

A theory of the absorption and the resonance-enhanced diffraction of soft x-rays by anisotropic ferrous magnetic moments in FeNb_2O_6

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 4261

(<http://iopscience.iop.org/0953-8984/9/20/021>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 08:44

Please note that [terms and conditions apply](#).

A theory of the absorption and the resonance-enhanced diffraction of soft x-rays by anisotropic ferrous magnetic moments in FeNb₂O₆

Stephen W Lovesey[†] and Hans Grimmer[‡]

[†] ISIS Facility, Rutherford Appleton Laboratory, Oxfordshire OX11 0QX, UK

[‡] Laboratory for Neutron Scattering, ETH-Z and PSI, CH-5232 Villigen PSI, Switzerland

Received 28 January 1997

Abstract. Some of the interesting magnetic properties of ferrous niobate have recently been attributed to the orbital angular momentum of the iron atom. In the present work, the spin and orbital components of the magnetic moment are shown to make distinctive appearances in the resonant contribution to the scattering length for the electrostatic scattering of x-rays, from which the dichroic signals in the attenuation coefficient and the Bragg diffraction cross-section are derived. Quantitative predictions are made for the circular and linear dichroic signals of ferrous atoms in FeNb₂O₆, and these are compared to the corresponding signals predicted for free ferrous atoms. In all cases, the analytic expressions for the dichroic signal possess a relatively simple structure.

1. Introduction

A recent analysis of a large body of empirical data on the magnetic properties of ferrous niobate, FeNb₂O₆, has led to the view that the ferrous atom (3d⁶) has a magnetic moment which is far from being spatially isotropic. One set of measures of the degree of anisotropy in the moment are departures of the principal components of its gyromagnetic factor from the value of 2.0 achieved by a free electron. The latter value is obtained for all of the principal components of the gyromagnetic factor of a ferric atom (3d⁵) with the orbital singlet state ⁶S. In stark contrast to a ferric atom, the components of the gyromagnetic factor of the ferrous atom in FeNb₂O₆ are predicted by Heid *et al* (1996) to be $g_x = 2.0$, $g_y = 2.37$ and $g_0 = 3.09$. The anisotropy in the moment of the ferrous atom is attributed to the perturbation of the orbital of its extra electron, relative to the spherically symmetric half-filled shell of a ferric atom, by the (ligand) crystal-field potential. One anticipates that the same physical mechanism creates significant magnetoelastic effects, and possibly even a hybridization of the lattice modes of vibration with the spin-wave excitations, which has previously been observed in FeF₂ and FeCl₂ (Lovesey and Loveluck 1977). The evidence offered by Heid *et al* (1996), to the effect that the orbital magnetic moment on the ferrous atom is significantly different from zero and anisotropic, is a new development in accounts of the magnetic properties of FeNb₂O₆.

Emerging experimental techniques that use beams of x-rays from accelerator sources might be quite useful in further studies of FeNb₂O₆, and similar magnetic materials. In particular, we have in mind two techniques, which utilize the L-absorption edges of the iron atom to probe its magnetic state, because they have the scope to give separate access to

the spin and orbital contributions of the moment and they are now relatively easy to apply. One technique is based on the dichroic effect in the attenuation coefficient and the second is resonance-enhanced Bragg diffraction. A theoretical framework for the two techniques can be formulated in terms of the resonant contribution to the scattering length for the electrostatic scattering of x-rays.

In this paper, we provide theoretical results pertaining to FeNb_2O_6 that enable one to predict its dichroic signals and scattering cross-section. These probes of magnetism rely on the electric dipole absorption event, in which a hole from the partially filled 3d valence shell is transferred to an initially full 2p core orbital. The energies of the L_2 and L_3 absorption edges, separated by several eV, are in the region of 0.71 keV, and this energy corresponds to an x-ray wavelength = 17.5 Å.

Below a temperature of 4.9 K, FeNb_2O_6 displays long-range antiferromagnetic order with a (non-collinear and canted) magnetic configuration $F_x C_z$ (the notation used here is defined, for example, by Bertaut 1963). For this magnetic phase, we show that because there is no net magnetic moment the dichroic signal for circular polarization in the primary beam of x-rays is zero. The signal is non-zero for a new phase induced by the application of a magnetic field, of about 1 T, in which, under the influence of the field, the moments reorientate and produce a net moment for the sample, in the direction of the field. (The magnitude of the critical magnetic field at which the phase transition takes place, and the magnitude of the induced magnetic moment, depend on the direction of the field relative to the axes of the crystal structure.) On the other hand, the dichroic signal for linear polarization in the primary beam of x-rays is found to be non-zero for both of the magnetic phases that we have mentioned. Above the ordering temperature and in the absence of an applied magnetic field the circular dichroic signal is zero, and the linear dichroic signal is non-zero. The dependence of the cross-section for Bragg diffraction by FeNb_2O_6 on the temperature and an applied magnetic field is readily deduced from what we have already said about the dependence of the dichroic signals on these variables.

In the next section we very briefly introduce the formulation of the absorption and resonance-enhanced scattering of x-rays used in the subsequent work, which is due to Lovesey and Balcar (1996, 1997). The main feature of the formulation is the reduction of the resonant component of the scattering length to an expression in terms of standard atomic variables, at the expense of having to mimic the full energy spectrum for dipole-allowed transitions, from the equilibrium state of the ferrous atom to the plethora of (virtual) quasi-discrete intermediate states, by just two components which are identified by the two possible values of the total angular momentum of the core state that appears in the intermediate states. As with any formulation of the scattering length that one might choose to employ, it is required to possess a good description of the magnetic atom in question in the form of a wave function for its valence shell. The construction of the wave function for a ferrous atom in FeNb_2O_6 , which is based on the model of the material proposed by Heid *et al* (1996), is the task described in section 3. Our version of the scattering length for the resonant scattering of x-rays is found in section 4, and section 5 is given over to a discussion of the dichroic signals derived from it. The corresponding signals for a free ferrous atom (${}^5\text{D}_4$) are listed in section 6, for both completeness and also as a frame of reference in which to assess the influence of the crystal-field potential in the dichroic signals for FeNb_2O_6 given in section 5. A brief discussion of our findings follows immediately, in section 7.

2. Scattering length

In our work we use for the theory of absorption and resonance-enhanced scattering of x-rays the formulation put forward by Lovesey and Balcar (1996, 1997); hereafter, these two papers are referred to as I and III (paper II in the series treats an E2 absorption event, which is not of immediate interest). It is not our aim in this section to give anything bordering on a review of the formulation. Rather, we give the minimum of the information which appears necessary to enable the reader to follow the subsequent discussions.

The primary radiation has an energy $E = 2\pi\hbar c/\lambda$, wave vector \mathbf{q} and a polarization vector ε . The corresponding quantities for the secondary radiation are distinguished by a prime. It is understood that the energy of the primary radiation is tuned close to a resonance which is characterized by its mean energy, Δ , and the total angular momentum, \bar{J} , of the state created by the hole transferred in the absorption event from the valence shell to a core state. For 3d valence electrons and an electric dipole (E1) absorption event, $\bar{J} = \frac{3}{2}(L_3)$ or $\bar{J} = \frac{1}{2}(L_2)$. The total decay width of a resonance is Γ .

Let the absorbing atoms be at positions in the crystal sample which are defined by vectors $\{\mathbf{R}\}$. Spatial coherence in the scattering process, e.g. the condition for Bragg diffraction, arises from the phase factors $\exp(i\mathbf{k} \cdot \mathbf{R})$ in which the scattering wave vector $\mathbf{k} = \mathbf{q} - \mathbf{q}'$.

For E close to Δ , the mean value of the resonant contribution to the scattering length is

$$\langle f \rangle = -\left(\frac{2\pi e}{\lambda}\right)^2 \left\{ E - \Delta + \frac{i}{2}\Gamma \right\}^{-1} \sum_{\mathbf{R}} \exp\{i\mathbf{k} \cdot \mathbf{R} - W(\mathbf{k})\} \langle Z(\mathbf{R}) \rangle \quad (2.1)$$

where $\exp\{-W(\mathbf{k})\}$ is the Debye–Waller factor. The amplitude of the resonant process, denoted by $\langle Z(\mathbf{R}) \rangle$, is a purely real quantity, and in the following work it is calculated using an atomic model of the valence electrons in a ferrous atom found in ferrous niobate. The amplitude factor depends on the magnetic properties of the crystal, the polarization vectors ε and ε' , and the square of the radial integral $\langle R \rangle$ for an E1 absorption event.

The cross-section for Bragg diffraction is proportional to $|\langle f \rangle|^2$. The attenuation coefficient, and the dichroic signals, are derived from the imaginary part of $\langle f \rangle$ when it is evaluated for a forward-scattering geometry and averaged with respect to states of polarization in the primary beam. We will denote the corresponding amplitude by $\langle Z \rangle_0$. The attenuation coefficient is then proportional to $\delta(E - \Delta)\langle Z \rangle_0$, where the delta function for the energy is a good approximation when the energy Γ is vanishingly small.

For a free atom, whose magnetic properties are specified by the three quantum numbers SLJ , $\langle Z \rangle$ is equal to one diagonal matrix of a sum of three spherical tensor operators, whose matrix elements are simple functions of Racah unit tensors. An example of this type is briefly discussed in section 6. The situation is rarely appropriate for salts containing 3d transition-metal atoms, since the crystal-field potential is a perturbation with an intermediate strength and stronger than the spin–orbit interaction. In consequence, the ground-state wave function of the transition-metal atom contains several atomic components, with coefficients determined by the crystal-field potential and spin–orbit interaction, and the corresponding amplitude factor is a sum of several matrix elements. Great simplification to the structure of the amplitude factor arises when all of the atomic components in the wave function are drawn from one J -manifold. A manifestation of the simplification is the option to use the method of operator equivalents, which is standard practice in the interpretation of many other experimental methods.

3. The wave function of a ferrous atom

In the ordered magnetic state of FeNb_2O_6 there are two non-equivalent sites for the ferrous atoms. We use local principal axes for the sites, in which the y -axes are common to both sites, and the two z -axes enclose an angle 2ϕ . The ferrous magnetic moments lie in the parallel x - z planes. Note that Heid *et al* (1996) refer to $90 - \phi$ as the canting angle. From the theoretical analysis they obtain in the local principal axes $g_x = 2.0$, $g_y = 2.37$ and $g_0 = 3.09$.

The ground-state wave function of a ferrous atom which is subjected to a crystal-field potential that possesses an octahedral symmetry can be constructed, to a good approximation, from the three non-degenerate orbitals that span the Γ_5 space. Using a standard notation, the three purely real, orthogonal and normalized orbitals are denoted by $|xy\rangle$, $|yz\rangle$ and $|zx\rangle$. In terms of the orbital angular momentum states $|L = 2, M_L\rangle = |M_L\rangle$ the three orbitals are here taken to be

$$\begin{aligned} |xy\rangle &= -\frac{i}{\sqrt{2}}(|2\rangle - |-2\rangle) \\ |yz\rangle &= \frac{i}{\sqrt{2}}(|1\rangle + |-1\rangle) \quad |zx\rangle = -\frac{1}{\sqrt{2}}(|1\rangle - |-1\rangle). \end{aligned} \quad (3.1)$$

Following the analysis by Heid *et al* (1996), we shall assume that the ground state is represented by $|yz\rangle$ and additions of $|zx\rangle$ and $|xy\rangle$ brought in by the action, within the Γ_5 space, of the spin-orbit interaction.

The spin-orbit interaction is treated as a linear perturbation on the state which is described as a product of $|yz\rangle$ and the spin state $|S = 2, M\rangle = |M\rangle$. A straightforward calculation leads to a wave function for the ground state of a ferrous atom which is

$$|\psi, M\rangle = |yz, M\rangle - \frac{i}{2}M(g_0 - 2)|zx, M\rangle + \frac{i}{2}(g_y - 2) \sum_{M'} \langle M' | S_y | M \rangle |xy, M'\rangle. \quad (3.2)$$

In terms of the spin-orbit interaction parameter, λ , and the separations in energy of the orbitals $|zx\rangle$ and $|xy\rangle$ from $|yz\rangle$ we have

$$g_0 - 2 = -2\lambda/e(zx) \quad (3.3a)$$

and

$$g_y - 2 = -2\lambda/e(xy). \quad (3.3b)$$

Inserting in these formulae the values of the parameters derived by Heid *et al* (1996), namely, $\lambda = -99$, $e(zx) = 182$ and $e(xy) = 540$, all in units of cm^{-1} , one recovers for g_0 and g_y the values previously quoted by us. Of course,

$$\langle \psi, M | L_z | \psi, M \rangle = (g_0 - 2) \langle \psi, M | S_z | \psi, M \rangle \quad (3.4a)$$

and, for $\alpha = x$ and y ,

$$\langle \psi, M + 1 | L_\alpha | \psi, M \rangle = (g_\alpha - 2) \langle \psi, M + 1 | S_\alpha | \psi, M \rangle. \quad (3.4b)$$

In the light of these results, one can conclude that the wave function specified in (3.2) gives a tolerable description of the model for a ferrous atom in FeNb_2O_6 developed by Heid *et al* (1996).

In the next section, the wave function is used to calculate the amplitude factor which appears in the mean value of the scattering length. For the case in hand, the mean value of the amplitude factor is equal to its diagonal matrix element averaged over the degeneracy in the spin magnetic quantum number, M . Since $S_z |M\rangle = M |M\rangle$, the average over M gives the average value of S_z and the average over M^2 gives the average value of S_z^2 .

4. The amplitude factor

The amplitude factor in the scattering length is a sum of three terms that are labelled by the rank, K , of a spherical-tensor operator. Thus, the matrix element of each term obeys the Wigner–Eckart theorem for a tensor of rank K . When, as in the present case, one calculates matrix elements in the SL -basis, since for 3d transition-metal atoms subject to a crystal field this basis is more convenient to use than the SLJ -basis, for a given K the Wigner–Eckart theorem separately applies to the spin and orbital operators. The matrix elements of the spin and orbital operators in the amplitude factor are coupled, via a Clebsch–Gordan coefficient, to produce a matrix element of a tensor of rank K . The complete details of the formulation are found in paper III, together with values of the Racah unit tensors for 3d⁶, 5D.

We have calculated the amplitude factor, $\langle Z \rangle$, using the wave function for a ferrous atom which is defined in (3.2). In the results of the calculation we have kept all terms in the matrix elements except those which are quadratic in the departure of the gyromagnetic factor from the spin-only value, and this level of approximation in the matrix elements is consistent with the construction of the wave function. The amplitude factor for one of the two non-equivalent magnetic sites is the sum of the following three terms, in which $\bar{J} = 1 \pm \frac{1}{2}$:

(i) $K = 0$:

$$\frac{1}{45} \langle R \rangle^2 (\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon}) \left\{ 4(2\bar{J} + 1) \pm \frac{1}{2} \left[(g_0 - 2) \langle S_z^2 \rangle + \frac{1}{2} (g_y - 2) (S(S + 1) - \langle S_z^2 \rangle) \right] \right\} \quad (4.1)$$

(ii) $K = 1$:

$$\frac{i}{15} \langle R \rangle^2 (\boldsymbol{\varepsilon}' \times \boldsymbol{\varepsilon})_z \langle S_z \rangle \left\{ \frac{1}{4} (g_0 - 2) (2\bar{J} + 1) \pm \frac{5}{6} \left[1 - \frac{3}{20} (g_y - 2) \right] \right\} \quad (4.2)$$

(iii) $K = 2$:

$$-\frac{1}{90} \langle R \rangle^2 \left\{ (\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon} - 3\varepsilon'_x \varepsilon_x) (2\bar{J} + 1) \pm \left[\frac{1}{2} (\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon} - 3\varepsilon'_y \varepsilon_y) (g_y - 2) \right. \right. \\ \left. \left. \times (S(S + 1) - \langle S_z^2 \rangle) + (\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon} - 3\varepsilon'_z \varepsilon_z) (g_0 - 2) \langle S_z^2 \rangle \right] \right\}. \quad (4.3)$$

In these expressions, $\langle S_z \rangle$ and $\langle S_z^2 \rangle$ are the thermal average values of the enclosed spin operators. In the absence of a magnetic field, $\langle S_z \rangle$ in FeNb₂O₆ decreases with increasing temperature and vanishes at the Néel temperature. At zero temperature $\langle S_z \rangle = S$ and $\langle S_z^2 \rangle = S^2$ (these estimates do not include the zero-point fluctuations which exist in ordered antiferromagnets). Well above the Néel temperature $\langle S_z^2 \rangle = S(S + 1)/3$, and paper I contains the leading-order correction to this result as a function of the ratio of the single-site anisotropy constant to the temperature. The contributions to (4.1)–(4.3) made by the spin moment of the ferrous atom are identified by setting to zero the orbital contributions, and this is achieved by replacing g_y and g_0 by the spin-only value of 2.0.

Looking at (4.1) and (4.3), the two terms formed with tensors of an even rank, the thermodynamic information in both terms appears as $\langle S_z^2 \rangle$. The terms also share the feature for $g_y = g_0 = 2.0$, the spin-only gyromagnetic factor, that they are independent of the thermodynamic properties of the ferrous atom. For $K = 0$ the useful information in the amplitude factor is in the part that has opposite signs at the L₂ and L₃ absorption edges. The coefficient of $2\bar{J} + 1$ is exactly the same as we find for a free atom, and the appropriate result is found in paper III. On the other hand, in the term $K = 2$ the coefficient of $2\bar{J} + 1$ reflects the spatial symmetry of the principal orbital in the ground-state wave function. The

coefficient in (4.3) is correct for the orbital $|yz\rangle$, of course, while if the principal orbital is $|zx\rangle$ or $|xy\rangle$ the coefficient is replaced by $(\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon} - 3\varepsilon'_y \varepsilon_y)$ or $2(\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon} - 3\varepsilon'_z \varepsilon_z)$, respectively. Note that for unpolarized x-rays the polarization factors in (4.3) are individually equal to zero when a spatial average is taken.

Not surprisingly, perhaps, the term $K = 1$ is significantly different from the even-rank terms, which we have just discussed. First, we note that (4.2) is proportional to the spin moment, and so the term is zero in the paramagnetic phase. In this phase, the term can be made non-zero by applying a magnetic field. The coefficient of $2\bar{J} + 1$ is proportional to the component of the orbital moment which lies along the z -axis. Lastly, we note that (4.2) is 90° out of phase with the even-rank terms.

Taken together with the information given by Heid *et al* (1996) on the magnetic structure of FeNb_2O_6 , the results (4.1)–(4.3) enable one to calculate the structure factor for resonance-enhanced Bragg diffraction. The technical headache of averaging $|\langle f \rangle|^2$ with respect to states of the polarization in the primary beam is addressed in paper I. In the remaining part of this paper we only discuss the linear and circular dichroic signals in the attenuation coefficient predicted for FeNb_2O_6 .

5. Dichroic signals

Dichroic signals, derived from the attenuation coefficient, contain information on the spatial anisotropy in the magnetic moment distribution of the absorbing atoms. As references against which to assess this information it is useful to consider the signals for a free atom, and the isotropic contribution to the attenuation coefficient of the crystal. A free atom is considered in the next section, and here we start with the isotropic contribution to the attenuation coefficient calculated with the ferrous wave function defined in section 3.

As we mentioned in section 2, the integrated intensity in the attenuation coefficient is proportional to $\langle Z \rangle_0$, which is formed by averaging the amplitude factor with respect to states of the polarization in the beam of x-rays incident on the sample. Of course, the isotropic signal is independent of the polarization, and it seems to be conventional to define this signal as the $K = 0$ term of $\langle Z \rangle_0$ multiplied by a factor of three. From (4.1), we find for the isotropic signal so defined the result

$$\frac{1}{15} \langle R \rangle^2 \left\{ 4(2\bar{J} + 1) \pm \frac{1}{2} \left[(g_0 - 2) \langle S_z^2 \rangle + \frac{1}{2} (g_y - 2) (S(S + 1) - \langle S_z^2 \rangle) \right] \right\}. \quad (5.1)$$

One practical use of the isotropic signal is to normalize the dichroic signals, to which we now turn our attention.

The dichroic signals are defined to be the differences in $\langle Z \rangle_0$ for equal and opposite values of the polarization in the primary beam of x-rays. To describe the polarization we use a Stokes vector, \mathbf{P} . At a synchrotron source of radiation it is sufficient to use $\mathbf{P} = (0, P_2, P_3)$ where $P_2^2 + P_3^2 \leq 1$. We adopt the convention used by Lovesey and Collins (1996), in which P_2 is the mean helicity, with $P_2 > 0$ representing right-handed and $P_2 < 0$ left-handed states of circular polarization, and P_3 is a measure of the linear polarization.

The linear and circular dichroic signals are taken to be

$$\Delta Z(\text{L}) = \langle Z(P_3) \rangle_0 - \langle Z(-P_3) \rangle_0 \quad \text{and} \quad \Delta Z(\text{C}) = \langle Z(P_2) \rangle_0 - \langle Z(-P_2) \rangle_0. \quad (5.2)$$

The average values of the products of polarization vectors needed to derive $\Delta Z(\text{C})$ and $\Delta Z(\text{L})$ from (4.2) and (4.3) are given in paper I. We will assume that the beam of x-rays

is parallel to the x - z plane, which contains the magnetic moments in FeNb_2O_6 ; cf. figure 1, and figure 12 in the paper by Heid *et al* (1996).

From (4.3) and (5.2),

$$\Delta Z(L) = \frac{1}{30} \langle R \rangle^2 P_3 \left\{ -(2\bar{J} + 1) \cos^2 \varphi \pm \left[\frac{1}{2} (g_y - 2) (S(S + 1) - \langle S_z^2 \rangle) - (g_0 - 2) \langle S_z^2 \rangle \sin^2 \varphi \right] \right\}. \quad (5.3)$$

In this result, φ is the angle between the z -component of the local principal axes and the direction of propagation of the beam of x-rays, and the angle is depicted in the left-hand panel of figure 1.

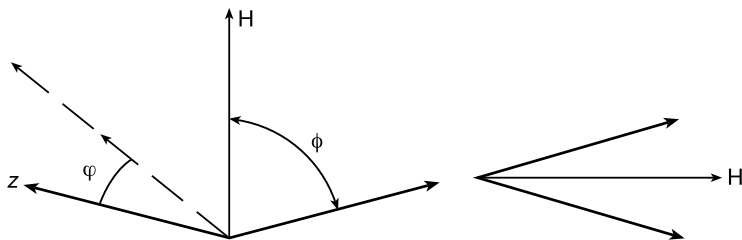


Figure 1. The figure depicts the arrangements of the applied magnetic field, denoted by \mathbf{H} , the x-ray beam and the z -components of the two sets of local principal axes. All of the vectors lie in the plane defined by the crystal a - and c -axes. The left-hand panel describes a field applied along the c -axis, and the right-hand panel describes a field applied along the a -axis. The spin configurations associated with the two panels are $C_x F_z$ for $\mathbf{H} \parallel c$, and $F_x C_z$ for $\mathbf{H} \parallel a$.

The total signal from a crystal is (5.3) plus the corresponding signal from the second, non-equivalent ferrous atom. The second signal is derived from (5.3) by taking φ to have the value $\varphi - 2\phi$. If the strong external field is applied along the c -axis of the crystal, the value to be given to ϕ is 65.9° , and if it is applied along the a -axis, the appropriate value is 24.1° . The two cases are illustrated in the two panels in figure 1, and figure 14 in the paper by Heid *et al* (1996) contains isometric drawings of the spin configurations. The quoted values of ϕ are expected to be good estimates when the field strengths just exceed the critical values required to induce changes in the spin configurations away from the fully compensated antiferromagnetic configuration. For weaker fields the appropriate value of ϕ is 90° , and the linear dichroic signals from the two non-equivalent atoms are equal. In this instance, and for $\varphi = 90^\circ$, the sum of the signals from the L_2 and L_3 absorption edges is zero, while the contribution to the difference in the two signals which is proportional to $g_0 - 2$ achieves its maximum value. The variation of $\Delta Z(L)$ with the angle φ can be used to separately measure $g_y - 2$ and $g_0 - 2$.

Deep in the paramagnetic phase and in the absence of a magnetic field $\langle S_z^2 \rangle = S(S+1)/3$, to a good approximation. In this instance, all ferrous atoms are equivalent and one replaces $\cos^2 \varphi$ and $\sin^2 \varphi$ by their average values of $\frac{1}{2}$.

The circular dichroic signal defined in (5.2) is derived from the result (4.2), and one finds

$$\Delta Z(C) = -\frac{2}{15} \langle R \rangle^2 \langle S_z \rangle P_2 \cos \varphi \left\{ \frac{1}{4} (g_0 - 2) (2\bar{J} + 1) \pm \frac{5}{6} \left[1 - \frac{3}{20} (g_y - 2) \right] \right\}. \quad (5.4)$$

Clearly, the signal is zero if the primary beam contains no circular polarization, or if the propagation of the beam is at right angles to the z -component of the local principal axes.

The signal from the second, non-equivalent atom is obtained from (5.4) by replacing φ by the angle $\varphi - 2\phi$. If the spin configuration is a fully compensated antiferromagnetic arrangement, described by the choice $\phi = 90^\circ$, the total signal from the crystal is zero. In the presence of a strong magnetic field, such that $\phi \neq 90^\circ$, the total signal is different from zero. Looking at (5.4) we see the coefficient of $2\bar{J} + 1$ is proportional to $g_0 - 2$. Hence, if the multiplying factors are known, the total signal from the L_2 and L_3 absorption edges directly gives a measure of $g_0 - 2$, i.e. the orbital magnetic moment in the direction of the z -component of the local principal axes.

6. Free-atom signals

To help appreciate the effect of the local environments on the dichroic signals from the ferrous atoms in FeNb_2O_6 , which are modelled by the wave function defined in section 3, we give here the corresponding signals predicted for a free ferrous atom. In this instance, the state of the atom is completely specified by the quantum numbers SLJ , and for $3d^6$ the values obtained by application of Hund's rules are $S = L = 2$ and $J = 4$. The Racah unit tensors for this state are listed in paper III.

In place of (5.1) we get for a free atom an isotropic signal:

$$\frac{1}{15} \langle R \rangle^2 \{4(2\bar{J} + 1) \pm 2\}. \quad (6.1)$$

The coefficients of $2\bar{J} + 1$ in (5.1) and (6.1) are the same. It is also interesting to note that, if we use in (5.1) $\langle S_z^2 \rangle = 4$ together with the quoted values for g_y and g_0 , the difference in the isotropic signals at the L_2 and L_3 absorption edges is slightly larger than the value predicted by (6.1), for a free atom, and it is slightly smaller for $\langle S_z^2 \rangle = S(S + 1)/3$, which is appropriate at a temperature much in excess of the ordering temperature.

The linear and circular dichroic signals for a free ferrous atom are

$$\Delta Z(L) = \frac{1}{30} \langle R \rangle^2 P_3 \sin^2 \varphi \{-(2\bar{J} + 1) \pm 2\} \quad (6.2)$$

and

$$\Delta Z(C) = -\frac{4}{15} \langle R \rangle^2 P_2 \cos \varphi \left\{ \frac{1}{4}(2\bar{J} + 1) \pm \frac{1}{3} \right\}. \quad (6.3)$$

In evaluating (6.2) and (6.3) we have used $\langle J_z \rangle = 4$ and $\langle J_z^2 \rangle = 16$. Comparing (5.3) and (6.2), and (5.4) and (6.3), the effect on the signals of the spatial anisotropy of the ferrous moment in FeNb_2O_6 is most apparent in the linear signal. Here, the dependence of the total signal, related to the coefficient of $2\bar{J} + 1$, on the angle φ is changed by the action of the crystal field from $\sin^2 \varphi$, in the free atom, to $\cos^2 \varphi$. In section 4 we comment on the coefficient and how it depends on the spatial symmetry of the principal orbital in the wave function of the ferrous atom.

7. Discussion

We have used the formulation of the resonant contribution to the scattering length for x-rays due to Lovesey and Balcar (1996, 1997) to obtain a relatively simple analytic expression for it that is appropriate for the model of FeNb_2O_6 put forward by Heid *et al* (1996). The expression for the scattering length is a basis for a discussion of the dichroic signals in the attenuation coefficient and the diffraction cross-section realized at the L absorption edges of the ferrous atoms. It has been shown that both the linear and the circular dichroic signals

contain useful information about the anisotropic ferrous magnetic moment. Measurements of the two signals certainly will provide a stringent test of the model.

The entire scattering length enters the cross-section for resonance-enhanced Bragg diffraction, whereas the two dichroic signals are related to two different parts of it. Another feature which makes diffraction a somewhat less incisive experimental tool than dichroic signals is that the cross-section for diffraction is proportional to the square of the absolute value of the scattering length, while the dichroic signals are simply proportional to its imaginary part. Further discussion of the relative merits of the two experimental techniques is given by Lovesey and Collins (1996).

Acknowledgments

The continued interest of Dr S P Collins and Dr U Staub in our work is appreciated. Much of the contribution to the paper by one of us (SWL) was made while a guest of Dr W Fischer at the Paul Scherrer Institute.

References

- Bertaut E F 1963 *Magnetism* vol III (New York: Academic)
- Heid C, Weitzel H, Bourdarot F, Calemczuk R, Vogt T and Fuess H 1996 *J. Phys.: Condens. Matter* **8** 10 609
- Lovesey S W and Balcar E 1996 *J. Phys.: Condens. Matter* **8** 10 983
- 1997 *J. Phys.: Condens. Matter* **9** 4237
- Lovesey S W and Collins S P 1996 *X-ray Scattering and Absorption by Magnetic Materials* (Oxford: Clarendon)
- Lovesey S W and Loveluck J M 1977 *Dynamics of Solids and Liquids by Neutron Scattering (Springer Topics in Current Physics 3)* (Berlin: Springer)