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A neutron diffraction study of weak ferromagnetism in nickel fluoride

P J Brown† and J B Forsyth‡

† Institut Laue–Langevin, Grenoble, France

‡ SERC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK

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Abstract. Polarised neutron diffraction data have been collected from single crystal samples of NiF_2 at 4.2 K and in an external field of 1.4 T. Subsidiary unpolarised neutron experiments carried out at a number of wavelengths have determined the extinction parameters and these have been used to correct the observed, polarised-beam flipping ratios. The geometry of the polarised neutron experiment was such that one group of reflections gives information solely on the distribution of the weak ferromagnetism, which corresponds to some 0.03 $\mu B/Ni^{2+}$ ion. The other reflections contain magnetic scattering from the antiferromagnetic component of the moment. Measurement of the flipping ratio of the 111 reflection has enabled us to verify the absolute configuration of the canted magnetic moments with respect to their octahedron of fluorine neighbours. The observations are compared to a calculation based on a model ground state wavefunction for the Ni^{2+} ion in the rutile structure and indicate that, although this model accounts qualitatively for the magnetic scattering, there are very significant discrepancies particularly in the low-angle data. It is concluded that a more sophisticated model including covalent transfer of spin to the fluorine ligands is required to give a satisfactory explanation of the scattering associated with the weak ferromagnetism in NiF_2.

1. Introduction

Accurate neutron diffraction measurements of the magnetic scattering intensity from ordered magnetic materials can provide a direct measure of the magnetic moment density throughout the unit cell. In general, the magnetisation contains contributions from both the spin and orbital moment of the magnetic electrons and it will be modified, for ions of the transition elements, by the presence of covalency. Alperin (1961, 1962) was the first to make such measurements by collecting unpolarised neutron diffraction intensities from both powdered and single crystal samples of antiferromagnetic NiO. The e_g symmetry of the magnetisation, its low value and the expansion of the form factor relative to that for a spin-only free ion are quite well accounted for by the presence of the cubic crystalline field (Low 1958), some 10% orbital moment corresponding to a g value of 2.23 (Blume 1961), the introduction of spin-polarised Hartree Fock wavefunctions (Watson and Freeman 1960) and covalency (Hubbard and Marshall 1965).

To the best of our knowledge, there have been no form factor determinations for Ni^{2+} in any environment since the first experiment of Alperin (1961). However, Ni^{2+}

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compounds have been investigated by calculation perhaps more thoroughly than those of any other transition metal ion, particularly in the case of NiF_6^{4-}. The pioneering study of this complex in $KNiF_3$ by Sugano and Shulman (1963) was further improved by, among others, Ellis *et al* (1968), Soules *et al* (1971) and Wachters and Nieuwpoort (1972).

We now report a study of magnetic neutron scattering from NiF_2 which we have sought to interpret on the basis of the current understanding of the ground state wavefunction for the Ni^{2+} ions. NiF_2 has the added interest of being one of the small group of weakly ferromagnetic ionic compounds. We have used the high sensitivity offered by the polarised beam to study the spatial distribution of this ferromagnetism.

2. The magnetic structure of NiF_2

Nickel fluoride has the rutile structure illustrated in figure 1. The unit cell is tetragonal, space group $P4_2/mnm$ with $a = 4.710$ Å, $c = 3.118$ Å. The atoms occupy the following positions:

Ni in 2a at $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

F in 4f at $\pm(x, x, 0; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2})$ with $x \sim 0.30$.

Below its Néel temperature of 73.2 K, NiF_2 forms a slightly canted antiferromagnetic structure in which the moments lie in the basal plane close to the $\langle 100 \rangle$ directions (Moriya 1960). The single-ion anisotropy introduces a small angle δ between the moments and the axial directions of some 0.9° as shown in figure 1. The sense of δ has been deduced by Moriya (1960) from the torque measurements of Matarrese and Stout (1954) and by Shulman (1961) from NMR experiments: it is such that the moments make an angle of $45° + \delta$ to the fluorine ligand at the same height in the unit cell. If the ferromagnetic moment is aligned along [010] then the antiferromagnetic component on the atom at the origin of the unit cell points along $[\bar{1}00]$.

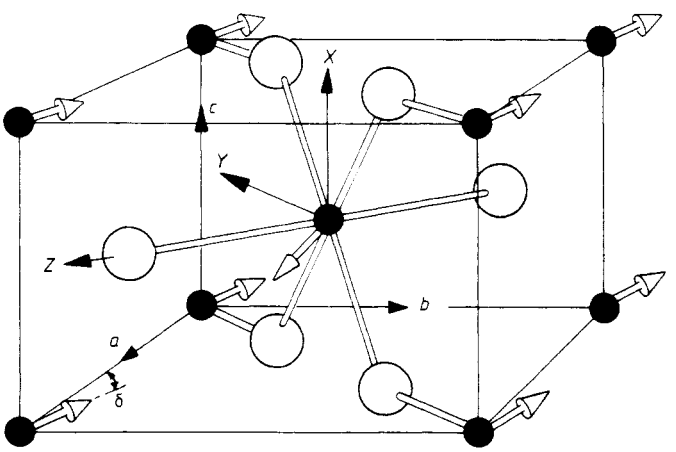

Figure 1. The tetragonal unit cell of NiF_2, which has the rutile structure. The directions of the magnetic moments on the nickel ions at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are indicated by open arrows: they lie in the basal plane and are inclined to the a axis by an angle δ. Each nickel ion is octahedrally coordinated by fluorine atoms and the quantum axes X, Y and Z are shown for the ion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

Precision x-ray measurements by Haefner *et al* (1966) have shown that there is a very small difference between the lattice constants $\boldsymbol{a}$ and $\boldsymbol{b}$ below the Néel temperature

$$a = 4.64844(4) \qquad b = 4.64719(4) \qquad c = 3.0743 \text{ Å}$$

where $\boldsymbol{a}$ is the direction of the weak ferromagnetic moment. Our diffraction measurements are insensitive to this small departure from tetragonality.

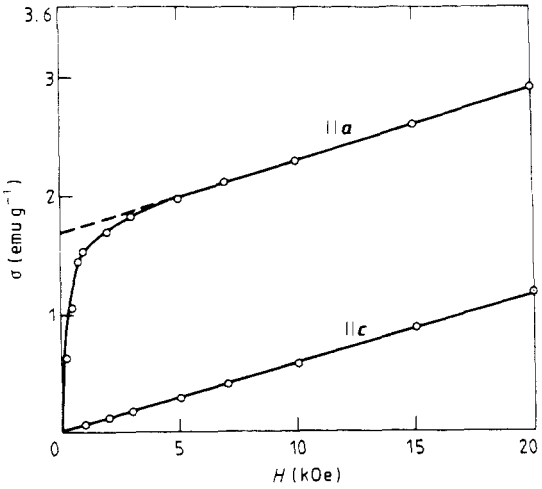

Figure 2. Magnetisation curves for NiF_2 at 4.2 K with the magnetic field applied parallel and perpendicular to the tetragonal axis (after Joenk and Bozorth 1965).

The susceptibility and ferromagnetic moment σ of NiF_2 have been the subject of a number of studies (Joenk and Bozorth 1965, Cooke *et al* 1965 and Borovik-Romanov *et al* (1973). The value of σ lies in the range 161–178 emu mol^{-1} corresponding to some 0.03 μB/NiF_2. In zero field some domains have their net moment parallel to $\boldsymbol{a}$ and the others parallel to $\boldsymbol{b}$. When a sufficiently strong field is applied parallel to $\boldsymbol{b}$, the domains parallel to $\boldsymbol{a}$ are swept away; a further increase in the field strength then causes a linear increase in the canting angle and ferromagnetic moment of the material (figure 2).

3. Polarised neutron diffraction measurements at 4.2 K

The principal objective of the present study has been to determine the spatial distribution of the weak ferromagnetism in NiF_2. Since the magnetic scattering which arises from a ferromagnetic distribution contributes to the nuclear reflections, the polarised beam technique can be used to determine the magnetic scattering amplitudes through measurements of the flipping ratios R for incident neutron spins parallel and then antiparallel to the magnetisation direction in the crystal

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

with

$$\boldsymbol{Q}(\boldsymbol{K}) = \hat{\boldsymbol{K}} \times \boldsymbol{M}(\boldsymbol{K}) \times \hat{\boldsymbol{K}}$$

Here, $N(\boldsymbol{K})$ and $\boldsymbol{M}(\boldsymbol{K})$ are the nuclear and magnetic structure factors for a given reflection with scattering vector $\boldsymbol{K}$ and $\hat{\boldsymbol{P}}$ is a unit vector parallel to the beam polarisation.

Two approximately equi-axed single crystal specimens were selected from a flux-grown sample provided by B M Wanklyn, Clarendon Laboratory. Oxford. The sample weights were 125 and 28 mg and they were oriented with [010] vertical in the liquid helium cryostat of the D3 polarised neutron diffractometer at the ILL, Grenoble. An external applied field of up to 1.4 T is provided by an electromagnet and an initial experiment was conducted to verify that the application of a modest field of some 0.1 T did indeed result in removal of domains with weak ferromagnetism along [100] or $[\bar{1}00]$, as suggested by the bulk measurements illustrated in figure 2. The integrated intensity of the purely magnetic reflections (100) and (300) were monitored as the field was increased. In principal the intensity should be reduced to zero, since the antiferromagnetic component of the remaining domain is parallel to the scattering vector. In fact, a residual intensity was observed which amounted to some 15% of that from the unmagnetised equidomain crystal, and this remained after the field increased beyond 0.1 T. The residual intensity was subsequently shown to be the result of multiple Bragg scattering and it remains at temperatures above the Néel point.

In the limit of spherically symmetric moment distributions centred on the cations, the antiferromagnetic component of the moment in the NiF_2 will contribute only to reflections with $h + k + l$ odd. Of these, those with either h or $k = 0$ will be purely magnetic and the rest will be mixed with nuclear intensity coming from the fluorine anions. Although the principal objective of the experiment is to study the weak ferromagnetism in NiF_2, this is not unrelated to the absolute magnetic configuration which is accessible through flipping ratio measurements on these latter mixed nuclear and magnetic reflections. The existence of the external magnetic field parallel to [010] ensures that the antiferromagnetic part of the moment lies along [100].

The antiferromagnetic part of the magnetic interaction vectors $\boldsymbol{Q}$ for hkl reflections with $k \neq 0$ have components parallel to the [010] polarisation direction and therefore have polarisation-dependent cross sections. We measured a flipping ratio of 0.683 ± 0.002 for the 111 reflection. The observation that this ratio is less than unity provides direct confirmation of the spin configuration deduced by Moriya (1960) and Shulman (1961), since it shows that the moment on the magnetic ion at the origin is rotated from $[\bar{1}00]$ towards [010].

The ferromagnetic moment contributes to all nuclear reflections but its contribution to the reflections with $h + k + l$ odd will be masked by the much larger antiferomagnetic scattering. We must therefore confine our measurements to the $h + k + l$ even reflections: for some of these we can take advantage of the fact that no aspherical antiferromagnetic moment can contribute if $\boldsymbol{Q}(\boldsymbol{K}) \cdot \boldsymbol{P} = 0$. In practice, this occurs for the $\{h0l\}$ reflections if the ferromagnetic moment is aligned by a magnetic field parallel to [010], which is also the direction of $\boldsymbol{P}$.

The flipping ratios of 23 independent reflections out to $\sin\theta/\lambda = 0.6$ Å^{-1} were measured from both crystals in an external field of 1.4 T. As many equivalent reflections were measured as the normal beam, zero and higher layer geometry allowed, even though those from different layers are not strictly magnetically equivalent. In several cases, unexpected differences between exactly equivalent reflections suggested the presence of multiple scattering effects, so those measurements were repeated at several different wavelengths and, in some cases, as a function of rotation about the scattering vector. The D5 diffractometer was used in the latter case and for measurements to the shortest wavelength (0.5 Å).

4. Extinction

Comparison of the observed reflection peak heights showed that severe extinction was present in both crystals. The physical interpretation of the observations is therefore critically dependent on a proper correction for this effect. The correction of magnetic structure factors, obtained by polarised neutron diffractometry, when the magnetic scattering is much weaker than the nuclear has been considered by Delapalme *et al* (1978). They show that the flipping ratios close to unity are much less variable with wavelength than are the integrated intensities. Rough estimates of the integrated intensities from our samples showed that, for the larger crystal, extinction was important in all reflections and that its magnitude precluded a sufficiently accurate treatment. No further account was taken of the data from the larger crystal and the results quoted in the rest of the paper pertain to measurements on the smaller sample. We based our extinction correction for these data on a model derived from accurate integrated intensity measurements at three wavelengths (0.84, 0.53 and 0.40 Å) made at 90 K on the D9, hot-source diffractometer at the ILL. These data were reduced to structure factors and used in a least-squares refinement. The parameters of the model were three scale factors (one for each wavelength), the fluorine positional parameter, two isotropic temperature factors and a mosaic spread parameter to take account of the extinction. The extinction was treated within the Becker–Coppens (1974) theory. It was found necessary to fix the domain radius at a large value, equivalent to type I behaviour, and the best fit was given by a Lorentzian angular distribution of mosaic blocks. The final crystallographic parameters are

Mosaic spread	$0.77 \pm 0.06 \times 10^4$ radians $^{-1}$
Nickel isotropic temperature factor	0.50 ± 0.02 Å $^{-2}$
Fluorine x parameter	0.3037 ± 0.0002
Fluorine isotropic temperature factor	0.62 ± 0.02 Å $^{-2}$

The overall agreement factor was 4.5% and no significant improvement occured when the temperature factors were allowed to be anisotropic.

Delapalme *et al* (1978) showed that the correction to be applied to the observed magnetic structure factors is

$$M_{\text{corrected}} = M_{\text{obs}}\left(1 + \frac{N}{2y}\frac{\mathrm{d}y}{\mathrm{d}N}\right)^{-1}$$

where y is the extinction correction which relates the kinematical and the observed intensities.

$$I_{\text{observed}} = yI_{\text{kinematical}}.$$

The derivative $\mathrm{d}y/\mathrm{d}N$ was calculated from the refined extinction model and the correction factors are listed in table 1 for a range of reflections with widely different intensities and for the five different wavelengths used in the experiment. The relative insensitivity to wavelength of the larger corrections is clearly demonstrated. After correction for extinction, the magnetic structure factors for the same reflection measured at different wavelengths were in most cases in good agreement. In a few instances, individual measurements which were significantly different from the means were rejected as being affected by multiple scattering.

The correction factors applied to 110 and 220, though not the largest, result in magnetic structure factors greater than that attributable to the bulk magnetisation. These reflections are just those ones with scattering vectors most inclined to the (010) plane (45°), and we therefore thought it prudent to check the extinction correction for this extreme case. A comparison was made between flipping ratio measurements of the reflections measured with [010] vertical and with [1$\bar{1}$0] vertical at 80 K and in an applied

Table 1. The extinction correction factor $(1 + N/2y\ \mathrm{d}y/\mathrm{d}N)^{-1}$ for some reflections from NiF_2 at the five different wavelengths used in the experiment. The nuclear structure factors N in units of 10^{-12} cm are also given.

				Extinction corrections for various wavelengths λ(Å)				
h	k	l	N	$\lambda = 0.90$	$\lambda = 0.84$	$\lambda = 0.80$	$\lambda = 0.72$	$\lambda = 0.50$
1	1	0	2.2762	2.2089	2.1745	2.1458	2.0736	1.7655
2	2	0	3.2538	2.1745	2.1500	2.1279	2.0681	1.7810
2	1	1	2.5270	2.0528	2.0079	1.9730	1.8911	1.5916
1	1	2	2.1702	1.8486	1.7963	1.7582	1.6751	1.4130
4	1	1	1.7249	1.5655	1.5178	1.4849	1.4171	1.2314
3	1	0	1.3805	1.5214	1.4741	1.4421	1.3775	1.2065
4	2	2	1.4602	1.4025	1.3620	1.3348	1.2811	1.1463
1	0	1	1.3142	1.6937	1.6377	1.5992	1.5200	1.2987
2	0	0	0.3429	1.0715	1.0626	1.0569	1.0463	1.0226
0	0	2	4.0406	2.2183	2.2126	2.2041	2.1725	1.9391
3	0	1	3.6770	2.1687	2.1506	2.1331	2.0825	1.8119
2	0	2	0.3474	1.0439	1.0381	1.0344	1.0278	1.0133
4	0	0	2.3386	1.8273	1.7777	1.7413	1.6610	1.4045
4	0	2	2.2273	1.6990	1.6513	1.6169	1.5426	1.3178

field of 4.6 T. In these conditions, the magnetisation arises solely from aligned paramagnetism amounting to $104 \times 10^{-3}\ \mu_B$/cell, and the scattering vectors in the second orientation now lie in the (010) plane. After correction for this geometrical difference, the observed magnetic structure factors were equivalent to ±5%, which was the accuracy of measurement. Moreover, their values were now consistent with the magnetisation and an Ni^{2+}, 3d form factor. This experiment confirms the validity of the extinction correction even in the non-zero layer geometry.

5. Contributions to the magnetic structure factors

The magnetic structure factors deduced from the flipping ratios assuming that they arise solely from magnetisation directed along [010] are plotted against sin θ/λ in figure 3. The extinction corrections described in the previous section have been applied. The bulk magnetisation at 1.4 T corresponds to $98.5 \times 10^{-3}\ \mu_B$/cell. The dependence on sin θ/λ of the magnetic structure factors is by no means smooth and, as has already been remarked, the values for the (110) and (220) reflections are significantly greater than the total magnetisation. This result suggests that the assumption made above is not justified and that these data contain contributions from the much larger, antiferromagnetic component of the magnetisation. The two important ways by which the antiferromagnetic

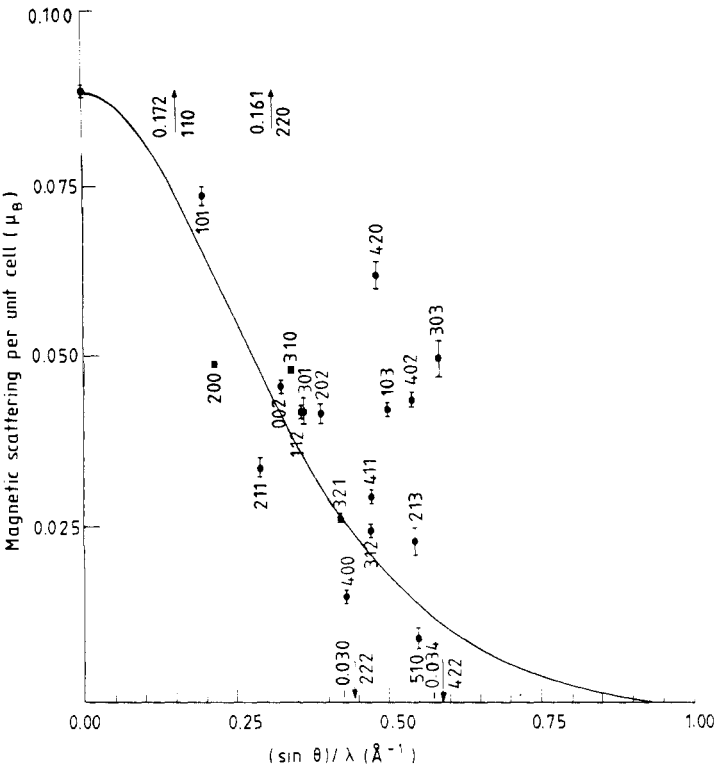

Figure 3. Comparison of the magnetic scattering in the $(h + k + l)$ even reflections of NiF_2 with that which would be given by Ni^{2+} ions with a spin-only form factor. The four values which lay outside the limits of the graph are indicated by vertical arrows.

moment may contribute to these reflections are through the asymmetric components contributing to nonzero layer reflections (see § 3) and through higher multipoles of magnetisation parallel to [010] introduced by spin–orbit coupling. The latter effect was first discussed for S state ions by Kaplan (1964) and it should be most important in the higher-order reflections. The anomalously high scattering in the low-angle 110 and 220 reflections must come from the former effect. It is therefore not possible to treat asymmetric components of the antiferromagnetic moment as small perturbations of the ferromagnetic scattering in those reflections in which both contributions are present. However, the majority of reflections measured have sin θ/λ values at which any covalent contribution to the magnetic scattering will be small, and hence the characteristic features of the data illustrated in figure 3 must be a property of the single-ion magnetisation density at all but the lowest angles.

6. The Ni^{2+} ion in an orthorhombic crystal field

The Ni^{2+} ion in NiF_2 is coordinated by an octahedron of fluorine ions with orthorhombic symmetry. We will describe the wavefunction of the nickel ion at $(\frac{111}{222})$ in the unit cell with respect to the axes shown in figure 1 (X parallel to [001]; Y parallel to $[\bar{1}10]$). With

this choice, the Z quantum axis is directed towards a vertex of the octahedron whereas the other two axes pass through the mid-points of perpendicular edges.

The crystal field can be separated into a dominant octahedral part and a smaller orthorhombic distortion leading to inequivalence of all three quantum axes. The Ni^{2+} ion has a $(3d)^8$ configuration giving a ^3F ground state separated by some $14000\,cm^{-1}$ from a ^3P state. The octahedral field splits ^3F into an orbital singlet Γ_2 and two orbital triplets Γ_5 and Γ_4. The Γ_2 state has the lowest energy, some $10^4\,cm^{-1}$ below Γ_5. The orthorhombic distortion of the cubic field lifts the degeneracy of both Γ_5 and Γ_4 states, but the potentials involved are much smaller than those associated with the cubic components of the field, so it is permissible to use a perturbation treatment to evaluate the mixing of Γ_5 into the ground state by spin–orbit coupling. The eigenvectors of Γ_5 in an orthorhombic field can be written as

$$\Psi_A = \frac{\sqrt{5}}{4}(|1\rangle + |-1\rangle) - \frac{\sqrt{3}}{4}(|3\rangle + |-3\rangle)$$

$$\Psi_B = \frac{\sqrt{5}}{4}(|1\rangle - |-1\rangle) + \frac{\sqrt{3}}{4}(|3\rangle - |-3\rangle)$$

$$\Psi_C = \frac{1}{\sqrt{2}}(|2\rangle + |-2\rangle).$$

We define Δ_A, Δ_B and Δ_C as the energies of these three states with respect to the ground state Γ_2, which is given by

$$\Psi_G = \frac{1}{\sqrt{2}}(|2\rangle - |-2\rangle).$$

With the quantum axes defined in figure 1, the appropriate combination of spin and orbital functions which lead to a spin-only moment equally inclined to the Y and Z quantum axes is

$$\Phi_G = -\frac{1}{4}(\sqrt{2}-1)(|2,1\rangle - |-2,1\rangle) + \frac{i}{2\sqrt{2}}(|2,0\rangle - |-2,0\rangle)$$
$$+\frac{1}{4}(\sqrt{2}+1)(|2,-1\rangle - |-2-1\rangle)$$

and the orthogonal function

$$\Phi_Y = \frac{1}{2\sqrt{2}}(|2,1\rangle - |-2,1\rangle) - \frac{i}{2}(|2,0\rangle - |-2,0\rangle) + \frac{1}{2\sqrt{2}}(|2,-1\rangle - |-2,-1\rangle)$$

can be used to introduce a small component of spin moment parallel to the applied field in the experiment, midway between the Z and $-Y$ axes.

The states of Γ_5 which are mixed into Φ_G are

$$\Phi_A = \frac{1}{\sqrt{3}}(\sqrt{2}|A,0\rangle + \frac{i}{\sqrt{2}}|A,1\rangle - \frac{i}{\sqrt{2}}|A,-1\rangle)$$

$$\Phi_B = \frac{1}{\sqrt{2}}(|B,0\rangle + \frac{i}{\sqrt{2}}|B,1\rangle + \frac{i}{\sqrt{2}}|B,-1\rangle)$$

$$\Phi_C = \frac{1}{\sqrt{6}}((\sqrt{2}-2)|C,1\rangle + (\sqrt{2}+1)|C,-1\rangle)$$

where A, B and C stand for the orbital functions Ψ_A, Ψ_B and Ψ_C. The amounts of admixture are given by $\sqrt{3}\lambda/\Delta_A$, $\sqrt{2}\lambda/\Delta_B$ and $\sqrt{3}\lambda/\Delta_C$ respectively.

The equilibrium orientation of the spin in the Y, Z plane comes from a balance between the exchange interaction, which acts to align the spin on the ion at $(0, 0, 0)$ anti-parallel to that on the ion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, the spin–orbit interaction which favours parallelism between the spin and orbital moments and the action of the applied magnetic field. This equilibrium is considered in detail by Moriya (1960), who shows that in zero field the inclination of the spin on the origin ion to the Z quantum axis is given by α, where

$$\cos\alpha = \frac{-1}{\sqrt{2}}(1 - x/(1 + x^2)^{1/2})^{1/2}, \qquad \left(x = \frac{2E\eta}{8J_1}\right).$$

Here E is one of the orthorhombic crystal field parameters and J_1 the exchange integral between the corner and body-centre atoms. The parameter E can be written, in terms of the energies Δ_A etc and the spin–orbit coupling parameter λ, as

$$E = 4\lambda^2\left(\frac{1}{\Delta_C} - \frac{1}{\Delta_A}\right) \qquad \eta = (1 - 1/2S)$$

Since x is small, $\cos\alpha$ can be written to first order as

$$\cos\alpha \approx -\frac{1}{\sqrt{2}}(1 - \tfrac{1}{2}x)$$

so that the angle of inclination of the spins to the crystallographic $\boldsymbol{a}$ or $\boldsymbol{b}$ axes is $x/2$. This inclination can be represented, to first order, by mixing the function Φ_Y with amplitude $x/2\sqrt{2}$ into the ground state. Thus the ground state of the ion in zero magnetic field can be represented as

$$= \mathcal{N}\left(\Phi_G + \frac{\lambda^2}{2\sqrt{2}J_1}\left(\frac{1}{\Delta_C} - \frac{1}{\Delta_A}\right)\Phi_Y + \frac{\sqrt{3}\lambda}{\Delta_0}\Phi_C + \frac{\sqrt{3}\lambda}{\Delta_A}\Phi_A + \frac{\sqrt{2}\lambda}{\Delta_B}\Phi_B\right)$$

where $\mathcal{N}$ is a normalising factor.

Estimates of the crystal field parameters obtained from susceptibility, ESR and infrared transmission measurements are compared by Joenk and Bozorth (1964). They suggest $D \sim 4$ and $E \sim 1.7\ \text{cm}^{-1}$ with a mean g value of 2.33. Taking $\lambda = 250\ \text{cm}^{-1}$ and $8J_1 = 95\ \text{cm}^{-1}$, the amplitudes of the functions Φ_Y, Φ_C, Φ_A and Φ_B are calculated as 0.0063, 0.0709, 0.0766 and 0.0621 in zero applied field. We estimate from the susceptibility that the amplitude of Φ_Y should increase to 0.0117 in the 1.4 T field of the experiment.

7. Calculation of magnetic scattering amplitudes

A technique for calculating magnetic scattering amplitudes from a ground state wavefunction was outlined by Brown *et al* (1973) and the expression for the orbital density corrected by Brown and Forsyth (1977). In these publications the components of the magnetic scattering amplitude were expressed as the amplitudes of the spherical har-

monic expansion with respect to the scattering vector ($\boldsymbol{K}$) thus:

$$\underset{(i=x,y,z)}{\boldsymbol{M}_i(\boldsymbol{K})} = 4\pi \sum_{l=0,2,4}^{l} \sum_{m=-l}^{l} i^l \{\boldsymbol{S}_i(lm) f_l(K) + \boldsymbol{L}_i(lm) g_l(K)\} Y_m^{*l}(\hat{\boldsymbol{K}}) \tag{1}$$

where $f_l(K)$, $g_l(K)$ are the spin and orbital radial form factors respectively and the $\boldsymbol{S}_i(lm)$, $\boldsymbol{L}_i(lm)$ are coefficients which depend on the actual form of the eigenvectors of the wavefunction and their matrix elements of spin and orbital angular momentum. An alternative way of setting out the result given above is to evaluate the contribution which each eigenvector contributes to a particular component of the magnetic structure factor. Taking this approach one can write

$$\underset{(i=xyz)}{\boldsymbol{M}_i(\boldsymbol{K})} = \sum_j \sum_k c_j c_k^* \boldsymbol{F}_{ijk}(\boldsymbol{K}).$$

Here the c_j are the coefficients of the eigenvectors used to describe the wavefunction and the $\boldsymbol{F}_{ijk}(\boldsymbol{K})$ are coefficients which depend on the form of the eigenvectors involved, the radial magnetisation distribution, the magnitude and direction of the scattering vector but are independent of the amplitudes of the eigenfunctions. By analogy with equation (1) above one can write

$$\boldsymbol{F}_{ijk}(\hat{\boldsymbol{K}}) = 4\pi \sum_{l=0,2,4}^{l} \sum_{m=-l}^{l} i^l \{\boldsymbol{S}_{ijk}(lm) f_l(K) + \boldsymbol{L}_{ijk}(lm) g_l(K)\} Y_m^{*l}(\hat{\boldsymbol{K}}).$$

Here the $\boldsymbol{S}_{ijk}(lm)$ and $\boldsymbol{L}_{ijk}(lm)$ are evaluated in exactly the same way as the $\boldsymbol{S}_i(lm)\boldsymbol{L}_i(lm)$ in equation (1) but include only terms introduced by the eigenvectors i and j and are independent of all the coefficients. This way of proceeding is appropriate if the way in which the magnetic structure factors depend on the coefficients of the eigenvectors is to be determined. The magnetic structure factor $\boldsymbol{M}(\boldsymbol{K})$ for a single ion is the Fourier transform of a real, centrosymmetric magnetisation density and is therefore itself real. Hence

$$c_j c_k^* \boldsymbol{F}_{ijk}(\boldsymbol{K}) = (c_k c_j^* \boldsymbol{F}_{ikj}(\boldsymbol{K}))^*$$

so that

$$\boldsymbol{F}_{ijk}(\boldsymbol{K}) = \boldsymbol{F}_{ikj}^*(\boldsymbol{K})$$

and

$$\boldsymbol{M}_i(\boldsymbol{K}) = \sum_j (\mathrm{Re}|c_j|^2 \boldsymbol{F}_{ijj}(\boldsymbol{K}) + \sum_{k>j} 2\,\mathrm{Re}(c_j c_k^* \boldsymbol{F}_{ijk}(\boldsymbol{K})))$$

writing $c_j = a_j + ib_j$ and $\boldsymbol{F}_{ijk} = \boldsymbol{A}_{ijk} + i\boldsymbol{B}_{ijk}$

$$\frac{\partial \boldsymbol{M}_i(\boldsymbol{K})}{\partial a_i} = \sum_j \boldsymbol{A}_{ijk}(\boldsymbol{K}) a_j + \boldsymbol{B}_{ijk}(\boldsymbol{K}) b_j = \sum_j \mathrm{Re}(\boldsymbol{F}_{ijk}(\boldsymbol{K}) c_j^*)$$

$$\frac{\partial \boldsymbol{M}_i(\boldsymbol{K})}{\partial b_i} = \sum_j \boldsymbol{A}_{ijk}(\boldsymbol{K}) b_j - \boldsymbol{B}_{ijk}(\boldsymbol{K}) a_j = -\sum_j \mathrm{Im}(\boldsymbol{F}_{ijk}(\boldsymbol{K}) c_j^*).$$

This demonstrates that the partial derivative of the magnetic structure factors with respect to the amplitudes of the eigenfunctions depends only on the factors $\boldsymbol{F}_{ijk}$ and the values of the other amplitudes. For a given set of data and a fixed form for the eigenfunctions, the factors $\boldsymbol{F}_{ijk}$ need be determined once and once only, and then will allow

calculation of the structure factors for any combination of amplitudes. Since the derivatives are relatively simple it should be possible to carry out a least-squares fit of the amplitudes to a set of measurements.

8. Refinement of the Ni^{2+} wavefunction

The components $\boldsymbol{M}(\boldsymbol{K})$ cannot be determined directly from the observations in the present experiment, except in the case of the *h*0*l* reflections. We have chosen to compare theory with experiment in terms of the quantity γ', where

$$\gamma' = \boldsymbol{Q}(\boldsymbol{K}) \cdot \hat{\boldsymbol{P}}/N \qquad (= M/N \text{ when } \hat{\boldsymbol{P}} \text{ is parallel to } \boldsymbol{Q}(\boldsymbol{K})).$$

For small magnetic scattering, perfect beam polarisation and flipping efficiency (ε)

$$\gamma' = (R - 1)/4.$$

In the presence of extinction and imperfect polarisation or flipping efficiency, γ' can be derived from the observed R using the relationship

$$\gamma' = (R - 1)\left(1 + \frac{N}{2y}\frac{\mathrm{d}y}{\mathrm{d}N}\right)^{-1} \frac{1}{2|P|(1 + \varepsilon)}.$$

We calculate the values of γ' for the measured reflections and the wavefunctions derived in § 6 with radial part given by Clementi and Roetti (1974) for Ni^{2+}, using the equivalence

$$-\hat{\boldsymbol{K}} \times \boldsymbol{M}(\hat{\boldsymbol{K}}) \times \hat{\boldsymbol{K}} = (\boldsymbol{M}(\hat{\boldsymbol{K}}) \cdot \hat{\boldsymbol{K}})\hat{\boldsymbol{K}} - \boldsymbol{M}(\hat{\boldsymbol{K}})$$

so

$$\boldsymbol{Q}(\hat{\boldsymbol{K}}) \cdot \hat{\boldsymbol{P}} = -\sum_{(i=xyz)} \left[\left(\sum_{(l=xyz)} \boldsymbol{M}_l(\boldsymbol{K}) \cdot \hat{\boldsymbol{K}}_l\right)\boldsymbol{K}_i - \boldsymbol{M}_i(\boldsymbol{K})\right] \cdot \hat{\boldsymbol{P}}_i.$$

The results are compared with the observations in table 2. The improved agreement with respect to a simple spherically symmetric model is striking. However there remain some sizeable discrepancies between observed and calculated values, and the large value (32) given by a chi-squared test suggests that these differences may be physically significant. To find out whether these differences could be removed by changes of the parameters, a least-squares refinement of the coefficients of Φ_Y, Φ_A, Φ_B and Φ_C was carried out. The derivaties of γ' with respect to the amplitudes a_j are given by

$$\frac{\partial\gamma'}{\partial a_j} = \sum_{i=x,y,z} \frac{\partial\gamma'}{\partial \boldsymbol{M}_i(\boldsymbol{K})} \cdot \frac{\partial \boldsymbol{M}_i(\boldsymbol{K})}{\partial a_j} = \frac{1}{N}\sum_{i=x,y,z} -(\hat{\boldsymbol{K}} \cdot \hat{\boldsymbol{P}} - \hat{\boldsymbol{P}}_i)\frac{\partial \boldsymbol{M}_i(\boldsymbol{K})}{\partial a_j}.$$

The refinement gave values for the coefficients

$$\Phi_Y = 0.020 \pm 0.003$$

$$\Phi_A = 0.066 \pm 0.008$$

$$\Phi_B = 0.066 \pm 0.008$$

$$\Phi_C = 0.070 \pm 0.008$$

and a value of chi-squared of 20. The γ' values given by these parameters are listed in the final column of table 2.

Table 2. A comparison of γ' observed with the values calculated for three different models. $\Delta\gamma'_{obs}$ are the estimated errors in the observations. The values of χ^2 ($=\Sigma(\gamma'_{obs}-\gamma'_{calc}/\Delta\gamma')^2/(n-v)$, where n is the number of observations and v is the number of variables) do not include contributions from 110 and 220.

hkl	sin θ/λ	γ'_{obs}	$\Delta\gamma'_{obs}$	γ' calculated spherical	resonance	refined
200	0.215	0.1648	0.0174	0.2067	0.1978	0.1670
400	0.430	0.0068	0.0011	0.0116	0.0043	−0.0006
110†	0.152	0.0397	0.0007	0.0154	0.0185	0.0170
310	0.340	0.0353	0.0010	0.0263	0.0375	0.0309
510	0.548	0.0032	0.0016	0.0059	0.0061	0.0018
220†	0.304	0.0283	0.0009	0.0066	0.0210	0.0199
420	0.481	0.0348	0.0019	0.0115	0.0554	0.0507
101	0.195	0.0750	0.0020	0.0540	0.0628	0.0558
301	0.361	0.0135	0.0010	0.0099	0.0114	0.0085
211	0.290	0.0176	0.0016	0.0164	0.0153	0.0119
411	0.472	0.0183	0.0013	0.0115	0.0132	0.0076
121	0.290	0.0031	0.0041	0.0080	0.0069	0.0045
321	0.420	0.0373	0.0021	0.0346	0.0451	0.0328
002	0.324	0.0120	0.0006	0.0116	0.0169	0.0139
202	0.389	0.1469	0.0063	0.1003	0.1925	0.1566
402	0.539	0.0203	0.0012	0.0058	0.0165	0.0123
112	0.354	0.0216	0.0017	0.0164	0.0252	0.0199
312	0.470	0.0196	0.0022	0.0148	0.0196	0.0122
022	0.389	0.0660	0.0057	0.0685	0.1088	0.0740
222	0.445	−0.0077	0.0018	0.0060	−0.0024	−0.0056
422	0.580	−0.0247	0.0019	0.0062	−0.0119	−0.0172
103	0.498	0.0377	0.0027	0.0197	0.0418	0.0326
303	0.584	0.0162	0.0013	0.0035	0.0149	0.0122
013	0.498	0.0380	0.0039	0.0190	0.0364	0.0261
213	0.543	0.0133	0.0017	0.0071	0.0192	0.0145
123	0.543	0.0057	0.0017	0.0064	0.0148	0.0095
χ^2				47	32	20

† Not included in χ^2 test.

9. Discussion

Although the parameter changes indicated by the least-squares refinement give a significantly better fit to the neutron scattering data, the results are at variance with the conclusions of the previous investigations quoted in § 6. They lead to energies Δ_A, Δ_B, Δ_C of 6600, 5400 and 6200 ± 800 cm^{-1} respectively, giving $E \sim 2$, $D \sim 7$ and $\tilde{g} = 2.3$. The equal values of the coefficients of Φ_A and Φ_B imply that the orbital component of the moment lies essentially parallel to the antiferromagnetic spin moment and the net ferromagnetic moment comes almost entirely from the spin canting term Φ_Y which is increased from its starting value. This result might suggest that equally good agreement might be obtained by omitting the Φ_A, Φ_B and Φ_C terms altogether since Φ_B contributes nothing to the net moment and the combined moment due to Φ_A and Φ_C contributes nothing to the ferromagnetic moment. This hypothesis was tested by refining the coefficient a_y in the spin-only wavefunction

$$\Psi_{\text{spin only}} = \mathcal{N}(\Phi_G + a_y\Phi_Y).$$

The refinement gave $a_y = 0.018 \pm 0.003$ essentially the same as in the complete refinement but with a value of chi-squared of 41. This demonstrates that the orbital terms $\Phi_A\Phi_B\Phi_C$ in the wavefunction make a significant contribution to the magnetic scattering at nonzero angle and contribute positively to the agreement between observed and calculated γ' values. In the same way, a test was made to check whether the function Φ_B, which has zero moment in all three principal directions, makes a significant contribution to the γ' values. A refinement carried out leaving out this function gave a final χ^2 value of 35, showing that contributions of Φ_B to the magnetic scattering cannot be neglected.

The polarised neutron scattering measurements can be said to support the interpretation of the weak ferromagnetism in NiF_2 as due to spin–orbit coupling, they lend support also to the general form of the ground state wavefunction of the nickel ion derived from other measurements. As far as the neutron results are concerned however, the amplitudes giving best agreement between the observations and the model wavefunction lead to values of the crystal field parameters D and E very different from those obtained from magnetisation and resonance results. It is also clear that the high χ^2 value of 20 shows that the model wavefunction is still not adequate to account completely for the magnetic scattering. The major effect which has not been introduced into the model wavefunction is covalency; the model assumes that all the moment is confined to the Ni^{2+} ion. The effect of covalent transfer of moment from the nickel to the fluorine on the magnetic scattering is twofold: firstly the associated delocalisation of the ferromagnetic moment will reduce the scattering which follows the Ni^{2+} form factor and enhance the scattering at low $\sin\theta/\lambda$; the second process will affect those hkl reflections for which $k \neq 0$ and comes from the antiferromagnetic moment transferred to fluorine ions which, having the symmetry of the ligands, can scatter in the $h + k + l$ even reflections. In both cases the transferred moment is associated with s and p fluorine functions which have form factors which fall off rapidly with $\sin\theta/\lambda$; if therefore the disagreement between the observations and the model is due to covalency then the degree of disagreement should be less at the higher $\sin\theta/\lambda$ values.

In order to test this hypothesis the measured reflections were divided into two groups corresponding to $\sin\theta/\lambda$ values greater and less than 0.4 $Å^{-1}$ and the effective χ^2 values for each of these two groups calculated. In the case of the refined model, the χ^2 values for the two groups were essentially equal, whereas for the model based on the published crystal field parameters the χ^2 for the low-angle group was 56 and for those with $\sin\theta/\lambda > 0.4$ it was 19. This result suggests that the effects of covalency on the magnetic scattering are sufficiently strong at low angles to falsify the refinement of the parameters of the ionic wavefunction. A refinement based on the high angle group of reflections only indicated no significant change in the parameters and gave no appreciable reduction in the value of χ^2. It must therefore be concluded that the simple ionic model considered here does not fit the magnetic scattering sufficiently well to enable its parameters to be determined with any more certainty than has already been achieved in magnetisation and resonance studies. Further interpretation of these magnetic scattering data must await a more sophisticated model for the magnetic electrons in NiF_2, including the effects of covalent transfer of spin from the nickel to the fluorine ions.

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