Resonant (1s → 3d) x-ray Bragg diffraction by transition-metal compounds

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Abstract

Structure factors for Bragg diffraction of x-rays enhanced by electric quadrupole absorption (1s → 3d) are calculated for several configurations of the resonant ions found to exist in transition-metal compounds. The configurations include the spontaneous order (fully compensating and non-collinear antiferromagnetism) and field-induced states of ferrous niobate, and paramagnetic iron pyrite. The calculation is couched in terms of spherical tensors, which describe the orbital magnetism of 3d electrons, and highlights the essential components contributing to the results, namely, use of an atomic model for the resonant contribution to the x-ray scattering length, the influence of the elements of symmetry pertinent to a resonant ion and the crystal structure, and linear and circular polarization effects. Spatial anistotropy in the 3d orbital moments leads to charge-forbidden reflections. Associated structure factors are calculated as functions of the canting angle of the principal axis, and the (azimuthal) angle of rotation of the crystal about the Bragg wavevector. In the model for ferrous niobate the orbital moment arises from a conventional mechanism based on the spin-orbit coupling. An interpretation of diffraction data for vanadium sesquioxide implies, for this material, that orbital magnetism is not enslaved to spin magnetism.

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1. Introduction

Properties of a magnetic material are ultimately determined by charge, orbital and spin degrees of freedom of the valence electrons. Concerning orbital degrees of freedom these are often subjugated to spins. Such is the case when orbital magnetism in the first approximation is created by the action of the spin-orbit interaction, being quenched at zeroth order by the local electrostatic potential. In other cases, which include Mott insulators, orbital and spin degrees of freedom must be treated on an equal footing; see [1 – 3] and references therein.

There is a growing awareness of the feasibility and need to separately determine orbital magnetism and ordering rather than merely infer them from lattice distortions and spin properties. A tendency to accept inference as the best one can do for orbital properties stems from confidence, established through several decades of research, in our ability to measure lattice and spin properties. However, the availability today of sophisticated diffraction instruments supplied with photons from a synchrotron source beckons a reappraisal of the status quo.

Experimental methods based on the Bragg diffraction of x-rays from a synchrotron source offer much to the investigation of electron correlations in magnetic materials [4]. At high incident energies, well above the region of atomic resonances, the method is similar to magnetic neutron diffraction except that a beam of x-rays reveals the ordering of spin moments whereas neutrons reveal the ordering of magnetic moments. Operating at lower incident energies, but still clear of atomic resonances, x-ray diffraction gives information on the ordering of spin and orbital moments. Unfortunately, the magnetic signals in x-ray diffraction are relatively weak, e.g. in the limit of high incident energies the ratio of the magnetic and charge signals for diffraction from planes of reflection separated by a distance d is (λ_o/d) where the Compton wavelength $\lambda_o = 0.0243$Å. Problems encountered in measuring weak signals are mitigated by tuning the incident x-ray energy to an inner-shell absorption edge of a magnetic ion, with the immediate benefit of signal enhancement from the resonance which can be as much as a few orders of magnitude. The enhancement comes at a price, though, that includes operating at an incident energy

not ideal for diffraction and the need to rely on a theoretical framework for the interpretation of data. If the energy of the resonance Δ (keV) is too small the wavelength = (12.4/Δ) Å will barely match *d* in the Bragg condition and, also, evacuated flight paths become essential to reduce absorption.

Regarding 3d transition-metal compounds, there is much to be said in favour of tuning to the K-shell absorption edge. For ions ranging from vanadium to copper the energy of this absorption edge corresponds to wavelengths ranging from 2.3 Å to 1.4 Å which are well suited for Bragg diffraction. There is also a case in favour of exploiting the electric quadrupole event (E2) even though the signal enhancement is less than that enjoyed by an electric dipole event (E1). As a function of incident energy the observed E2 spectral line-shape is found to be simple and similar to a single oscillator, which is in marked contrast to quite complicated line-shapes associated with E1 events [5 - 7]. This empirical evidence on the E2 line-shape suggests that it is reasonable to appeal to an atomic model for the interpretation of the diffracted signal. From such a model one learns that resonant x-ray Bragg diffraction enhanced by an E2 event at the K-shell absorption edge (1s $\rightarrow$ 3d) is directly related to the orbital moments of the 3d valence electrons [8].

Using an atomic model to describe enhanced x-ray Bragg diffraction for an E2 event we are able to give a full account of the information that could be available through an investigation of 3d transition-metal compounds. By way of an interesting and challenging example we give results for the calculated structure factor of ferrous niobate [9], and briefly expand on a previously published short account of the structure factor for vanadium sesquioxide which successfully accounts for available experimental observations [7, 10].

The magnetic moment on the ferrous ion in $FeNb_2O_6$ is highly anisotropic and it contains a large orbital component, e.g. the principal element of the gyromagnetic factor = 3.09. In zero external magnetic field the configuration of the moments below 4.9K is non-collinear, and the eight ferrous ions in the magnetic unit cell make up a fully compensating antiferromagnetic structure with a F_xC_z–arrangement of the moments. The canting angle of the ferrous moment is attributed to the octahedral

environment of the oxygen ions. A sufficiently large field applied along the a- or c-axis induces a transition to a state with a net ferromagnetic component. At 2.0K the critical fields for the transition are 0.9T along a and 1.85T along c. In the following text we report the calculated structure factors appropriate for the fully compensating antiferromagnetic structure and the two field-induced structures. In all three cases we predict the information gained from azimuthal-angle scans (in which the crystal is rotated about the Bragg vector) and the variation of the structure factor with respect to the canting angle as it varies with the strength of the applied field.

Charge-forbidden Bragg reflections are particularly valuable sources of information on the orbital moments. This class of reflections include those called Templeton and Templeton scattering [11-13], which arise from anisotropy in the moments referred to the crystallographic axes. We calculate the charge-forbidden structure factors for (paramagnetic) iron pyrite for which [111] is the principal axis of a resonant (iron) ion with site symmetry $\bar{3}(C_{3i})$. When permitted by the crystal structure, alignment of the Bragg wavevector and the symmetry axis of rotation yields a periodicity in the azimuthal-angle scan equal to the degree of the rotation axis [5, 19]. A second subset of the reflections are due to the magnetic moments. In the example based on ferrous niobate, we consider both spontaneous magnetic order and field-induced magnetic order. For this material azimuthal-angle scans do not reflect the two-fold axis of rotation that passes through the site occupied by the resonant ion, i.e. the structure factors are not simple functions of $\cos(2\psi)$ or $\sin(2\psi)$ where ψ is the angle of rotation about the Bragg vector. Instead, the calculated scans depend on several harmonics in ψ, and the rather complicated dependence on ψ is traced to the spatial anisotropy of the orbital moments when referred to the crystallographic axes.

As we mention at the start of the section, broadly speaking orbital magnetism is either subjugated to spin magnetism or largely an independent degree of freedom. Ferrous niobate belongs to the first class of materials and vanadium sesquioxide is a Mott insulator. In the ordered magnetic phase of V_2O_3 vanadium ions occupy sites that have no symmetry. The spontaneous magnetic moment is not orientated along a crystallographic axis which is a feature common to V_2O_3 and $FeNb_2O_6$, although the configuration of moments in V_2O_3 is believed to be collinear. An interpretation [10]

of the resonant x-ray Bragg diffraction data available for V_2O_3 [7] implies that the orbital moment of the vanadium ion is essentially determined by the trigonal symmetry of the high-temperature crystal structure. In the proposed model, orbital magnetism is not enslaved to spin magnetism and the spatial symmetry element for the orbital moments is the three-fold (trigonal) axis of rotation. The presence of the latter in azimuthal-angle scans is not immediately obvious because Bragg wavevectors for charge-forbidden reflections are not parallel to the trigonal axis. Using the observed values for the magnetic moment and canting angle, and spin $S = 1$ the orbital moment along the trigonal axis has the value $-1.3\mu_B$.

The following two sections record general features of the resonant scattering length and the atomic model used to estimate its behaviour for transition metal ions. In particular, section 3 includes a summary of the rules governing the behaviour of the atomic tensor (which is equivalent to an orbital moment) subject to elements of symmetry which enter the definition of a unit-cell structure factor. Specific results for ferrous niobate are recorded in sections 4 and 5 together with the construction of the structure factor that describes an azimuthal-angle scan. Section 6 is given over to a discussion of the unit-cell structure factors appropriate for the field-induced magnetic configurations and the fully-compensating antiferromagnetic configuration achieved in zero applied and a temperature less than 4.9K. In many ways less complicated is the Templeton and Templeton scattering by iron pyrite which is discussed in section 7. General findings are gathered in section 8.

2. The resonant scattering-length

The resonant contribution to the scattering length is denoted by f, and its mean value, which is equal to its time-averaged value, is $< f >$. Let us label intermediate states engaged in the resonance event by η. These states are non-equilibrium states of the resonant ion and have a life-time = $(\hbar/\gamma_\eta)$, and they are of no interest to us apart from their unavoidable role in f. If the energy of the incident x-rays and the energy of the resonance are E and Δ_η, respectively, a contribution to $< f >$ is of the form,

$$\sum_{\mu} p_{\mu} \sum_{\eta} \frac{\left\langle \mu \left| B^{+} \right| \eta \right\rangle \left\langle \eta \left| B \right| \mu \right\rangle}{(E - \Delta_{\eta} + \frac{i}{2}\gamma_{\eta})}. \qquad (2.1)$$

Here, p_{μ} is the thermal (Boltzmann) factor for the equilibrium state of the sampled labelled μ.

For the electric dispole (E1) events $B = R^{\alpha}$ and for electric quadrupole (E2) events $B = R^{\alpha}R^{\beta}$ where **R** is the position operator and α and β label Cartesian components. As a function of Cartesian labels E2 events contain 81 quantities. Since $< f >$ is a bulk quantity Neumann's Principle applies to it, and the symmetry elements for $< f >$ include the symmetry elements of the point group of the site occupied by the resonant ion. In consequence, the number of independent quantities is usually reduced. For example, if a two-fold axis of rotation passes through the site an E2 event in the paramagnetic state of the sample is described by at most 13 independent quantities.

The question naturally arises as to how to relate the independent quantities to properties of the material [14,15]. One way toward addressing this question is to use an atomic model to calculate the matrix elements in the numerator of (2.1), and this is the approach adopted here. Calculations based on an atomic model are performed in terms of irreducible spherical tensors. There is then a bridge to cross between spherical tensors and Cartesian tensors and matrices used implementing the initial approach. Sticking with the example of an E2 event and a resonant ion at a site containing a two-fold axis of rotation, in the Cartesian language the 13 independent quantities are arranged in the form of a 6 x 6 matrix in order to facilitate calculations [14]. The matrix in question is equivalent to a linear combination of irreducible spherical tensors in which the coefficients are determined by symmetry properties inherent in the matrix, e.g. the two-fold axis of rotation and the demand for invariance with respect to reversal of the direction of time.

3. An atomic model for < *f* >

The absence of much structure in the spectral line-shape [5 – 7] suggests that an adequate description of the resonant enhancement of the diffracted signal might be found by decoupling the resonant energy denominator from the matrix elements to create a simple oscillator. The matrix elements are summed over the quantum labels of the intermediate states that contribute to the resonance in question. Implementing this simplification, and considering E almost matched to the resonance energy, Δ, the scattering length is proportional to,

$$\frac{F(\boldsymbol{\tau})}{(E-\Delta+\frac{\mathrm{i}}{2}\Gamma)}\ , \tag{3.1}$$

where Γ is the width of the resonance. In (3.1), $F(\tau)$ is a unit cell structure factor evaluated for the reciprocal lattice vector τ. With use of an atomic model for the states of the resonant ion, $F(\tau)$ is calculated without approximation [8, 16]. One has,

$$F(\boldsymbol{\tau}) = \sum_{\mathbf{d}} \left\langle Z(\mathbf{d}) \right\rangle \exp(\mathrm{i}\mathbf{d}\cdot\boldsymbol{\tau}), \tag{3.2}$$

where the sum is over the positions of ions in the magnetic unit cell (we omit in (3.2) the Debye-Waller factor which might depend on the position of the ion). For an E2 event, $<Z(\mathbf{d})>$ is the sum of at most five scalar products, and in our chosen notation,

$$\left\langle Z(\mathbf{d}) \right\rangle = \sum_{K=0}^{4} (2K+1)^{1/2}\, \mathbf{H}^{(K)} \cdot \left\langle \mathbf{T}^{(K)}(\mathbf{d}) \right\rangle, \tag{3.3}$$

in which the spherical tensor $\mathbf{H}^{(K)}$ is determined by the conditions of the incident and diffracted beams. For a 1s $\rightarrow$ 3d absorption event $<\mathbf{T}^{(K)}>$ is proportional to an orbital moment of the 3d valence shell. A spherical tensor of rank K has $(2K + 1)$ components and,

$$\mathbf{H}^{(K)} \cdot \left\langle \mathbf{T}^{(K)} \right\rangle = \sum_{m=-K}^{K} (-1)^m H^{(K)}_{-m} \left\langle T^{(K)}_{m} \right\rangle . \tag{3.4}$$

The scattering length and the structure factor are scalar quantities. Hence, a symmetry property of $\langle \mathbf{T}^{(K)} \rangle$ is matched by a corresponding symmetry property of $\mathbf{H}^{(K)}$ thereby leaving $\langle f \rangle$ unchanged by the operation in question. Examples include: (1) $\langle \mathbf{T}^{(K)} \rangle$ and $\mathbf{H}^{(K)}$ are both invariant with respect to the operation of inversion which changes the sign of all spatial coordinates and (2) for K odd $\langle \mathbf{T}^{(K)} \rangle$ and $\mathbf{H}^{(K)}$ are both odd with respect to the change in direction of time.

The procedure used to construct the structure factor (3.2) is based on a knowledge of $\langle \mathbf{T}^{(K)} \rangle$ at one site in the cell and the chemical and magnetic symmetry elements of the unit cell. The following rules apply to $\langle \mathbf{T}^{(K)} \rangle$ and the orbital moments (the behaviour of the orbital moment is deduced from the invariance of the commutation relation for angular momentum $[L_x, y] = iz$, and two more obtained by cyclic permutation of Cartesian labels, or alternatively using the differential form of angular momentum operators). Reflection in the y–z plane results in (x, y, z) $\rightarrow$ (–x, y, z), (L_x, L_y, L_z) $\rightarrow$ (L_x, $-L_y$, $-L_z$) and one finds $\left\langle T_m^{(K)} \right\rangle \rightarrow (-1)^K \left\langle T_{-m}^{(K)} \right\rangle$. Reflection in the x – z plane gives $\left\langle T_m^{(K)} \right\rangle \rightarrow (-1)^{m+K} \left\langle T_{-m}^{(K)} \right\rangle$ and reflection in the x–y plane gives $\left\langle T_m^{(K)} \right\rangle \rightarrow (-1)^K \left\langle T_m^{(K)} \right\rangle$, and the corresponding changes in (x, y, z) and (L_x, L_y, L_z) are deduced by cyclic permutation of labels from the changes induced by reflection in the y–z plane. The act of inversion results in (x, y, z) $\rightarrow$ (–x, –y, –z) and leaves unchanged both **L** and $\left\langle T_m^{(K)} \right\rangle$. A two-fold rotation is equivalent to inversion followed by reflection in the plane perpendicular to the axis of rotation, and this identity yields the changes in $\left\langle T_m^{(K)} \right\rangle$ created by a two-fold rotation. Lastly, one needs an identity that is derived from the required invariance of the Hamiltonian to a change in the direction of time. Let **H** denote the applied field or the direction of the spontaneous moment at the site in question. One finds that changing the direction of time multiplies $\left\langle T_m^{(K)} \right\rangle$ by $(-1)^K$ and reverses the polarity of **H**, i.e. $\left\langle T_m^{(K)} \right\rangle_{\mathbf{H}} = (-1)^{(K)} \left\langle T_m^{(K)} \right\rangle_{-\mathbf{H}}$.

Using standard definitions [17] of orbital moments one finds, for 3d ions,

$\left\langle \mathbf{T}^{(1)} \right\rangle = \left\langle \mathbf{L} \right\rangle / \sqrt{30}$, $\left\langle \mathbf{T}^{(2)} \right\rangle = \frac{1}{3}(\frac{2}{35})^{1/2} \left\langle \mathbf{Q} \right\rangle$, $\left\langle \mathbf{T}^{(3)} \right\rangle = \left\langle \mathbf{\Lambda} \right\rangle / (3\sqrt{70})$, and $\left\langle \mathbf{T}^{(4)} \right\rangle = \left\langle \Upsilon \right\rangle / (18\sqrt{70})$ where, respectively, **Q**, Λ and Υ are operators for the orbital quadrupole, octupole and hexadecapole.

4. The orbital moments in ferrous niobate

A wealth of experimental data on the magnetic properties of ferrous niobate have been successfully interpreted in terms of a Hamiltonian that includes a crystal-field potential, spin-orbit interaction, exchange interaction between spin moments and dipole-dipole coupling between the magnetic moments [9]. (The two many-particle interactions are treated in a mean-field approximation.) The ferrous ion is situated on a two-fold axis of rotation that coincides with the crystallographic b-axis, and the ordered magnetic moments lie in the plane perpendicular to this axis. Referring to Figs. 1 and 2 the moment at site [1] in the unit cell makes an angle ϕ with respect to the c-axis.

The following expressions for $\left\langle T_m^{(K)} \right\rangle$ in the principal axes (ξ, η, ζ) are obtained using a wavefunction for the ferrous ion calculated to first-order in the spin-orbit interaction. The expressions involve 3j-symbols and standard reduced matrix elements $\left(\theta \| V(K) \| \theta\right)$ which are tabulated, for example, in reference [8]. One finds for K = 1 and 3,

$$(2K+1)^{1/2} \left\langle T_m^{(K)} \right\rangle_{(\xi\eta\zeta)} = -\left(\theta \| V(K) \| \theta\right) \delta_{m,0} \left\langle L_\zeta \right\rangle \begin{pmatrix} 2 & K & 2 \\ -1 & 0 & 1 \end{pmatrix}, \tag{4.1}$$

where $\left\langle L_\zeta \right\rangle = \left(g_\zeta - 2\right) \left\langle S_\zeta \right\rangle$, $\left\langle S_\zeta \right\rangle$ is the mean value of the spin moment and g_ζ = 3.09. The corresponding result for K even is,

$$(2K+1)^{1/2} \left\langle T_m^{(K)} \right\rangle_{(\xi\eta\zeta)} = -\left(\theta \| V(K) \| \theta\right) \left\{ \delta_{m,0} \begin{pmatrix} 2 & K & 2 \\ -1 & 0 & 1 \end{pmatrix} + \frac{1}{2}\left(\delta_{m,2} + \delta_{m,-2}\right) \right.$$

$$\left. \begin{pmatrix} 2 & K & 2 \\ -1 & 2 & -1 \end{pmatrix} \right\}. \tag{4.2}$$

From these expressions,

$$\langle Q_0 \rangle = \frac{3}{2}, \langle Q_{\pm 2} \rangle = -\left(\frac{3}{2}\right)^{3/2}$$
$$\langle \Lambda_0 \rangle = -6\langle L_\zeta \rangle$$
$$\langle \Upsilon_0 \rangle = 24, \langle \Upsilon_{\pm 2} \rangle = 6\sqrt{10},$$

and all other values are zero. These results apply to the principal axes.

Results for $\langle T_m^{(K)} \rangle$ in the crystal axes (a, b, c) are derived from (4.1) and (4.2) by rotation by ϕ about the b-axis, which is parallel to the η-axis and illustrated in Fig. 2. Thus,

$$\langle T_m^{(K)} \rangle_{(\mathrm{abc})} = \sum_q d_{mq}^{(K)}(\phi) \langle T_q^{(K)} \rangle_{(\xi\eta\zeta)}, \tag{4.3}$$

where $d_{mq}^{(K)}(\phi)$ is a component of the standard rotation matrix [18]. A rotation by π about the b-axis changes (4.3) to,

$$\sum_q d_{mq}^{(K)}(\phi)(-1)^{K+q} \langle T_{-q}^{(K)} \rangle_{(\xi\eta\zeta)}, \tag{4.4}$$

and it is at once clear from (4.2) that for K even $\langle T_m^{(K)} \rangle_{(\mathrm{abc})}$ is unchanged by the rotation, as it should be. For K odd one must add to the consideration the effect on the orbital moment of a rotation by π about the b-axis, namely, $(L_\mathrm{a}, L_\mathrm{b}, L_\mathrm{c}) \rightarrow (-L_\mathrm{a}, L_\mathrm{b}, -L_\mathrm{c})$, and the observation $\langle L_\mathrm{b} \rangle = 0$. In consequence, rotation by π about the b-axis together with reversal in the direction in time is the full symmetry operation under which $\langle T_m^{(K)} \rangle_{(\mathrm{abc})}$ is invariant, and the full operation is described by (4.4) multiplied by an additional $(-1)^K$.

5. Structure factors for ferrous niobate

Our numbering of ferrous ions in the magnetic unit cell is provided in Fig. 1, and the corresponding spatial phase factors required in the structure factor (3.2) are listed in Table I. The table also includes [9] the observed orientation of the magnetic moment which has a saturation value = 4.5 μ_B; the principal axis is inclined at an angle $\phi = 65.9°$ to the c-axis, and (+, 0, +) = (4.06, 0, 1.85)μ_B together with $g_\xi = 2.0$ and $g_\zeta = 3.09$.

A rotation by π about the c-axis relates the chemical environments at sites [1] and [2]. The rotation leads to a moment (–, 0, +) at site [2] while according to the entry in Table I the observed moment lies in the opposite direction. The required moment (+, 0, –) is obtained from (–, 0, +) by reversing the polarity, which amounts to multiplying the atomic spherical tensor by $(-1)^K$. Hence, the tensor appropriate for site [2] in the structure factor is,

$$(-1)^K \; (-1)^m \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} .$$

The chemical environments at sites [3] and [4] are obtained, respectively, from site [1] by reflections in planes perpendicular to the b- and a-axes, and the moment orientation carried by the reflections coincides with the observed moment. As far as the chemical environments are concerned [5] ≡ [1], [6] ≡ [2], [7] ≡ [3] and [8] ≡ [4]. Factors of $(-1)^K$ at sites [5], [7] and [8] produce spherical tensors consistent with the observed magnetic moments. Assembling all the factors one finds that,

$$\Psi = \sum_{\mathbf{d}} \left\langle T_m^{(K)}(\mathbf{d}) \right\rangle_{(\mathrm{abc})} \exp(\mathrm{i}\mathbf{d}\cdot\boldsymbol{\tau}), \tag{5.1}$$

is non-zero for $k + K$ an even integer, i.e. there is a selection rule acting on the sum of the rank of the spherical tensor and the Miller index k.

Taking $k = 2n$ (and K even) the value of (5.1) is,

$$\Psi = 4(-1)^n \cos(\alpha) \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} \left\{ 1 + (-1)^{h+n+m} \right\}, \tag{5.2}$$

and for $k = 2n + 1$ (and K odd) the corresponding result is,

$$\Psi = -4\mathrm{i}(-1)^n \cos(\alpha) \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} \left\{ 1 - \mathrm{i}(-1)^{h+n+m} \right\}. \tag{5.3}$$

In arriving at these expressions we have used $\left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} = (-1)^m \left\langle T_{-m}^{(K)} \right\rangle_{(\mathrm{abc})} = \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})}^*$ which is derived from (4.3). (While the second equality, involving the complex conjugate of $\left\langle T_m^{(K)} \right\rangle$, might at first sight appear to follow immediately from the standard definition of spherical harmonics in fact this is not the case, and in general it need not be satisfied.) The structure factor (3.2) describing the fully compensating antiferromagnet obtained in zero field below is 4.9K is derived from (5.2) or (5.3).

As might be expected, structure factors describing field-induced ferromagnetic states are significantly simpler than those just encountered. First we consider a field applied along the a-axis. Above the critical field four of the eight moments in the magnetic cell change their orientation; the field-induced state is derived from the entries in Table I by making the following changes (–, 0, +) → (+, 0, +) and (–, 0, –) → (+, 0, –), and for $\left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})}$ it amounts to the introduction of an additional phase $(-1)^m$ at each of the four sites. The corresponding value of (5.1) can be different from zero for $k = 2n$. This reflection condition, or extinction rule, arises because the magnetic unit cell is now identical to the chemical unit cell, as illustrated in Fig. 3. Above the critical field in the a-direction, and taking $k = 2n$, the structure factor is derived from the expression,

$$\Psi = 2(-1)^n \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} \left\{ 1 + (-1)^{K+m+h+n} \right\} \left\{ \mathrm{e}^{\mathrm{i}\alpha} + (-1)^{h+n} \mathrm{e}^{-\mathrm{i}\alpha} \right\}. \tag{5.4}$$

We discuss this result after giving the corresponding result for a field along the c-direction.

The moment configuration achieved by a field exceeding the critical value for the c-direction is illustrated in Fig. 4 and it is derived from Table I by making the changes (–, 0, –) → (–, 0, +) and (+, 0, –) → (+, 0, +) and these changes translate $\left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} \rightarrow (-1)^K \left\langle T_{-m}^{(K)} \right\rangle_{(\mathrm{abc})}$. The calculated structure factor is different from zero for $k = 2n$ and $h + n$ an even integer, and it is constructed from the result,

$$\Psi = 4(-1)^n \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} \left\{ \mathrm{e}^{\mathrm{i}\alpha} + (-1)^m \mathrm{e}^{-\mathrm{i}\alpha} \right\}. \tag{5.5}$$

The additional extinction rule $h + n$ even governing diffraction is identical with the extinction rule for charge scattering which can be derived from Table I, i.e. the field-induced ferromagnetic state achieved by a field along the c-axis does not generate charge-forbidden reflections. Returning our attention to (5.4) which describes a field-induced net moment along the a-axis, the charge-allowed reflections arise from atomic tensors with $K + m$ even, and charge-forbidden reflections arise from $K + m$ odd. As we shall see, additional selection rules on $K + m$ arise from the polarization states in the incident and final channels of scattering.

To complete the calculation of the structure factor (3.2) one needs values of the spherical tensor $\mathbf{H}^{(K)}$ which describes the geometry of the experiment. Our coordinates for the experimental arrangement (x, y, z) are defined in Fig. 5, and we evaluate $\mathbf{H}^{(K)}$ in these coordinates. The scalar product (3.4) clearly has $\mathbf{H}^{(K)}$ and $\langle \mathbf{T}^{(K)} \rangle$ referred to a common set of axes and one has (x, y, z) coincide with the crystal axes (a, b, c). The non-zero values of $H_m^{(K)}, m \geq 0$ are listed in Table II. The remaining non-zero values are derived from the entries by using the identity

$$H_{-m}^{(K)} = (-1)^{K+m} \left\{ H_m^{(K)} \right\}^*. \tag{5.6}$$

For the unrotated channel of scattering ($\sigma'\sigma$), in which the polarization perpendicular to the plane of scattering is unchanged by the scattering event, $m = 0, \pm 2$ and one finds $H_{\pm 2}^{(3)} = 0$. In contrast to the values of $H_m^{(K)}$ for the unrotated channel, the

values of $H_m^{(K)}$ in the rotated channel ($\pi'\sigma$) are not purely real and non-zero values are found for $m = \pm 1, \pm 3$.

6. Discussion of the ferrous niobate structure factors

The observed fully compensating antiferromagnetic structure of ferrous niobate requires a unit cell which is doubled along the b-axis relative to the chemical unit cell. Reflections (h, k, l) that can be indexed with respect to the chemical unit cell therefore have k even. Writing $k = 2n$ the reflection condition, also called an extinction rule, for scattering by spherical distributions of charge is known to be $h + n$ even, cf. Table I. The so-called charge-allowed reflections with $h + n$ even are not sensitive to spatial anisotropy in the charge and the magnetic contributions to resonant diffraction. For this reason charge-allowed reflections are not taken up in the subsequent discussion of calculated structure factors for ferrous niobate. We shall start the discussion by looking at the field-induced ferromagnetic states because they are indexed relative to the chemical unit cell ($k = 2n$) and have relatively simple calculated structure factors.

The results for structure factors to be discussed in this section are created by bringing together in the definition (3.2) the quantities labelled Ψ in section 5 and the spherical tensor $\mathbf{H}^{(K)}$ whose elements are found in Table II. We elect not to report details of the algebra and, instead, focus on the results and their interpretation. One feature of great interest is the dependence of diffraction on states of polarization in the incident and scattered beams of photons.

Field-induced moment along the c-axis

The configuration of the moments is illustrated in Fig. 4. Starting from the magnetic unit-cell structure factor, which contains eight ferrous ions, we found in the previous section the selection rule $k = 2n$ applies to the present case, i.e. the configuration is indexed relative to the chemical unit cell and we use this construction in Fig. 4. The calculated structure factor has a null value for charge-forbidden

reflections, and the structure factor for charge-allowed reflections is created from (5.5).

Field-induced moment along the a-axis

Starting from the magnetic unit-cell structure factor we have found the selection rule $k = 2n$, and the configuration of moments illustrated in Fig. 3 is consistent with this finding. For charge-forbidden reflections the calculated structure factor can be different from zero and it is created from the expression derived from (5.4) on setting $h + n$ odd, namely

$$\Psi = 4\mathrm{i}(-1)^n \sin(\alpha)\left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} \left\{1-(-1)^{K+m}\right\}, \tag{6.1}$$

where α is a spatial phase factor defined in Table I. When the crystal and experimental axes coincide, making the σ-polarization perpendicular to the a – b plane, the structure factor is,

$$F(\boldsymbol{\tau}) = 4\mathrm{i}\sin(\alpha)\sum_{K,m}(-1)^m (2K+1)^{1/2} H_{-m}^{(K)} \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} \left\{1-(-1)^{K+m}\right\}. \tag{6.2}$$

Here $n = 0$ and one has $\tau = (h, 0, 0)$ with h an odd integer. The spherical tensor $\mathbf{H}^{(K)}$ is determined by the experimental geometry, and the conditions of the incident and final beams of photons. In particular it depends on the Bragg angle θ included in Fig. 5.

The structure factor (6.2) evaluated for the unrotated ($\sigma'\sigma$) and rotated ($\pi'\sigma$) is,

$$F_{\sigma'\sigma}(\boldsymbol{\tau}) = -2\left\langle L_\zeta \right\rangle \sin\alpha \sin 2\theta \cos\phi \cos 2\phi, \tag{6.3}$$

and,

$$F_{\pi'\sigma}(\boldsymbol{\tau}) = -2\mathrm{i}\sin\alpha \cos\theta \cos 2\theta \sin 2\phi, \tag{6.4}$$

where ϕ measures the inclination of the preferred magnetic axis, labelled ζ, relative to the c-axis and $\langle L_\zeta \rangle = (g_\zeta - 2)\langle S_\zeta \rangle$ is the orbital magnetic moment.

As the magnetic field applied along τ is steadily increased beyond its critical value the canting angle ϕ approaches $\pi/2$, and for the fully saturated ferromagnetic states $\phi = \pi/2$ and scattering in both channels is reduced to zero. Scattering in the $(\sigma'\sigma)$ channel survives at elevated temperatures with $\langle S_\zeta \rangle$ determined by the magnitude of the applied field. Tensors $\langle T_m^{(K)} \rangle_{(\mathrm{abc})}$ with $m \neq 0$ contribute in the rotated channel. In consequence, diffraction in the $(\pi'\sigma)$ channel is due to spatial anisotropy in the orbital moments referred to the crystallographic axes (the result (6.4) vanishes for $\phi = 0$ and $\pi/2$), and such a term is often called Templeton and Templeton scattering [11-13]. One might cite the factor $\sin 2\phi$ in (6.4) as evidence that the origin of the scattering is anisotropy in the orbital moments in the crystal axes, for the scattering vanishes should the principal axis ζ coincide with either the a-axis or the c-axis.

The 90° phase shift in the two channels is present because one contribution is determined by even-rank atomic tensors and the other is determined by odd-rank atomic tensors. The origin of this state of affairs is the selection rule $K + m$ odd in (6.2) with m even for $(\sigma'\sigma)$ and m odd for $(\pi'\sigma)$. A manifestation of the phase shift is that a completely linearly polarized incident x-ray beam acquires circular polarization on scattering; conversely, the cross-section for diffraction is sensitive to circular polarization in the incident beam. The mean helicity [4] in the final beam P_2' for a completely linearly polarized incident beam ($P_3 = 1$) is related to the structure factor by the expression,

$$P_2' \propto \mathrm{Im.}\{F_{\sigma'\sigma}^* F_{\pi'\sigma}\}. \qquad (6.5)$$

For the fully saturated ferromagnetic state $P_2' = 0$.

In summary, the scattering that contributes to charge-forbidden reflections consists of purely magnetic scattering in the unrotated channel and Templeton and Templeton scattering in the rotated channel. The difference in the origins of contributions to the two channels results in a sensitivity in scattering to circular polarization.

In an azimuthal-angle scan the crystal is rotated by ψ about τ = (*h*, 0, 0). We find,

$$F_{\sigma'\sigma}(\boldsymbol{\tau}) = -2\left\langle L_\zeta \right\rangle \sin(\alpha)\sin 2\theta \cos\phi\cos\psi(2\cos^2\phi - \cos^2\psi - 1), \qquad (6.6)$$

and,

$$F_{\pi'\sigma}(\boldsymbol{\tau}) = -\sin(\alpha)\left\{ 2i\cos\theta\sin 2\phi\cos\psi(\cos 2\theta\cos^2\psi - \sin^2\psi) + \left\langle L_\zeta \right\rangle \cos\phi\sin\psi \right.$$

$$\left. \left[\cos 3\theta\,(1 - 3\cos^2\phi\cos^2\psi) + \cos\theta(\cos^2\phi\sin^2\psi - 3\sin^2\phi)\right] \right\}. \qquad (6.7)$$

As expected, these expressions evaluated for ψ = 0 reduce to (6.3) and (6.4) and evaluated for $\phi = \pi/2$ both (6.6) and (6.7) are zero. At a general setting of the crystal the rotated scattering contains charge and magnetic contributions. For $\psi = \pi/2$ the moments are contained in the plane of scattering, and for this setting the scattering is in the rotated channel and its character is purely magnetic.

A feature of (6.6) and (6.7) to be noted is the absence of a signature of the two-fold axis of rotation that passes through the site of the ferrous ion. The quite complicated ψ-dependence of (6.6) and (6.7) arises because of spatial anisotropy in the orbital moments, referred to the crystallographic axes.

By way of illustrating this point one can consider a simple collinear arrangement of moments. In keeping with the style adopted for the section, we will not give any specific results for such a system although the algebra involved is straightforward. A ferrous moment (+, 0, +) in the a – c plane is described by $\left\langle T_m^{(K)} \right\rangle_{(abc)}$ and a moment aligned in the opposite direction is described by

$(-1)^{K+m} \left\langle T_{-m}^{(K)} \right\rangle_{(\mathrm{abc})} = (-1)^K \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})}$. The structure factor for two oppositely aligned moments, e.g. sites [1] and [3] in Table I and Fig. 1, is created from,

$$\left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})} \pm (-1)^K \left\langle T_m^{(K)} \right\rangle_{(\mathrm{abc})},$$

where the + (–) sign is for a charge (antiferromagnetic) reflection. Using (4.3) and,

$$\left\langle T_m^{(K)} \right\rangle = \sum_q \exp(\mathrm{i}q\psi) d_{mq}^{(K)}\left(\frac{\pi}{2}\right) \left\langle T_q^{(K)} \right\rangle_{(\mathrm{abc})}, \tag{6.8}$$

one readily calculates the corresponding structure factor. Equation (6.8) gives the atomic tensor rotated so as to align the crystal c-axis with τ and the geometry is illustrated in Fig. 5. As already implied, the result for the model in question is not a function solely of $\cos(2\psi)$ or $\sin(2\psi)$, and like (6.6) and (6.7) it contains odd harmonics. Not surprisingly, there are no odd harmonics of ψ in the structure factor calculated for the arrangement in which the principal axis ζ is aligned with the Bragg vector, denoted here by the x – axis, viz. Fig. 5. For the simple two-ion collinear model we have described the desired arrangement is achieved by setting $\phi = 0$, and for this ϕ the azimuthal-angle scan meshes with the two-fold axis of rotation because of the selection rule $m = q$ in (4.3), i.e. $d_{mq}^{(K)}(0) = \delta_{m,q}$.

Spontaneous magnetic order in zero field (fully compensating antiferromagnet)

The results (5.2) and (5.3) are the starting points for the present discussion. We will focus on the purely magnetic scattering which is described by (5.3). Taking $\tau = (0, 2n + 1, 0)$ the b-axis is aligned with the x-axis of the experimental geometry. It is to be noted that a ferrous ion sits on a two-fold axis of rotation which coincides with the b-axis, and the magnetic moments lie in the a-c plane. Clearly, rotation of the crystal by ψ about τ has the effect of adding ψ to the canting angle ϕ. The addition of the two angles is brought about by the addition theorem for rotation matrices [18].

Let $\beta_{\pm} = \psi \pm \phi$. We find,

$$F_{\sigma'\sigma}(\boldsymbol{\tau}) = (-1)^n \cos(\alpha) \sin 2\theta \left\langle L_\zeta \right\rangle [\cos\beta_+ \cos 2\beta_+ - \mathrm{i}(-1)^n \cos\beta_- \cos 2\beta_-], \qquad (6.9)$$

and,

$$F_{\pi'\sigma}(\boldsymbol{\tau}) = (-1)^n \cos(\alpha) \cos\theta \left\langle L_\zeta \right\rangle [\{\sin\beta_+ [\cos^2\beta_+ + \cos 2\theta(1 - 3\cos^2\beta_+)]\} - \mathrm{i}(-1)^n \{\beta_+ \to \beta_-\}]. \qquad (6.10)$$

In purely magnetic scattering there is no evidence from azimuthal-angle scans of the two-fold axis of rotation in the unit cell. Because of the phase shift between the contributions to (6.9) and (6.10) in β_+ and β_- the diffracted signal couples to circular polarization.

The calculated structure factors presented in this section offer a means of testing the properties reported for ferrous niobate [9] to an extent hitherto not possible. In this regard, we remind the reader that our expressions for the atomic tensor are correct at the first level of approximation in the spin-orbit coupling. Previously [8] it has been demonstrated that some contributions to scattering can be zero at this level of approximation so more accurate calculations for ferrous niobate might be necessary to completely interpret experimental data.

7. Structure factors for iron pyrite

Results for x-ray diffraction from FeS_2 enhanced by absorption at the K-edge of iron have been reported by Kokubun et al. [20]. Weak features in the intensity at the pre-edge of scattering strongly enhanced by electric dipole (E1) absorption behave differently in azimuthal-angle scans and the authors suggest this is due to some E2 absorption at the pre-edge. Our calculated structure factors support this view and point the way to further possible tests.

Components entering the calculation of structure factors for diffraction by the iron ions are gathered in Table III. The atomic tensor appropriate to an ion is obtained by application of rules given in section 3, e.g. ions at [000] and [0 ½ ½] are related by a c-glide operation and the element essential in finding the atomic tensor for [0 ½ ½] is reflection in the a-c plane. The charge-forbidden reflections which have been studied are (0, 0, *l*) and (0, *l*, *l*) with *l* an odd integer. Assembling from Table III the factors appearing in Ψ, equation (5.1), one finds,

$$\Psi(0,0,l) = \{1-(-1)^m\}\{< T_m^{(K)} >_{(\mathrm{abc})} + < T_{-m}^{(K)} >_{(\mathrm{abc})}\}, \tag{7.1}$$

and,

$$\Psi(0,l,l) = \{1-(-1)^m\}\{< T_m^{(K)} >_{(\mathrm{abc})} - < T_{-m}^{(K)} >_{(\mathrm{abc})}\}. \tag{7.2}$$

Here, *K* is taken to be an even integer because iron pyrite is not magnetically ordered at room temperature. Evidently *m* is an odd integer and so *K* = 2 and 4; these findings constitute one possible definition of Templeton and Templeton scattering.

The site symmetry is $\bar{3}(\mathrm{C}_{3i})$. Hence, the possible values of the projection label *q* in $< T_q^{(K)} >_{(\xi\eta\zeta)}$ are *q* = 0 and ± 3. We assume that in the principal axes the atomic tensor is purely real and thus $< T_q^{(K)} >_{(\xi\eta\zeta)} = (-1)^q < T_{-q}^{(K)} >_{(\xi\eta\zeta)}$. The principal axis is [111] and,

$$< T_m^{(K)} >_{(\mathrm{abc})} = \exp(\mathrm{i}\tfrac{m\pi}{4}) \sum_q d_{mq}^{(K)}(\beta) < T_q^{(K)} >_{(\xi\eta\zeta)}, \tag{7.3}$$

with $\cos\beta = (1/3)^{1/2}$ and $\sin\beta = (2/3)^{1/2}$. Unlike the situation for ferrous niobate, the atomic tensors $< T_m^{(K)} >_{(\mathrm{abc})}$ for iron pyrite contain an imaginary component.

To describe diffraction at τ = (0, 0, *l*) the c-axis of the crystal is aligned with the x-axis of the experimental geometry. Secondly, an azimuthal-angle scan is rotation of the crystal by ψ about the x-axis, as illustrated in Fig. 5. The two rotations are

described by an appropriate rotation matrix [18] and one finds the result (6.8). With $\psi = 0$ the b- and y-axes are aligned. When (6.8) is applied in (7.1) the values of q are ± 1 and ± 3.

The structure factors to be discussed are derived from (3.4), (6.8) and (7.1). They are expressed in terms of the octupole ($K = 2$) and hexadecapole ($K = 4$) moments of the iron 3d-shell, and components allowed by site symmetry ($\bar{3}$) are $\langle Q_o \rangle$, $\langle \Upsilon_o \rangle$ and $\langle \Upsilon_{+3} \rangle = -\langle \Upsilon_{-3} \rangle$. The two independent components of the hexadecapole enter as the linear combination,

$$< \Gamma >= \tfrac{1}{9}\{< \Upsilon_o > + (\tfrac{7}{10})^{1/2} < \Upsilon_{+3} >\}. \qquad (7.4)$$

For (0, 0, l) we find $F_{\sigma'\sigma}(\tau) = 0$ and,

$$F_{\pi'\sigma}(\boldsymbol{\tau}) = \tfrac{1}{21}\cos\theta \sin\psi \{2 < Q_o > (1 - 2\cos 2\theta) + < \Gamma > [1 - (6 - 7\sin^2\psi)\cos^2\theta]\}. \qquad (7.5)$$

The dependence on ψ, namely, $\sin\psi$, of the octupole contributions to $F_{\pi'\sigma}(\tau)$ is the same as that predicted for E1 enhanced diffraction [20]. Hence, in terms of an azimuthal-angle scan it is the hexadecapole in E2 that distinguishes it from E1. The contribution from the octupole is seen in (7.5) to vanish for a Bragg angle $\theta = 30°$, and with $\tau = (0, 0, l)$ this condition is almost achieved with iron pyrite and $l = 3$.

Lastly, we consider $\tau = (0, l, l)$ and l odd, and [011] aligned with the x-axis. For $\psi = 0$ the a- and z-axes are aligned. Equation (7.2) is the starting point for the calculation of structure factors. Orientation of the crystal to the required position in the experimental co-ordinates (x, y, z) and rotation by ψ about the x-axis lead to,

$$< T_m^{(K)} >= \exp(i\tfrac{m\pi}{2}) \sum_{qq'} \exp(i\tfrac{3\pi q'}{4})\, d_{qq'}^{(K)}\, (\tfrac{\pi}{2})\, d_{q'm}^{(K)}(\psi) < T_q^{(K)} >_{(abc)}, \qquad (7.6)$$

and when used in (7.2) $q = \pm 1$ and $q = \pm 3$. While the sum on q' is equivalent to a single rotation matrix, as in all previous examples, the presence of the phase factor denies it being a simple function of ψ. In consequence, for $\tau = (0, l, l)$ and a general ψ we do not have for the structure factors simple algebraic expressions.

It can be shown that for $\psi = 0$ and $\pi/2$ the structure factor $F_{\sigma'\sigma}(\tau)$ is zero, and its values at ψ and $\psi + \pi$ are the same. Taking $\psi = \pi/4$,

$$F_{\sigma'\sigma}(\boldsymbol{\tau}) = \tfrac{\sqrt{2}}{21} \sin^2\theta \{< Q_o > + \tfrac{3}{4} < \Gamma >\}. \qquad (7.7)$$

Expressions for $F_{\pi'\sigma}(\tau)$ are particularly complicated. This structure factor is the same at $\psi = \pi/2$ and $\psi = 3\pi/2$ (in these settings the b-c plane is perpendicular to the plane of scattering) and for arbitrary ψ it is not the same at ψ and $\psi + \pi$. Setting, respectively, $\psi = 0$, $\pi/4$ and $\pi/2$ we find:

$$F_{\pi'\sigma}(\boldsymbol{\tau}) = -\tfrac{1}{21} \sin(\theta + \tfrac{\pi}{4}) \{2 < Q_o > (1 - 2\sin 2\theta) + \tfrac{1}{2} < \Gamma > (3 + \sin 2\theta)\}, \qquad (7.8)$$

$$F_{\pi'\sigma}(\boldsymbol{\tau}) = \tfrac{1}{21} \cos\theta \{< Q_o > (1 - 2\cos 2\theta) + \tfrac{1}{16} < \Gamma > (7\sqrt{2}\sin 2\theta + 11\cos 2\theta - 9)\}, \qquad (7.9)$$

and,

$$F_{\pi'\sigma}(\boldsymbol{\tau}) = -\frac{1}{21\sqrt{2}} \sin\theta \{2 < Q_o > (1 + 2\cos 2\theta) + \tfrac{1}{4} < \Gamma > (5\cos 2\theta - 1)\}. \qquad (7.10)$$

These few expressions for $\tau = (0, l, l)$ provide an orientation to the behaviour of $F_{\pi'\sigma}(\tau)$ as a function of ψ and the Bragg angle.

The observed pre-edge features [20] possess structure on the scale of the energy resolution available in the experiment. The features are not well separated from the main intensity, attributed to E1 enhanced diffraction, which raises the real possibility that their character is largely E2 together with some E1. For $\tau = (0, 0, l)$ the significant aspect in the observed intensities is a decrease on changing from $l = 1$ to l

= 3, and this could be due to the very small contribution from $< Q_o >$ to $F_{\pi'\sigma}(\boldsymbol{\tau})$ at $l = 3$. With τ = (0, l, l) the azimuthal-angle scan at the best separated pre-edge feature is distinctly different from that expected for E1 enhanced diffraction. Intensities are not reported for each channel of scattering, and data can be compared to ($|F_{\sigma'\sigma}|^2 + |F_{\pi'\sigma}|^2$). General aspects of the observations are in accord with calculated structure factors. For $\psi = \pi/2$ the observed intensity is essentially zero. Using this evidence in (7.10) we find $< \Gamma > \sim -6.5 < Q_o >$, and then the maximum intensity is at $\psi = 0$. As weak maximum at $\psi = \pi/4$ could be due to a contribution to scattering in the unrotated channel. A fully satisfactory confrontation between experiment and theory could be made with high resolution data observed in the rotated and unrotated channels of scattering, with an adequate account of absorption corrections.

8. Summary

The material presented here on resonant x-ray diffraction by a magnetic material was conceived with several objectives in mind, comprising a description of the atomic model used, a discussion of various inherent symmetry properties, and the calculation of structure factors for the interpretation of experimental data.

First, the resonance enhanced contribution to the scattering length $\langle f \rangle$ is not immediately related to atomic variables of interest in the investigation of material properties. (This feature of $\langle f \rangle$ distinguishes it from the non-resonant part of the scattering length, and the magnetic scattering length for neutron beams.) However, a representation of the resonant contribution in terms of atomic variables can be achieved at the expense of undertaking an approximation [8, 10, 16]. The approximate form of $\langle f \rangle$, based on an atomic model, is appealing to work with since it gives vent to physical intuition as to the quantities controlling diffraction, and it gives a simple framework within which to relate observations to results obtained by other experimental techniques. The limitations imposed by the approximation need to be assessed by testing predictions against experimental results, and completely numerical calculations, e.g. results from multiple-scattering theories [21].

Secondly, the magnetic ion – at the focus of interest – is part of a crystal structure and influenced by the symmetry of its environment. The discussion of the symmetry relations between equivalent ions is another necessary ingredient of the presentation, together with the influence of the experimental setup and the polarization conditions of the photons.

The building blocks are brought together to demonstrate a step by step procedure for assembling the structure factors pertinent for any crystal containing magnetic ions. These structure factors are subject to the appropriate reflection conditions, or extinction rules, and display the signatures for charge-allowed and charge-forbidden, or purely magnetic, diffraction. This leads to a characterization of the physical content to be recovered from the Bragg reflections of the material in question [10].

A big component of this work is represented by a worked example of the various structure factors calculated for three magnetic configurations encountered in $FeNb_2O_6$ [9] under different experimental conditions. The discussion of $FeNb_2O_6$ is facilitated by the availability of extensive data, obtained from magnetic neutron diffraction and complementary measurements, in which the magnetic structure and the anisotropy properties of the Fe-ion have been determined. A second worked example is appropriate for FeS_2 which is not magnetically ordered.

Disentangling the geometric conditions of the scattering process from the properties of the valence shell that accepts the photo-excited core electron facilitates a discussion of the symmetry operations connecting equivalent sites in the unit cell [8, 16]. In this context, it is important to note that the atomic tensor, which describes properties of the valence shell in terms of orbital moments, necessarily exhibits the transformation properties of an axial quantity. In order to obtain the correct moment orientation at a specific magnetic site it may, in some cases, be necessary to use a time-reversal operation on top of the symmetry operations inherent in the chemical unit cell. The transformations produce, for each site, corresponding phase factors which are then taken into account together with the usual phase factors deriving from the positions occupied by the ions in the unit cell.

One result found here for $FeNb_2O_6$ and also in a previous investigation of V_2O_3 [10] is the coupling of structural and orbital properties in diffraction signals. The coupling appears in the form of selection rules on Miller indices (h, k, l) for a reflection and the rank K and component index m ($-K \leq m \leq K$) of the orbital moments of the valence shell. For example, in diffraction by the fully compensating antiferromagnetic configuration of $FeNb_2O_6$ the signal is zero unless $K + k$ is an even integer, while in the case of V_2O_3 charge-forbidden reflections are believed to satisfy K odd and $h + m$ even. (In E1 and E2 absorption events the maximum values of K are 2 and 4, respectively.)

Charge related diffraction at a charge-forbidden reflection, which is due to spatial anisotropy, can be accompanied by magnetic related diffraction. A signature of this diffraction, frequently called Templeton and Templeton diffraction after its discoverers [11 – 13], is its appearance in the channel of scattering in which linear polarization is rotated, through 90° from initially being perpendicular to the plane of scattering. However, this is not a general rule and it is valid for particular materials and Bragg reflections. By way of an example, we have shown for FeS_2 and $\tau = (0, l, l)$ that Templeton and Templeton scattering appears in the unrotated channel of scattering. In the case of $FeNb_2O_6$ the origin of Templeton and Templeton diffraction is made explicit through a dependence on the orientation of principal axes relative to crystallographic axes.

Use of principal axes to facilitate the description of non-magnetic properties of crystals is well established [14]. Less well-known, perhaps, is their use for magnetic properties [15] and properties described by spherical tensors, as in the present work.

Spatial anisotropy in the orbital moments of the resonant ions in $FeNb_2O_6$ and FeS_2 is manifest in azimuthal-angle scans, in which the crystal is rotated about the Bragg vector. Calculated structure factors have a quite complicated dependence on the azimuthal angle, because of the anisotropy. In particular, for $FeNb_2O_6$ the azimuthal angle does not mesh with the two-fold axis that passes through the site occupied by the resonant ion and produce a four-fold periodicity in the intensity

regarded as a function of azimuthal angle [5]. We have illustrated the destruction by anisotropy of coherence between the azimuthal angle and an axis of rotation by reporting results for a simple collinear configuration of moments.

Circular polarization can be created in the diffraction of a completely linearly polarized incident beam of photons if amplitudes for the rotated and unrotated channels of scattering are shifted in phase such that the imaginary part of the product of the amplitudes is different from zero. This can be achieved with $FeNb_2O_6$ with the two configurations of the magnetic moments. In one configuration there is a 90° phase shift between the amplitude in the rotated ($\pi'\sigma$) and the unrotated ($\sigma'\sigma$) channels of scattering due to pure charge and purely magnetic contributions, respectively. A second configuration generates reflections for which both channels carry purely magnetic signals, and the necessary phase shift between them arises from the actual nature of the configuration.

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Table I

Quantities entering the structure factor of ferrous niobate. Definitions: $\tau = (h, k, l)$, $\alpha = 2\pi ky + \frac{\pi}{2} l$, and $\beta = \alpha - \frac{\pi}{2} k$. The sum of spatial phase factors is the structure factor for charge scattering, and the result for $k = 2n$ is $4 \cos(\alpha)\{1 + (-1)^{h+n}\}$. Hence charge
allowed diffraction is indexed by $k = 2n$ and $h + n$ even.

Ion	Spatial phase factor	Observed moment in zero field	Atomic phase factor
[1] $e^{i\beta}$	(+, 0, +)	1	
[2] $(-1)^h e^{-i\alpha}$	(+, 0, −)	$(-1)^{K+m}$	
[3] $e^{-i\beta}$	(−, 0, −)	$(-1)^K$	
[4] $(-1)^h e^{i\alpha}$	(+, 0, −)	$(-1)^{K+m}$	
[5] $(-1)^k e^{i\beta}$	(−, 0, −)	$(-1)^K$	
[6] $(-1)^{h+k} e^{-i\alpha}$		(−, 0, +)	$(-1)^m$
[7] $(-1)^k e^{-i\beta}$	(+, 0, +)	1	
[8] $(-1)^{h+k} e^{i\alpha}$	(−, 0, +)	$(-1)^m$	

Table II

Non-zero values of $H_m^{(K)}$ for the unrotated ($\sigma'\sigma$) and rotated ($\pi'\sigma$) channels of scattering for which $m = 0, \pm 2$ and $m = \pm 1, \pm 3$, respectively; the axes are defined in Fig. 5 and θ is the Bragg angle. $H_{-m}^{(K)} = (-1)^{K+m}\{H_m^{(K)}\}^*$.

K	m	$(\sigma'\sigma)$	m	$(\pi'\sigma)$
0	0	$\frac{1}{2\sqrt{5}}\cos 2\theta$		
1	0	$\frac{\mathrm{i}}{2\sqrt{10}}\sin 2\theta$	1	$-\frac{1}{4\sqrt{5}}\mathrm{e}^{-3\mathrm{i}\theta}$
2	0	$-\frac{1}{2\sqrt{14}}\cos 2\theta$	1	$\frac{1}{4}\left(\frac{3}{7}\right)^{1/2}\mathrm{e}^{-3\mathrm{i}\theta}$
	2	$\frac{1}{4}\left(\frac{3}{7}\right)^{1/2}$		
3	0	$-\frac{\mathrm{i}}{\sqrt{10}}\sin 2\theta$	1	$-\frac{1}{4}\left(\frac{3}{10}\right)^{1/2}\mathrm{e}^{-3\mathrm{i}\theta}$
			3	$-\frac{1}{4\sqrt{2}}\mathrm{e}^{-\mathrm{i}\theta}$
4	0	$-\left(\frac{2}{35}\right)^{1/2}\cos 2\theta$	1	$\frac{1}{4\sqrt{14}}\mathrm{e}^{-3\mathrm{i}\theta}$
	2	$-\frac{1}{2\sqrt{7}}$	3	$\frac{1}{4\sqrt{2}}\mathrm{e}^{-\mathrm{i}\theta}$

Table III

Quantities entering the structure factor of iron pyrite.

Site	Spatial Phase factor	Symmetry Operation	Atomic Tensor
[000]	1	Origin	$\left\langle T_m^{(K)} \right\rangle_{(abc)}$
[½ ½ 0]	$e^{i\pi (h+k)}$	b-glide (x → – x)	$(-1)^K \left\langle T_{-m}^{(K)} \right\rangle_{(abc)}$
[0 ½ ½]	$e^{i\pi (k+l)}$	c-glide (y → – y)	$(-1)^{m+K} \left\langle T_{-m}^{(K)} \right\rangle_{(abc)}$
[½ 0 ½]	$e^{i\pi (h+l)}$	a-glide (z → – z)	$(-1)^m \left\langle T_m^{(K)} \right\rangle_{(abc)}$

Figure Captions

1. The antiferromagnetic configuration of magnetic moments in ferrous niobate observed in zero field below the Néel temperature [9]; the crystal a – b plane is in the plane of the paper, and the moments are contained in the a – c plane, cf. Table I.

2. The relative orientation of the principal (ξ,η,ζ) and crystallographic (a,b,c) axes of ferrous niobate and the definition of the canting angle ϕ. Magnetic moments lie in the a – c plane.

3. The configuration of magnetic moments in ferrous niobate induced by a magnetic field applied in the a–direction [9]; moments lie in the a – c plane and the c-axis and this plane are perpendicular to the plane of the page.

4. The configuration of magnetic moments in ferrous niobate induced by a magnetic field applied in the c–direction, which is perpendicular to the plane of the page.

5. (x,y,z) axes define the experimental geometry. σ–polarization is perpendicular to the plane of scattering which contains the x-y axes. Photons are elastically scattered and deflected through an angle 2θ. The Bragg vector $\tau = \mathbf{q} - \mathbf{q}' = -\mathbf{x}$. In an azimuthal-angle (ψ) scan used in the investigation of iron pyrite [19] the crystal c-axis is aligned with **x** and the crystal b-axis and the y-axis enclose an angle ψ.

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