on the measurement of the diffracted intensities from a crystal maintained in a monochromatic neutron beam, with the neutron spins alternately up and down with respect to a magnetic field on the sample. A flipping ratio can then be defined $R = I^+/I^-$, in which I^+ and I^- are the diffracted intensities corresponding to the two spin states. For a centrosymmetric structure, this ratio is expressed in terms of the nuclear and magnetic structure factors $N(\underline{K})$, $M(\underline{K})$ with $\underline{Q}(\underline{K}) = \underline{K} \times \underline{M}(\underline{K}) \times \underline{K}$ as follows :

$$R = \frac{N(\underline{K})^2 + 2\mathrm{Re}[N(\underline{K})\ Q(\underline{K}).\hat{\underline{P}}] + Q(\underline{K})^2}{N(\underline{K})^2 - 2\mathrm{Re}[N(\underline{K})\ Q(\underline{K}).\hat{\underline{P}}] + Q(\underline{K})^2}$$

where $\underline{K}$ is the scattering vector and $\hat{\underline{P}}$ is the unit vector parallel to the polarisation. The necessary corrections for the background, extinction, efficiences of flipping and polarisation, and the $\lambda/2$ contribution are treated in several publications.

An antiferromagnet has to satisfy certain requirements in order to constitute a favourable case for study using polarised neutrons. The magnetic and nuclear unit cells should be identical, the structure factors should not be in phase quadrature, and the distribution of the antiferromagnetic domains is of primary importance. These are also the conditions for the occurrence and study of weak ferromagnetism.

The expression for the flipping ratios is modified in the presence of antiferromagnetic domains. Such domains are physically plausible on account of the lowering of the free energy expected as a result of the increased disorder and entropy. The domain walls are probably only a few lattice spacings thick and require imperfections such as vacancies or dislocations to stabilise them. They have been directly observed in some antiferromagnets using polarised neutron topography. Such studies are likely to prove of value in following their behaviour in magnetic fields.

In a uniaxial antiferromagnet, with the sublattice magnetisation directed along the main axis, 180° domains may exist, differing in the signs of the antiferromagnetic vectors $\underline{L}$. The weak ferromagnetic moments are linearly dependent on the components of $\underline{L}$ and a reversal of the weak moment must be accompanied by a rotation of the antiferromagnetic sublattices by 180°. If the fraction of the reversed spins on equivalent sites is given by $(1+\delta)/2$ the flipping ratio is given by

$$R = \frac{N^2 + M^2q^2 + 2\delta NM\ \underline{q}.\hat{\underline{P}}}{N^2 + M^2q^2 - 2\delta NM\ \underline{q}.\hat{\underline{P}}}$$

where F_N and F_M are the nuclear and magnetic structure factors, $\underline{q} = \hat{\underline{K}}(\hat{\underline{K}}.\hat{\underline{\xi}}) - \hat{\underline{\xi}}$ and $\hat{\underline{P}}$ is the direction of polarisation of the neutrons, $\hat{K}$ the unit scattering vector and $\hat{\underline{\xi}}$ the unit spin vector on the ion.

In the particular case of haematite [6], which we shall consider in some detail, the application of this relation is complicated by the fact that it is not uniaxial and there are three equivalent antiferromagnetic axes in the basal plane along which the spins can lie.

The spin axes are rotated by 120° in these trigonal domains. In the geometry chosen, the perpendicular component of the spin in the antiferromagnetic trigonal domains can be obtained by a measurement of the spin-flip fraction, which implies polarisation analysis of the diffracted beam.

Subsequently, the distribution of the ferromagnetic spin density in the unit cell can be estimated from the flipping ratios of the nuclear peaks which contain these contributions, and which are forbidden by the antiferromagnetic structure.

The antiferromagnetic domain walls are coupled with the ferromagnetic ones, since only then is the sense of $\underline{D}$ in the Dzyaloshinsky term invariant throughout the crystal. The antiferromagnetic domain population follows the field dependence of the magnetisation, and on saturation, a single domain is formed. The polarisation ratio

for the (210) reflection, which is sensitive to the domain population, was chosen by the authors for a study of these effects. It rose to a maximum of 2.2 as the field swept out the antiferromagnetic domain walls for which the easy direction was probably [10$\bar{1}$]. A gradual repopulation of these domains with spins more perpendicular to the field led to a subsequent decrease in R as $\hat{P}.q \to 0$. A reasonable correlation with the magnetisation data confirmed this picture.

The spin density of the canted moment was studied by measuring the flipping ratio of the forbidden reflections with (h+k+l) even, suitably chosen to maximise the effect. The covalent contribution from the iron-oxygen bonds was eliminated by working under conditions in which the interference term, proportional to $\hat{P}.q$ is zero. Only four reflections were finally measured, two of which were equivalent. The ferromagnetic component was found to have a distribution different from the antiferromagnetic component and it was suggested that the spin density was a vector function, probably as a result of the spin-orbit coupling.

The spatial distribution of the weak ferromagnetic moment in the S-state ion in $MnCO_3$ was measured by Brown and Forsyth [7] with considerable accuracy. It has a rhombohedral structure, and the Mn ions at 000 and 1/2 1/2 1/2 have nearly antiparallel spins, with the weak ferromagnetic moment in the basal plane.

The ferromagnetic distribution alone was studied by restricting the work to reflections of the type (hhl) with l even. The variation of the intensity of an antiferromagnetic reflection (001) with field at 4.2K gave an indication of the anisotropy and the orientation of the trigonal domains. This intensity was shown to follow the magnetisation curve closely. The flipping ratios of fourteen reflections were measured in two fields and at a neutron wavelength of 0.93 Å. The usual corrections were applied and, in addition, the integrated intensities of 46 reflections using unpolarised neutrons were compared with the calculated structure factors to show that no extinction was present.

From these results the projection of the ferromagnetic spin density down the [1$\bar{1}$0] direction was carried out. The comparison with circularly symmetrical form factors calculated for a radius of 1.0 Å using the form factor for Mn^{2+} ($3d^5$) show that 10% of the moment was transferred to the ligands in the high field (7.0 KOe) and about 20% in the lower one (1.57 KOe).

Data from the magnetisation curves allowed a separation of the spontaneous part from the field induced part and these values, suitably normalised, were used to calculate the Fourier projections corresponding to each contribution. The distributions were quite different, which is unexpected, since they are supposed to arise from the same mechanism of canting. In each case, the density of the moment on the Mn extends out towards the oxygen, but in different ways, Kaplan's calculations [8], showing that the spin-orbit coupling introduces a effect which is independent of the field, may account for much of this difference.

The field-dependent moment reflects the antiferromagnetically aligned moment and its deviation from circular symmetry can be attributed to covalency. The spin distribution associated with the orbitals between the manganese and the oxygen neighbours was calculated on the basis of the theory of Marshall and Hubbard. Regions of negative polarisation on the carbon atoms incompatible with the present models of covalency were postulated to explain the observed distribution [9].

Cobalt carbonate has a larger ferromagnetic moment due to the presence of the orbital moment. It was shown to be an antiferromagnet T_N = 18.1K, with a spontaneous ferromagnetic moment of 0.258 μ_B/mole at 0 K, by Borovik-Romanov and his collaborators. It has a rhombohedral unit cell and the weak ferromagnetic component is in the plane at right angles to the trigonal axes. The (hhl) reflections with l even are nuclear, with small ferromagnetic contributions which were measured using polarised neutrons [10] at 3.6 KOe, and at 4.6 KOe when the domains are fully aligned, as shown by the flipping ratio of the (110) reflection. The purely magnetic intensities, with l odd, were normalised on an absolute scale, after extinction corrections obtained from the stronger nuclear peaks.

The ground state wave function was defined by linear combinations of basis vectors functions conforming to the point group symmetry of the Co^{2+} ion in $CoCO_3$, and the

spin-orbit and trigonal distortion energies estimated from EPR were used to select the coefficients of the eigenfunctions. The magnetic scattering due to the antiferromagnetic structure was calculated for several angles of tilt and crystal field parameters. The best agreement was obtained with the moment in the basal plane- and unexpected result.

The effects of an exchange interaction and an applied field parallel to the spontaneous moment were also studied. The results resemble those obtained for $MnCO_3$. The normalised form factors indicate covalent effects and an elongation of the Co^{2+} moment towards the anion.

An elegant study of the weak ferromagnetism in a compound with the rutile structure is due to Brown and Forsyth (11). Below 73.2 K NiF_2 forms an antiferromagnetic structure in which the moments in the basal plane are canted at a small angle of 0.9° to the <100> directions. Moriya has shown that the mechanism responsible for this canting is that due to single ion anisotropy.

The weak ferromagnetic component was studied in a crystal in which domains were removed by an external field. All nuclear reflections contain a part of this ferromagnetic component, but those with (h+k+l) odd also contain a much larger interfering antiferromagnetic contribution. Hence only reflections with (h+k+l) even are chosen, and the need to eliminate the aspherical antiferromagnetic part by choosing $\underline{Q}(\underline{K}).\hat{\underline{P}} = 0$, limited the choice to (hOl) reflections. Careful corrections for multiple scattering and extinction were found necessary.

The Ni^{2+} ion was treated in an octahedral crystal field with a small orthorhombic distortion. The magnetic scattering was calculated using crystal field parameters from susceptibility, ESR and infra-red transmission. The results were compared with the measured values of $\underline{Q}(\underline{K}).\hat{P}/M$ for a refinement of the Ni^{2+} wave-function.

The best crystal field parameters were found to be in disagreement with the conclusions of other techniques. The effects of covalency were strong at low angles, and in its presence, the simple ionic model used in inadequate for a more detailed refinement.

Certain external influences can also induce a weak ferromagnetic moment or reorientation of the spins not necessarily canted, in antiferromagnetic crystals,which then lend themselves to a study by polarised neutrons. The enhanced piezomagnetism in CoF_2 is an example (12).

In conclusion, this technique, in combination with calculations of magnetic scattering based on plausible crystal field models, can throw light on the orientation of the spins and the detailed mechanism of phenomena in the field of weak ferromagnetism.

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