

Neutron diffraction by magnetic crystals, including V_2O_3 and DyB_2C_2 .

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Abstract: A theory of neutron scattering by magnetic ions is developed and applied to diffraction by crystals in which ions in the unit cell are not equivalent on account of a lack of translational symmetry in their environments. The development demonstrates a close connection between interpretations of neutron and resonant x-ray magnetic Bragg diffraction, in terms of an atomic model. Cross-sections for neutron diffraction by powders and single crystals, including polarization induced interference between nuclear and magnetic amplitudes, are considered. By way of illustrating the theoretical development, cross-sections are predicted for two materials, V_2O_3 and DyB_2C_2 , on the basis of findings from extensive studies, using resonant x-ray diffraction, of their spatially anisotropic distributions of charge and magnetization.

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I. Introduction

The determination of magnetization distributions by the Bragg diffraction of neutrons is not a new experimental technique but one that has developed over the past four decades [1]. It is a technique of paramount value in understanding modern magnetic materials whose complex properties can involve an interplay of charge, orbital and spin degrees of freedom of the valence electrons [2, 3]. A theoretical framework for the interpretation of neutron diffraction data has also been in place for some time, starting essentially with Trammell's work [4]. Resonant Bragg diffraction of x-rays has come to the fore as a complementary technique in the past decade [5] with the growing availability of intense, polarized and tuneable beams of x-rays from synchrotron sources. The instrumentation now available at synchrotron sources provides accurate and detailed information on charge and magnetization distributions. As examples of recent applications of resonant x-ray diffraction revealing new features of complex magnetic materials we will consider one 3d-transition compound, V_2O_3 [6], and one lanthanide compound, DyB_2C_2 [7, 8].

We calculate the intensity of neutrons diffracted from crystals that support long-range magnetic order. Ions in a unit cell are not equivalent due to a lack of translational symmetry in their environments. The present work is based on atomic models which have proved to be good starting points for the interpretation of a wealth of data on 3d-transition and lanthanide compounds. A theory of neutron diffraction, with full account of scattering by spin and orbital magnetic moments, is developed from previous work [9, 10] and applied to powder and single crystal samples. In the case of single crystal samples, information to be found from the interference of nuclear and magnetic amplitudes enabled by polarization in the primary neutron beam is also considered. One aim in the development is to expose common structure in frameworks for the interpretation of neutron diffraction and resonant x-ray diffraction data. To this end, we predict neutron diffraction signals for V_2O_3 and DyB_2C_2 on the basis of successful interpretations of available resonant x-ray diffraction data [11, 12]. Advantages of the neutron beam technique over the x-ray beam technique are seen in quality and quantity of data. For, at present, resonant x-ray Bragg diffraction does not provide absolute values of atomic quantities, and the energy of the resonance limits the number of Bragg reflections observed. The limit on data set by the resonance

energy can be quite severe for electric dipole resonance events that give direct access to the valence shell of 3d-transition and lanthanide ions, i.e. $2p \rightarrow 3d$ and $3d \rightarrow 4f$, for which x-ray wavelengths are of the order 17\AA and 10\AA , respectively.

Vanadium sesquioxide exhibits a first-order, ferroelastic structural phase transition, at a temperature in the range $150 - 160\text{K}$, at which the material changes from a metal to an insulator and from a paramagnet to a collinear antiferromagnet. The long-range magnetic order coexists with a monoclinic crystal structure with space group $I2/a$ (number 15) in which vanadium ions occupy sites $8(f)$ that possess no symmetry. The energy dependence of resonant x-ray scattering from V_2O_3 [6] at space-group forbidden reflections (Miller indices $h k l$ satisfy $h + k + l$ an odd integer) is strikingly different at reflections with even and odd values of h , and this feature has been shown to be due to a selection rule [11] that stems from the configuration of the V moments. The same theory [11] accounts for data collected in azimuthal-angle scans at space-group forbidden reflections.

Dysprosium borocarbide, while not quite so exotic as V_2O_3 , is a very interesting metallic conductor with a tetragonal crystal structure. The material displays a continuous structural phase-transition at $T_Q = 24.7\text{K}$ [7], at which the crystal symmetry is lowered to space group 136 from space group 127, and a magnetic transition at $T_c = 15.3\text{K}$ [8, 13] below which there is a net moment in the plane normal to the two-fold axis of rotation that passes through sites $4(c)$ occupied by Dy ions. The lattice distortion at T_Q is accompanied by the appearance of Templeton & Templeton scattering at reflections $(00l + \frac{1}{2})$. Magnetic neutron diffraction signals from powder samples appear at T_c [13, 14]. At the same temperature a signal is seen in resonant x-ray diffraction at the reflection (102) [8]. The resonant x-ray diffraction data for DyB_2C_2 is consistent with structure factors [12] calculated for the space group 136 and the configuration of Dy magnetic moments proposed by Yamauchi et al. [13].

Expressions for the amplitude and intensity of magnetic neutron diffraction are recorded in the next section, where they are developed for the standard atomic model of a magnetic material. We include a new expression for the intensity which highlights contributions made to scattering by anisotropic components of the

magnetization. Properties of the amplitude set in principal axes are given in section 3. Neutron diffraction by V_2O_3 is the subject of section 4, where we give an expression for the intensity expected from a single crystal. Use of the expression for the interpretation of experimental data should yield valuable information that can be compared directly with findings from ab initio calculations and results derived from complementary experiments. To illustrate the information content of the neutron intensity we evaluate our expression for a model V wavefunction, and our findings suggest intensities at some equivalent reflections have the potential to yield good quality information about the orbital magnetization. We also estimate the intensity of reflections first seen in resonant x-ray diffraction [6]. Our findings for DyB_2C_2 in section 5, based on a successful interpretation resonant x-ray diffraction experiments [12], include an estimate of the wavefunction that describes the Dy magnetization. We predict intensities to be compared with data collected on single crystal samples. A brief discussion of our main results appears in section 6, and material on the atomic spherical tensors at the heart of our theoretical framework is gathered in an Appendix.

II. Basics

The interaction between a neutron with spin \mathbf{s}_n and electrons with position, spin and momentum variables \mathbf{R}_j , \mathbf{s}_j and \mathbf{p}_j , respectively, is $\mathbf{s}_n \cdot \mathbf{Q}_\perp$ where,

$$\mathbf{Q}_\perp = \sum_j \exp(i\mathbf{k} \cdot \mathbf{R}_j) \left\{ \hat{\mathbf{k}} \times (\mathbf{s}_j \times \hat{\mathbf{k}}) - \frac{i}{\hbar k^2} (\mathbf{k} \times \mathbf{p}_j) \right\}. \quad (2.1)$$

Here, \mathbf{k} is the change on scattering in the wavevector of the neutron and $\hat{\mathbf{k}} = \mathbf{k}/k$. In an atomic model of a magnetic material the sum on j over electrons is partitioned into a sum over electrons in the valence shell of an ion and a sum over all ions. The magnetic amplitude observed in Bragg diffraction is the mean value of \mathbf{Q}_\perp , denoted here by $\langle \mathbf{Q}_\perp \rangle$, evaluated for magnetic ions in the unit cell. It has been shown that the magnetic amplitude can be written as,

$$\langle Q_{\perp,p} \rangle = (4\pi)^{1/2} \sum_{KK'} \sum_{qq'} Y_q^K(\hat{\mathbf{k}}) \Psi_q^{K'}(K) (KqK'q' | 1p). \quad (2.2)$$

In this expression the Clebsch-Gordan coefficient couples two spherical tensors, of rank K and K' , to form a tensor of rank one (a vector) and projection $p = 0, \pm 1$. The coefficient is zero unless K is equal to $|K' - 1|$, K' or $K' + 1$, and $p = q + q'$. Evidently, the geometric content of the magnetic amplitude is contained in spherical harmonics $Y_q^K(\hat{\mathbf{k}})$. The quantity $\Psi_q^{K'}(K)$ is the unit-cell structure factor,

$$\Psi_q^{K'}(K) = \sum_{\mathbf{d}} \exp(i\mathbf{k} \cdot \mathbf{d}) \langle T_q^{K'}(K) \rangle_{\mathbf{d}}, \quad (2.3)$$

where $\langle T_q^{K'}(K) \rangle_{\mathbf{d}}$ describes the valence shell of the ion at position \mathbf{d} in the cell. With a small value of k the atomic tensor $\langle \mathbf{T}^1 \rangle$ is proportional to the magnetic moment $\boldsymbol{\mu} = \langle \mathbf{L} + 2\mathbf{S} \rangle$. Additional properties of atomic spherical-tensors for neutron diffraction are gathered in an Appendix.

The interpretation of resonant x-ray diffraction, based on an atomic model, contains a quantity very similar to (2.2) [15]. The amplitude in this instance is a scalar, i.e. a tensor of rank zero. Introducing the identity $(KqK'q' | 00) \propto \delta_{K,K'} \delta_{q,-q'}$ in (2.2) the quantity which in x-ray diffraction corresponds to (2.2) is actually a scalar product of a geometric factor with the structure factor, where the geometric factor contains information on the condition of the primary and diffracted x-ray beams.

Returning to neutron diffraction, we recount the limiting value taken by the magnetic amplitude as \mathbf{k} tends to the forward direction. With $k \rightarrow 0$ one finds $\langle \mathbf{T}^1 \rangle \rightarrow \boldsymbol{\mu}/3$ and for one ion,

$$\langle \mathbf{Q}_{\perp} \rangle \rightarrow \frac{1}{2} \{ \boldsymbol{\mu} - \hat{\mathbf{k}}(\hat{\mathbf{k}} \cdot \boldsymbol{\mu}) \}. \quad (2.4)$$

Retaining the first correction to these limiting values leads to the so-called dipole approximation for $\langle \mathbf{T}^1 \rangle$ in which,

$$\langle \mathbf{T}^1 \rangle \sim \frac{1}{3} \{ 2 \langle \mathbf{S} \rangle \langle j_0(k) \rangle + \langle \mathbf{L} \rangle (\langle j_0(k) \rangle + \langle j_2(k) \rangle) \}. \quad (2.5)$$

In this expression $\langle j_n(k) \rangle$ is the Bessel function transform of order n of the radial component of the magnetization distribution. The components have the properties $\langle j_0(0) \rangle = 1$ and for $n > 0$ $\langle j_0(0) \rangle = 0$. For the interpretation of data gathered with a view to examining spatial anisotropy in the magnetization distribution higher-order $K' > 1$ atomic tensors are considered. The upper limit is set by the angular momentum of the valence shell; for a 3d-transition ion the maximum value of K' in (2.2) is 5, and for a lanthanide ion the corresponding value is 7.

The intensity observed in a powder pattern is interpreted in terms of,

$$I_{\text{powder}} = \frac{1}{4\pi} \int d\hat{\mathbf{k}} |\langle \mathbf{Q}_\perp \rangle|^2 = \sum_{KK'} \sum_{q'} \left(\frac{3}{2K'+1} \right) |\Psi_{q'}^{K'}(K)|^2. \quad (2.6)$$

This expression can be simplified by using a general property of the atomic tensor. If K' is an odd integer, then $K = K' \pm 1$, and,

$$\langle T_{q'}^{K'}(K'+1) \rangle = \left(\frac{K'}{K'+1} \right)^{1/2} \langle T_{q'}^{K'}(K'-1) \rangle. \quad (2.7)$$

If K' is even the only non-zero tensor occurs when $K = K'$.

Physical properties of the sample can impose restrictions on K' and usually one finds that K' is restricted to odd integers. There are two sources of restrictions. First, a property of states used to describe the valence shell can impose restrictions on K' . For example, if a 4f shell is adequately described by states with the same values of J , S and L then K' is odd, for atomic tensors with even K' are zero. Secondly, the configuration of magnetic moments can lead to a selection rule on K' in the structure factor. Such a case is V_2O_3 , which is a collinear antiferromagnet, and $\Psi^{K'}$ vanishes unless K' is odd.

Experiments on single crystals are interpreted in terms of $|\langle \mathbf{Q}_\perp \rangle|^2$. When K' is odd the single-crystal intensity can be written in a simple and appealing form, which has the geometric content expressed in terms of spherical harmonics $Y_m^l(\hat{\mathbf{k}})$ instead of products of spherical harmonics. We find from (2.2),

$$I_{\text{crystal}} = \left| \langle \mathbf{Q}_\perp \rangle \right|^2 = (4\pi)^{1/2} \sum_{K'I'} \sum_{q'r'} \sum_{lm} Y_m^l(\hat{\mathbf{k}}) G(K', I'; l) \quad (2.8)$$

$$(-1)^{r'} \Psi_q^{K'}(K'-1) \{\Psi_{r'}^{I'}(I'-1)\}^* \begin{pmatrix} K' & I' & l \\ q' & r' & m \end{pmatrix}.$$

Values of $G(K', I'; l)$ are listed in Table I, and satisfy the sum rule,

$$\sum_l (2l+1)^{1/2} \begin{pmatrix} K' & I' & l \\ 0 & 0 & 0 \end{pmatrix} G(K', I'; l) = 0. \quad (2.9)$$

3j-symbols in (2.8) and (2.9) are more convenient to use than Clebsch-Gordan coefficients;

$$\begin{pmatrix} K & I & l \\ q & r & m \end{pmatrix} = (-1)^{K-I-m} (2l+1)^{-1/2} (KqIr | l-m). \quad (2.10)$$

The quantity summed in (2.9) is also included in Table I. To demonstrate that the expression for the single-crystal intensity is purely real one uses $G(K', I'; l) = G(I', K'; l)$ and $(Y_m^l)^* = (-1)^m Y_{-m}^l$ together with an identity for interchanging two columns of a 3j symbol. The term in (2.8) with $l = m = 0$ is identical to the powder intensity derived from (2.6), because integration over the direction of \mathbf{k} sets equal to zero every term in (2.8) except the term $l = m = 0$. Terms in (2.8) with $l > 0$ represent the influence on scattering of anisotropy in the magnetization distribution.

A useful approximation to the intensity is obtained from the term in (2.8) with $K' = I' = 1$. The corresponding value of the structure factor $\Psi_{q'}^1(0)$ is a spherical

component of a vector Ψ^1 with real Cartesian components. Setting $K' = I' = 1$ in (2.8) it reduces to,

$$I_{\text{crystal}} = \frac{9}{4} \{ \Psi^1 \cdot \Psi^1 - (\hat{\mathbf{k}} \cdot \Psi^1)^2 \}. \quad (2.11)$$

The dipole approximation for the intensity is obtained from (2.11) on using in $\Psi_q^1(0)$ the appropriate approximation for the atomic tensor.

To interpret the interference between magnetic and nuclear amplitudes induced by polarization \mathbf{P} in the primary beam one needs to evaluate,

$$\mathbf{P} \cdot \langle \mathbf{Q}_\perp \rangle = \sum_{q=0, \pm 1} (-1)^q P_{-q} \langle Q_{\perp, q} \rangle. \quad (2.12)$$

The identity expresses the scalar product of \mathbf{P} and $\langle \mathbf{Q}_\perp \rangle$ in terms of their spherical components. Cartesian components of \mathbf{P} , say, are,

$$P_x = (P_{-1} - P_{+1})/\sqrt{2}, P_y = i(P_{-1} + P_{+1})/\sqrt{2}, \text{ and } P_z = P_0. \quad (2.13)$$

III Principal axes

In many cases the physical properties of an ion in a crystal are most conveniently addressed in a set of axes that are not the crystal axes, nor the axes used to define the geometry of the experiment. Let us label the second set of axes by Cartesian coordinates $(\xi\eta\zeta)$. We use Euler angles α , β and γ to define the second set of axes, used for calculations of atomic quantities, relative to the chosen crystal axes and find,

$$\langle T_q^K \rangle = \sum_r \langle T_r^K \rangle_{(\xi\eta\zeta)} D_{rq}^K(-\gamma, -\beta, -\alpha), \quad (3.1)$$

where D_{rq}^K is an element of the rotation matrix.

We will label $(\xi\eta\zeta)$ principal axes when atomic tensors $\langle T_r^K \rangle_{(\xi\eta\zeta)}$ for the model in question are zero unless $r = 0$. Alternatively, in principal axes atomic tensors are said to be diagonal, and the ζ - axis is called the axis of quantization.

It can be shown that the magnetic amplitude is zero if \mathbf{k} is parallel to the axis of quantization, i.e. for \mathbf{k} and ζ parallel $\langle \mathbf{Q}_\perp \rangle = 0$. This finding is a generalization of the standard result which says the intensity is zero when \mathbf{k} and the moment direction are parallel.

A second result of this nature is found in the value of $\mathbf{P} \cdot \langle \mathbf{Q}_\perp \rangle$ when \mathbf{P} and ζ are parallel. We find,

$$\hat{\zeta} \cdot \langle \mathbf{Q}_\perp \rangle = \sum_{K'} \left(\frac{3K'}{2K'+1} \right)^{1/2} \{ \Psi_0^{K'}(K'-1) \}_{(\xi\eta\zeta)} [P_{K'-1}(k_\zeta) - P_{K'+1}(k_\zeta)], \quad (3.2)$$

where K' is odd, and $k_\zeta = \hat{\mathbf{k}} \cdot \hat{\zeta}$ is the projection of the scattering wavevector on the axis of quantization. In arriving at (3.2) the term with $K = K'$ is found to vanish, and the two terms $K = K' \pm 1$ combine with the aid of (2.7) to give the very simple expression we report. The Legendre polynomial $P_n(x)$ satisfies $P_0(x) = 1$ and $P_n(1) = 1$. From the second property we see that scattering is zero should \mathbf{k} and ζ coincide, a result we anticipated. For $K' = 1$ and 3,

$$1 - P_2(x) = \frac{3}{2}(1 - x^2), \text{ and } P_2(x) - P_4(x) = \frac{7}{8}(1 - x^2)(5x^2 - 1). \quad (3.3)$$

IV. Vanadium sesquioxide

At room temperature vanadium sesquioxide has a trigonal (corundum) structure with space group 167 ($R\bar{3}c$). Lowering the temperature of the material induces distortions which include tilting of the trigonal (hexagonal- c) axis and reduction of the point-group symmetry of sites occupied by vanadium ions [16].

The space group of the low temperature monoclinic structure is number 15($I2/a$). This is a body-centred cell and Bragg wavevectors $\tau_m(hkl)$ for charge reflections have the necessary condition $h + k + l$ an even integer. (Miller indices h , k and l are integers.) The antiferromagnetic configuration of vanadium magnetic moments, displayed in Fig. 1, consists of sheets of moments with ferromagnetic alignment within $(010)_m$ layers, or hexagonal (110) layers, and moment reversal between adjacent layers [17]. The moments are orientated along some easy-axis in these layers, and we take ϕ as the canting angle with respect to the trigonal axis.

The trigonal basis vectors are $\mathbf{a}_h = a(1, 0, 0)$, $\mathbf{b}_h = a(-1/2, 1/2 \sqrt{3}, 0)$ and $\mathbf{c}_h = c(0, 0, 1)$ and the volume of the unit cell $= a^2 c \sqrt{3} / 2$. Following Dernier and Marezio [16] in the use of an I - centred cell, from these vectors we generate monoclinic basis vectors $\mathbf{a}_m = (0, \frac{1}{\sqrt{3}} 2 a, 1/3c)$, $\mathbf{b}_m = \mathbf{a}_h$ and $\mathbf{c}_m = (0, \frac{1}{\sqrt{3}} a, -1/3 c)$, and the volume of the cell $= a^2 c / \sqrt{3}$. The corresponding Bragg wavevector $\tau_m(hkl) \equiv (hkl)_m$ is,

$$\boldsymbol{\tau}_m(hkl) = \frac{1}{a} (k, \frac{1}{\sqrt{3}}(h+l), \frac{a}{c}(h-2l)). \quad (4.1)$$

We note that $(10\bar{1})_m$ is parallel to \mathbf{c}_h and $(2lkl)_m$ is normal to \mathbf{c}_h .

Referring to Fig. 1, the position coordinates of vanadium ions labelled (1) and (5) are (x, y, z) and $(-x, -y, -z)$, respectively, with $x = 0.3439$, $y = 0.0012$ and $z = 0.2993$ [16]. The positions of the pair (2) and (6) are related by a body-centre translation to the pair (1) and (5). The position coordinates of (3) and (7) are $(1/2 -x, y, -z)$ and $(1/2 +x, -y, z)$, respectively, and the pairs (4) and (8), and (3) and (7) are related by the body-centre translation. The body-centre translation $(1/2, 1/2, 1/2)_m = \frac{a}{2} (1, \sqrt{3}, 0)$ and $(1/2, 1/2, 1/2)_m \cdot \boldsymbol{\tau}_m(hkl) = 1/2 (h + k + l)$. It is convenient to define an angle $\nu = 2\pi (x, y, z)_m \cdot \boldsymbol{\tau}_m(hkl) = 2\pi (xh + yk + zl)$.

For the model of V_2O_3 we have described, in the previous paragraphs, $\Psi^{K'}$ can be different from zero for even values of $K' + (h + k + l)$, so there is a selection rule in the structure factor that links the rank of atomic tensors and the sum of Miller indices

[11]. Neutron magnetic diffraction is observed at reflections with $h + k + l$ an odd integer, i.e. space-group forbidden reflections, and the scattering amplitude is composed of tensors of rank $K' = 1, 3$ and 5 . One finds,

$$\Psi_{q'}^{K'}(K) = 4 \cos(\nu) \left\{ \langle T_{q'}^{K'}(K) \rangle + (-1)^h \langle T_{-q'}^{K'}(K) \rangle \right\}. \quad (4.2)$$

Moon [17] studied reflections with even h and established the configuration of moments illustrated in Fig. 1, in which \mathbf{V} moments are contained in the plane normal to \mathbf{b}_m and cant at angle $\phi \sim 70^\circ$ with respect to \mathbf{c}_h . Intensity observed with odd h using resonant x-ray diffraction [6] has been successfully interpreted using (4.2) [11]. Note that for odd h we have $\Psi_{q'}^{K'} = -\Psi_{-q'}^{K'}$ and there is no contribution to scattering from diagonal elements of the atomic tensor. Scattering observed at space-group forbidden reflections with odd h is the magnetic analogue of Templeton & Templeton x-ray scattering [18] by anisotropic charge distributions.

A. Magnetic reflections with even h

The atomic tensor in (4.2) is obtained from principal axes $(\xi\eta\zeta)$ using (3.1). It is assumed that the axis of quantization is contained in the plane $\mathbf{a}_m - \mathbf{c}_m$ and it encloses an angle ϕ with the trigonal axis. One finds,

$$\langle T_{q'}^{K'}(K) \rangle = \langle T_0^{K'}(K) \rangle_{(\xi\eta\zeta)} D_{q'0}^{K'}(-\frac{\pi}{2}, \phi, 0), \quad (4.3)$$

and the corresponding value of the structure factor is,

$$\Psi_{q'}^{K'}(K) = 8 \cos(\nu) \langle T_0^{K'}(K) \rangle_{(\xi\eta\zeta)} D_{q'0}^{K'}(-\frac{\pi}{2}, \phi, 0). \quad (4.4)$$

The last result follows because, according to (4.3), $\langle T_{q'}^{K'} \rangle = \langle T_{-q'}^{K'} \rangle$. (In consequence, for odd h the result (4.3) predicts null scattering.)

Using (4.4) in (2.8) we arrive at,

$$I_{\text{crystal}} = \{8 \cos(\nu)\}^2 \sum_{K'} \sum_l (2l+1)^{1/2} G(K', I'; l) P_l(\tau_\zeta) \langle T_0^{K'}(K'-1) \rangle_{(\xi\eta\zeta)} \quad (4.5)$$

$$\langle T_0^{I'}(I'-1) \rangle_{(\xi\eta\zeta)} \begin{pmatrix} K' & I' & l \\ 0 & 0 & 0 \end{pmatrix}.$$

On writing $\hat{\mathbf{r}}_m(h \ k \ l) = (t_1, t_2, t_3)$ one has $\tau_\zeta = t_2 \sin\phi + t_3 \cos\phi$. If $\hat{\mathbf{r}}_m$ and ζ are parallel $\tau_\zeta = 1$ and the intensity is zero by virtue of the sum rule (2.9) which is satisfied by $G(K', I'; l)$. On retaining in (4.5) the term $K' = I' = 1$, and neglecting all other terms in the sums on K' and I' , remaining terms $l = 0$ and $l = 2$ collapse to give,

$$I_{\text{crystal}} = \frac{9}{4} \{8 \cos(\nu)\}^2 (1 - \tau_\zeta^2) \langle T_0^1(0) \rangle_{(\xi\eta\zeta)}^2. \quad (4.6)$$

In arriving at this expression we use entries in Table I and for the Legendre polynomials the first entry in (3.3). The result (4.6) is consistent with the more general expression found in (2.11).

The intensity (4.5) contains the canting angle ϕ and three atomic tensors. These four unknown quantities can be inferred by fitting experimental data for intensities to (4.5). Values of the atomic tensors derived from a model of the V ion's wavefunction can then be tested against measured values.

We have calculated (4.5) using for $\langle T_0^{K'}(K'-1) \rangle_{(\xi\eta\zeta)}$ expressions derived from a model V wavefunction based on $3d^2$ and the configuration 3F , namely,

$$|G\rangle = |S=1, M_s=1\rangle \left\{ \epsilon |L=3, M_L=-3\rangle + (1-\epsilon^2)^{1/2} |L=3, M_L=1\rangle \right\}. \quad (4.7)$$

The value $\varepsilon = 0.671$ gives $\langle L_\zeta \rangle = -0.8$ and a V magnetic moment $\mu = 1.2\mu_B$ in agreement with the finding of Moon [17]. In the expression for $\langle T_0^{K'}(K'-1) \rangle_{(\xi\mu\zeta)}$ there are no contributions from cross-terms and one finds,

$$\begin{aligned} \langle T_0^{K'}(K'-1) \rangle_{(\xi\mu\zeta)} &= \varepsilon^2 \langle SM_s = 1LM_L = -3 | T_0^{K'}(K'-1) | SM_s = 1LM_L = -3 \rangle \\ &+ (1 - \varepsilon^2) \langle SM_s = 1LM_L = 1 | T_0^{K'}(K'-1) | SM_s = 1LM_L = 1 \rangle. \end{aligned} \quad (4.8)$$

Expressions for the two matrix elements, obtained by use of (A8), are listed in Table II. In our numerical estimates we use $\langle j_n(k) \rangle$ for V^{3+} from [19].

Regarding $\langle T_0^1(0) \rangle_{(\xi\eta\zeta)}$ that appears in the approximation (4.6) to I_{crystal} our model wavefunction gives,

$$\langle T_0^1(0) \rangle_{(\xi\eta\zeta)} = \frac{1}{3} \langle j_0(k) \rangle (3 - 4\varepsilon^2) + \frac{2}{105} \langle j_2(k) \rangle (19 - 74\varepsilon^2). \quad (4.9)$$

As anticipated in (2.5), the coefficient of $\langle j_0 \rangle / 3$ is the magnetic moment μ of the V ion.

A confrontation of experimental data for magnetic Bragg intensities with I_{crystal} listed in the second ($\varepsilon^2 = 0.45, \langle L_\zeta \rangle = -0.8$) and third ($\varepsilon^2 = 0.25, \langle L_\zeta \rangle = 0$) columns of Table III will help find the exact nature of the magnetization and settle the contribution to it made by the orbital moment. The value of the canting angle $\phi = 70^\circ$ is consistent with the interpretation of neutron and resonant x-ray diffraction data [11, 17].

Equivalent reflections, identified by a common value of $|\tau_m|$, are particularly valuable because uncertainty in the interpretation arising from uncertainty in $\langle j_n(k) \rangle$ is eliminated. One factor in the variation of I_{crystal} within a group of equivalent reflections is the value of the spatial phase ν , e.g. the difference in I_{crystal} between

$(210)_m$ & $(2\bar{1}0)_m$ is the difference in $\{\cos(v)\}^2$ at the two reflections. To a good approximation, $(210)_m$ & $(2\bar{1}0)_m$ and $(201)_m$ are a group of equivalent reflections and the difference in I_{crystal} at the partners $(210)_m$ & $(2\bar{1}0)_m$, and $(201)_m$ is striking and it is largely due to pronounced anisotropy in the magnetization. Two other groups of equivalent reflections that are very sensitive to anisotropy are $(003)_m$ & $(40\bar{1})_m$, and $(023)_m$ & $(02\bar{3})_m$, $(42\bar{1})_m$ & $(4\bar{2}\bar{1})_m$. These two groups of reflections are sensitive to the orbital magnetization, which is seen in the variation of the ratio in column five between I_{crystal} for $\langle L_\zeta \rangle = -0.8$ and $\langle L_\zeta \rangle = 0$. In this respect, we note that the last six reflections in Table III have intensity due to the orbital magnetization and so they appear to be particularly good sources of information.

B. Magnetic reflections with odd h

We have estimated the neutron scattering intensity at magnetic reflections with h odd by using atomic tensors inferred from a successful interpretation of resonant x-ray diffraction on magnetically ordered V_2O_3 . The intensity of scattering from a single crystal is derived from (2.8). For the reflections of interest here the nuclear structure factor is zero, and thus polarization in the primary beam of neutrons does not lead to mixed magnetic and nuclear reflections. Because the V magnetic moment is contained in the plane spanned by \mathbf{a}_m and \mathbf{c}_m $\Psi_{\pm 1}^1 = 0$. Our estimate of I_{crystal} is made with tensors of rank $K' = 3$ and the terms proportional to $\langle j_2(k) \rangle$. Terms we neglect are proportional to $\langle j_4(k) \rangle$, cf. Table II, which for $k \sim 0.6\text{\AA}^{-1}$ is very small compared to $\langle j_2(k) \rangle$ that we retain.

By way of orientation, first we consider the intensity (2.6) observed in a powder pattern. Setting $K' = 3$ and using (2.7),

$$I_{\text{powder}} = \frac{3}{4} \sum_{q'} \left| \Psi_{q'}^3(2) \right|^2 .$$

In the sum q' takes all values consistent with the rank $K' = 3$ of the tensor, but for odd h $\Psi_0^{K'} = 0$. Since the V ion occupies a site with no symmetry, site-symmetry plays no part in selecting values of the projection label q' on atomic tensors.

In (4.2) we set h odd and use $\langle T_{-q'}^{K'} \rangle = (-1)^{q'} \langle T_{q'}^{K'} \rangle^*$ and find,

$$\Psi_{+1}^3(2) = 8 \cos(\nu) \langle T_{+1}^3(2) \rangle',$$

$$\Psi_{+2}^3(2) = i 8 \cos(\nu) \langle T_{+2}^3(2) \rangle'',$$

$$\Psi_{+3}^3(2) = 8 \cos(\nu) \langle T_{+3}^3(2) \rangle'.$$

Values of the atomic tensors inferred from an interpretation of resonant x-ray diffraction data on V_2O_3 [6, 20] are listed in Table IV. Our knowledge of $\langle T_{+2}^3 \rangle''$ is not as good as that for $\langle T_{+1}^3 \rangle'$ and $\langle T_{+3}^3 \rangle'$. From entries in Table IV we find,

$$I_{\text{powder}} = 96 \cos^2(\nu) \left\{ \langle T_{+1}^3(2) \rangle'^2 + \langle T_{+2}^3(2) \rangle''^2 + \langle T_{+3}^3(2) \rangle'^2 \right\} \sim 0.31 \left\{ \langle j_2(k) \rangle \cos(\nu) \right\}^2.$$

Let us consider the reflection $(340)_m$ for which $\tau(340)_m = 0.90 \text{ \AA}^{-1}$, and $\cos(\nu) = 0.98$. Using [18] $\langle j_2(\tau) \rangle = 0.20$ we obtain for $(340)_m$ the estimate $I_{\text{powder}} \sim 0.011$. Table V contains estimates of intensities for single crystals derived from (2.8). Reflections $(122)_m$ and $(320)_m$ possess the same value of τ_m , as is evident by inspection of (4.1).

Spatial anisotropy in the intensities is highlighted in projections of $\langle \mathbf{Q}_\perp \rangle$. Accordingly, Table V contains some values of $\mathbf{m} \cdot \langle \mathbf{Q}_\perp \rangle$ for \mathbf{m} parallel to the trigonal axis \mathbf{c}_h and \mathbf{m} normal to the plane $\mathbf{a}_m - \mathbf{c}_m$ that contains the V magnetic moments. The amplitude $\hat{\mathbf{c}}_h \cdot \langle \mathbf{Q}_\perp \rangle$ is proportional to t_1 and vanishes for reflections $(h0l)$. In detail,

$$\begin{aligned}
\hat{\mathbf{c}}_h \cdot \langle \mathbf{Q}_\perp \rangle &= \sqrt{21} t_1 \cos(\nu) \left\{ \langle T_{+1}^3 \rangle' t_3 (15t_3^2 - 11) + 2\sqrt{10} \langle T_{+2}^3 \rangle'' t_2 (1 - 3t_3^2) \right. \\
&\quad \left. + \sqrt{15} \langle T_{+3}^3 \rangle' t_3 (t_1^2 - 3t_2^2) \right\}.
\end{aligned} \tag{4.9}$$

Expressions for other projections are even more complicated and we refrain from giving them.

V. Dysprosium borocarbide

Fig. 2 illustrates the sites and the configuration of Dy moments in the magnetic unit cell. According to findings for powder samples reported by Yamauchi et al. [13], two neighbouring Dy moments along the c -axis are mutually perpendicular and two neighbouring moments in the plane normal to the c -axis one almost oppositely aligned. This configuration of Dy moments and the space group 136 has led to a successful interpretation of resonant x-ray diffraction data [12]. Here we adopt the same information in calculations of intensities in magnetic neutron diffraction.

Calculated structure factors do not contain a selection rule on the rank of atomic tensors K' that require K' to be an odd integer, and even K' is allowed. However, tensors with even K' are zero if states describing the valence shell have the same values of the atomic quantum numbers J , S and L . Such is the case when valence states are drawn from one J – manifold and therefore in our interpretation there are no contributions to magnetic neutron scattering from atomic tensors with even K' .

The structure factor for Dy ions can be different from zero for even $K' + q'$, so in $\Psi_q^{K'}(K)$ we have odd K' and odd q' , and $q' = 0$ is not allowed [12]. It transpires that intensities are accurately described by the rank-one tensor Ψ_q^1 , $q' = \pm 1$, and we begin with our results for I_{crystal} derived from (2.8). Later we give the case for believing that $\Psi_q^{K'}$ with $K' > 1$ are safely neglected.

We introduce an atomic form factor,

$$F(k) = \{\langle j_0(k) \rangle + \frac{8}{15} \langle j_2(k) \rangle\}^2, \quad (5.1)$$

with the property $F(0) = 1$. Notice that the dipole approximation (2.5) has $\frac{1}{2}$ as the coefficient of $\langle j_2(k) \rangle$, whereas (5.1) is derived from the complete expression for the contribution of rank one and the coefficient $8/15$ is expected to be more accurate. For space-group allowed reflections (hkl : $h + k = 2n$) we find, following calculations reported in [12],

$$I_{\text{crystal}} = \mu_0^2 (\cos \phi - \sin \phi)^2 F(k) (1 - \hat{k}_a^2). \quad (5.2)$$

In this instance, the intensity is due to the net moment $\mu_0(\cos \phi - \sin \phi)$ that is aligned with the crystal a-axis and \hat{k}_a is the projection of $\hat{\mathbf{k}}$ on this axis. At space-group forbidden reflections ($00l + \frac{1}{2}$), and ($h0l$) with odd h , equivalent to ($0kl$) with odd k , we find,

$$I_{\text{crystal}}(00l + 1/2) = \mu_0^2 (\cos \phi - \sin \phi)^2 F(k) (1 - \hat{k}_b^2), \quad (5.3)$$

and,

$$I_{\text{crystal}}(h0l) = \mu_0^2 (\cos \phi + \sin \phi)^2 F(k) (1 - \hat{k}_b^2). \quad (5.4)$$

For two of the three classes of reflections $\hat{k}_b = 0$. Since $\phi \sim 30^\circ$ ($h0l$) with odd h index strong reflections in the magnetic neutron diffraction pattern. The intensity of reflections ($h0l + \frac{1}{2}$) with odd h , equivalent to ($0kl + \frac{1}{2}$) with odd k , is derived from (5.4) by putting \hat{k}_a in place of \hat{k}_b . In resonant x-ray diffraction reflections ($00l + \frac{1}{2}$) are mixed magnetic and charge [12, 21] and ($h0l$) with odd h are purely magnetic [8, 12].

By constructing a wavefunction for a Dy ion in magnetically ordered DyB₂C₂ we can assess the magnitude of tensors with $K' > 1$ relative to $K' = 1$ used to derive (5.2) – (5.4). In addition, we can more closely relate magnetic neutron and resonant x-ray diffraction.

A crystal-field potential for $J = 15/2$ and symmetry $2/m$ contains 8 distinct energy levels, each one spanned by a Kramers doublet. (The same is true for $4/m$ which is the site symmetry of a Dy ion in space group 127. Hence, both above and below the structural phase transition at $T_Q = 24.7\text{K}$ the action of the crystal-field potential lifts the 8-fold degeneracy, barring an accidental degeneracy.) Let us assume a separation of the first excited state from the ground state $>T_c = 15.3\text{K}$ so we can realistically describe a Dy ion by one Kramers doublet. We denote the two states in the doublet, that account for low temperature properties, by $|\psi\rangle$ and $|\bar{\psi}\rangle$ where $|\bar{\psi}\rangle$ is derived from $|\psi\rangle$ by application of the operator for time reversal. The degeneracy of the doublet is lifted by the onset of long-range magnetic order and the two energy levels are spanned by $|G\rangle$ and $|\bar{G}\rangle$ where,

$$|G\rangle = \frac{1}{\sqrt{2}}\{e^{i\delta}|\psi\rangle + |\bar{\psi}\rangle\}, \quad (5.5)$$

$$|\bar{G}\rangle = \frac{1}{\sqrt{2}}\{e^{-i\delta}|\bar{\psi}\rangle - |\psi\rangle\}, \quad (5.6)$$

and δ is the mixing angle. In the scenario we describe, magnetic properties of a Dy ion are mapped to a pseudo-spin $1/2$ with eigenstates $|G\rangle$ and $|\bar{G}\rangle$. For time-odd operators, like angular momentum J_α , time-reversed states have the property $\langle \psi|J_\alpha|\psi\rangle = -\langle \bar{\psi}|J_\alpha|\bar{\psi}\rangle$. Moreover, an ion with an odd number of electrons and half-integer J has the property $\langle \psi|J_z|\bar{\psi}\rangle = 0$ because $|\psi\rangle$ and $|\bar{\psi}\rangle$ have no states in common. The two properties lead to the result $\langle G|J_z|G\rangle = 0$, and the z-axis is parallel to the crystal c-axis and the axis of two-fold rotation symmetry. Mean values of J_x and J_y can be different from zero if $|\psi\rangle$ contains $|M = 1/2\rangle$, or $|M = -1/2\rangle$. From (5.5) it follows that,

$$\langle \mathbf{G} | J_\alpha | \mathbf{G} \rangle = \text{Re} \{ e^{-i\delta} \langle \Psi | J_\alpha | \bar{\Psi} \rangle \}. \quad (5.7)$$

Another feature required of $|\Psi\rangle$ is that it is a linear combination of states with M values that differ by ± 2 , on account of the site symmetry $2/m$. Looking at candidates for $|\Psi\rangle$ with minimal parameters one is led to consider linear combination of $|5/2\rangle$ and $|1/2\rangle$, or $|1/2\rangle$ and $|-3/2\rangle$. We find that,

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \{ |1/2\rangle + i|-3/2\rangle \}, \quad (5.8)$$

with,

$$|\bar{\Psi}\rangle = \frac{1}{\sqrt{2}} \{ |-1/2\rangle - i|3/2\rangle \}, \quad (5.9)$$

provides a realistic description of the magnetic properties of a Dy ion in DyB₂C₂. The 90° phase difference between the two components is required to satisfy the observation in resonant x-ray diffraction of Templeton & Templeton scattering at $(00l + 1/2)$.

Next, we examine the saturation moment predicted by (5.8) and (5.9). From $\mu = g\langle \mathbf{J} \rangle = (4/3) \langle \mathbf{J} \rangle$ we find,

$$\mu_0 = \frac{4}{3} \{ \langle \mathbf{G} | J_x | \mathbf{G} \rangle^2 + \langle \mathbf{G} | J_y | \mathbf{G} \rangle^2 \}^{1/2}, \quad (5.10)$$

with mean values obtained from (5.7). The dependence of μ_0 on the canting angle ϕ is derived from,

$$\tan \phi = \langle \mathbf{G} | J_y | \mathbf{G} \rangle / \langle \mathbf{G} | J_x | \mathbf{G} \rangle. \quad (5.11)$$

The maximum value $\mu_0 = 8.59$ is achieved with $\phi = 45^\circ$, which corresponds to a vanishing unit-cell magnetic moment. There is no consensus on actual values of ϕ and μ_0 determined by powder neutron diffraction [13, 14]. (Neutron diffraction data has been interpreted on the basis of space group number 127, which is not consistent with x-ray diffraction data and the model used here based on space-group number 136.) In the subsequent discussion we use $\phi = 34^\circ$ and the value $\mu_0 = 6.99$ which is derived from (5.8) – (5.11). These values of the canting angle and saturation moment are in line with values derived from the analysis of neutron diffraction data [13].

Let us review general properties of atomic quantities that enter the interpretation of diffraction data. First, atomic tensors of even-rank are purely imaginary and account for Templeton & Templeton scattering observed in x-ray diffraction at reflections indexed by $(00l + \frac{1}{2})$. Structure factors for space-group forbidden reflections vanish with $q' = 0$ whereas structure factors for space-group allowed reflections and $q' = 0$ are different from zero. We find [12] for $(00l + \frac{1}{2})$,

$$\Psi_{q'}^{K'}(K) = \{1 - e^{iq'\pi/2}\} \{ \langle T_{q'}^{K'}(K) \rangle + e^{iq'\pi/2} \langle T_{-q'}^{K'}(K) \rangle \}, \quad (5.12)$$

and for $(h0l)$ with odd h ,

$$\Psi_{q'}^{K'}(K) = \{1 + e^{iq'\pi/2}\} \{ \langle T_{q'}^{K'}(K) \rangle - e^{iq'\pi/2} \langle T_{-q'}^{K'}(K) \rangle \}. \quad (5.13)$$

Evaluated for $K = K' - 1$ and $K' = 1$, without approximation, these expressions are,

$$\Psi_{\pm 1}^1(0) = -\frac{i8\sqrt{2}}{9} \left(\frac{3}{4} \sqrt{7} \mp 1 \right) (\cos \delta \pm \sin \delta) \{ \langle j_0(k) \rangle + \frac{8}{15} \langle j_2(k) \rangle \}, \quad (5.14)$$

where the upper (lower) choice of signs are for reflections indexed by $(00l + \frac{1}{2})$ (reflections $(h0l)$ with odd h), and $\Psi_{-1}^1(0) = \Psi_{+1}^1(0)$. Using (5.14) in (2.11) we recover (5.3) and (5.4) when $\phi = 34^\circ$, $\mu_0 = 6.99$ and $\delta = 75.52^\circ$ which is obtained from (5.11). At space-group allowed reflections $\Psi_{q'}^1(0)$ is purely real and the two components allowed by the chemical structure and configuration of moments $\Psi_{\pm 1}^1(0)$

satisfy $\Psi_{+1}^1(0) = -\Psi_{-1}^1(0)$; in fact, $\Psi_{+1}^1(0)$ is equal to the imaginary part of (5.14) evaluated with the upper choice of signs.

In general, the atomic tensor $\langle T_{q'}^{K'}(K) \rangle$ is a linear combination of $\langle j_{K'-1}(k) \rangle$ and $\langle j_{K'+1}(k) \rangle$. For $K' > 1$ and our model Dy wavefunction we find coefficients of $\langle j_n(k) \rangle$ in $\langle T_{q'}^{K'}(K) \rangle$ that are very small compared to coefficients of $\langle j_0(k) \rangle$ and $\langle j_2(k) \rangle$ in $\langle T_{q'}^1(0) \rangle$. In consequence, (5.14) for $\Psi_{q'}^1(0)$ is very accurate. In part this result is due to the fact that we deal with an f^9 ion, and the orbital contribution to the tensor of rank three is identically zero. (The same result holds for f^2 , f^5 and f^{12} [10].) We find the coefficient of $\langle j_2 \rangle^2$ in $\Psi_{q'}^3(2)$ has values 0.0050 and 0.0022 for the reflections $(00l + \frac{1}{2})$ and $(h0l)$, respectively, that amount to corrections to $(8/15)^2$ in $F(k)$ of less than 2%. Coefficients of $\langle j_2 \rangle \langle j_4 \rangle$ and $\langle j_4 \rangle^2$ are 0.0036 and 0.0006, respectively, and these terms can be safely neglected compared to the ones appearing in $F(k)$.

Unlike the diffraction pattern of V_2O_3 , discussed in the previous section, the pattern of DyB_2C_2 contains (space-group allowed) reflections with overlapping magnetic and nuclear contributions. At these space-group allowed reflections, polarization \mathbf{P} in the primary beam of neutrons creates mixed magnetic and nuclear intensities. \mathbf{P} is taken to be parallel to the net magnetic moment. The magnetic amplitude in a mixed reflection is proportional to $\hat{\mathbf{a}} \cdot \langle \mathbf{Q}_\perp \rangle$ for which we find the result,

$$\hat{\mathbf{a}} \cdot \langle \mathbf{Q}_\perp \rangle = \mu_0 (\cos \phi - \sin \phi) \{F(k)\}^{1/2} (1 - \hat{k}_a^2). \quad (5.15)$$

VI. Discussion

In the context of an atomic model of a material, we have developed and applied a theoretical framework for magnetic neutron diffraction. The framework has the same formal structure as one used recently for the successful interpretation of resonant x-ray Bragg diffraction by magnetic crystals. A formal structure in the interpretation of diffraction data that is common to neutron and resonant x-ray techniques facilitates the comparison of results. By way of illustrating this advantage, we predict results for magnetic neutron diffraction by V_2O_3 on the basis of results from resonant x-ray diffraction by the material that reveal reflections not yet observed with the neutron technique. In a second example, we calculate intensities for magnetic neutron diffraction by DyB_2C_2 on the basis of results derived from resonant x-ray diffraction data.

A new expression we give for the intensity of neutrons magnetically diffracted by a single crystal is well suited to the identification of features due to spatial anisotropy in the distribution of magnetization. In this expression, the leading term is the intensity expected from a powder sample. Other general results include properties of the amplitude for magnetic diffraction when set in principal axes, where atomic spherical tensors describing the valence shell are diagonal. The atomic tensors have been expressed in terms of unit tensors that are widely used in atomic physics. The literature on the interpretation of x-ray dichroic signals and resonant diffraction already contains extensive tabulations of the unit tensors evaluated for 3d transition and lanthanide ions, and the results complement tabulations of closely related quantities that have been used in the interpretation of magnetic neutron diffraction signals.

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Appendix

The purpose of the appendix is to record key expressions for the atomic tensor and to relate work to previous findings. The reduced matrix element in the Wigner-Eckart theorem,

$$\langle JM | T_{q'}^{K'}(K) | J'M' \rangle = (-1)^{J-M} \begin{pmatrix} J & K' & J' \\ -M & q' & M' \end{pmatrix} (SLJ \| T^{K'}(K) \| S'L'J'), \quad (\text{A1})$$

is simply related to quantities $A(K, K')$ and $B(K, K')$ used previously [9, 10] in the spin and orbital matrix elements of $T^{K'}$, namely,

$$(SLJ \| T^{K'}(K) \| S'L'J') = (-1)^{K'+J'-J} (2J+1)^{1/2} \{A(K, K') + B(K, K')\}. \quad (\text{A2})$$

We will not review properties of $A(K, K')$ and $B(K, K')$ but refer the reader to references [9, 10] for this information. Tables of $A(K, K')$ and $B(K, K')$ for various ions are found in [10].

Let us, however, express the spin and orbital contributions to the reduced matrix element in terms of a standard reduced matrix element in atomic physics $W^{(ab)K'}$ used also in the interpretation of resonant x-ray diffraction. In $W^{(ab)K'}$ the integer a is the rank of its spin contribution, and b is the rank of its orbital contribution. Tables of $W^{(ab)K'}$, and $W^{(ab)}$ used in (A8), are found in [14].

Writing,

$$(SLJ \| T^{K'}(K) \| S'L'J') = Z_{\text{spin}}^{K'}(K) + Z_{\text{orb}}^{K'}(K), \quad (\text{A3})$$

we find,

$$Z_{\text{orb}}^{K'}(K'-1) = (-1)^{K'} i^{K'+1} \delta_{S,S'} \left\{ \langle j_{K'-1}(k) \rangle + \langle j_{K'+1}(k) \rangle \right\} \quad (\text{A4})$$

$$\left[\frac{2}{3}(K'+1) \right]^{1/2} (2l+1)^2 A(K', K', l) W^{(0K')K'} ,$$

where K' is an odd integer, l is the angular momentum of the valence shell ($l = 2$ and 3 , respectively, for 3d and lanthanide ions) and $A(K', K', l)$ is given in [9, 10]. $Z_{\text{orb}}^{K'}(K' \pm 1)$ satisfies (2.7) and $Z_{\text{orb}}^{K'}(K')$ is zero. The spin contribution in (A3) is slightly more complicated. Let us use,

$$D(K, K') = (-1)^l \langle j_K(k) \rangle (2l+1) \begin{pmatrix} l & K & l \\ 0 & 0 & 0 \end{pmatrix} \left[\frac{3}{2}(2K+1) \right]^{1/2} W^{(1K)K'} . \quad (\text{A5})$$

If K' is even, the only non-zero value of $B(K, K')$ occurs when $K = K'$, in which case

$$Z_{\text{spin}}^{K'}(K') = i^{K'} \left[\frac{1}{3}(2K'+1) \right]^{1/2} D(K', K'). \quad (\text{A6})$$

If K' is odd, then $K = K' \pm 1$ and $Z_{\text{spin}}^{K'}(K' \pm 1)$ satisfies (2.7). For $K = K' - 1$,

$$Z_{\text{spin}}^{K'}(K'-1) = i^{K'-1} \left[3(2K'+1) \right]^{-1/2} \left\{ (K'+1) D(K'-1, K') \right. \\ \left. - \left[K'(K'+1) \right]^{1/2} D(K'+1, K') \right\}. \quad (\text{A7})$$

The form of the Wigner-Eckart theorem quoted in (A1) is appropriate when working with states labelled by the total angular momentum J . In describing properties of a 3d-transition ion it is quite common to have states labelled by spin and orbital quantum numbers, $SM_S LM_L$, with,

$$|SM_S LM_L\rangle = \sum_{JM} (SM_S LM_L | JM) |JM\rangle .$$

By constructing a matrix element $\langle SM_S LM_L | T_{q'}^{K'} | SM'_S LM'_L \rangle$ and performing sums on JM and JM' one finds that the appropriate form of the Wigner-Eckart theorem is obtained by replacing the quantity,

$$(-1)^{J-M} \begin{pmatrix} J & K' & J' \\ -M & q' & M' \end{pmatrix} W^{(ab)K'}$$

by the expression,

$$(-1)^{a+b+q'} \left\{ \frac{2K'+1}{(2a+1)(2b+1)} \right\}^{1/2} W^{(ab)} \sum_{mn} \begin{pmatrix} a & K' & b \\ -m & q' & -n \end{pmatrix} \quad (\text{A8})$$

$$(-1)^{S-M_S} \begin{pmatrix} S & a & S' \\ -M_S & m & M'_S \end{pmatrix} (-1)^{L-M_L} \begin{pmatrix} L & b & L' \\ -M_L & n & M'_L \end{pmatrix}.$$

The reduced matrix elements $W^{(ab)}$ and $W^{(ab)K'}$ are related by a 9j symbol, and the general expression is,

$$W^{(ab)K'} = \left\{ \frac{(2J+1)(2K'+1)(2J'+1)}{(2a+1)(2b+1)} \right\}^{1/2} \begin{Bmatrix} S & S' & a \\ L & L' & b \\ J & J' & K' \end{Bmatrix} W^{(ab)}. \quad (\text{A9})$$

Properties of $W^{(ab)}$ that are relevant to the interpretation of neutron diffraction are discussed in reference [22].

Table II

Matrix elements $\langle T_0^{K'}(K'-1) \rangle = \langle SM_S LM_L | T_0^{K'}(K'-1) | SM_S LM_L \rangle$ with $S = 1$, $M_S = 1$, $L = 3$ and $M_L = -3$ and 1 that enter the evaluation of the intensity when the V ion wavefunction in V_2O_3 is modelled by (4.7).

$M_L = -3$:

$$\langle T_0^1(0) \rangle = -\frac{1}{3} \langle j_0(k) \rangle - \frac{22}{21} \langle j_2(k) \rangle$$

$$\langle T_0^3(2) \rangle = \frac{4}{7\sqrt{7}} \{ \langle j_2(k) \rangle + \langle j_4(k) \rangle \}$$

$$\langle T_0^5(4) \rangle = -\frac{1}{7} \left(\frac{15}{11} \right)^{1/2} \langle j_4(k) \rangle$$

$M_L = 1$

$$\langle T_0^1(0) \rangle = \langle j_0(k) \rangle + \frac{38}{105} \langle j_2(k) \rangle$$

$$\langle T_0^3(2) \rangle = \frac{4}{7\sqrt{7}} \left\{ \frac{1}{5} \langle j_2(k) \rangle + \frac{2}{3} \langle j_4(k) \rangle \right\}$$

$$\langle T_0^5(4) \rangle = -\frac{1}{7} \left(\frac{5}{33} \right)^{1/2} \langle j_4(k) \rangle$$

Table III

The second column contains I_{crystal} derived from (4.5) and atomic tensors (4.8) evaluated for $\epsilon^2 = 0.45$ which gives a V ion moment $\mu = 1.2\mu_B$. Values are listed with increasing magnitudes of selected Bragg wavevectors $\tau_m = (hkl)_m$, and the last three columns specify the unit vector $\hat{\tau}_m = (t_1, t_2, t_3)$. The third column contains I_{crystal} derived from (4.5) and (4.8) and $\epsilon^2 = 0.25$ which corresponds to a V ion moment with no orbital content $\langle L_{\zeta} \rangle = 0$ and $\mu = 2.0\mu_B$. The ratio of I_{crystal} for $\mu = 1.2\mu_B$ and $\mu = 2.0\mu_B$, normalized to unity at the strongest reflection $(010)_m$, is found in the fifth column. The canting angle $\phi = 70^\circ$.

Table IV

Values of atomic tensors of rank three for V ions in magnetically ordered V_2O_3 inferred from an interpretation of resonant x-ray Bragg diffraction [19].

$$\langle T_{+1}^3(2) \rangle' = (0.037 \pm 0.009) \langle j_2(k) \rangle$$

$$\langle T_{+2}^3(2) \rangle'' = (-0.017 \pm 0.014) \langle j_2(k) \rangle$$

$$\langle T_{+3}^3(2) \rangle' = (0.039 \pm 0.013) \langle j_2(k) \rangle$$

Table V

Estimates for V_2O_3 of the single-crystal intensity (2.8) and projections of the magnetic amplitude on \mathbf{c}_h and \mathbf{b}_m .

Reflection	I_{crystal}	$\hat{\mathbf{c}}_h \cdot \langle \mathbf{Q}_\perp \rangle$	$\hat{\mathbf{b}}_m \cdot \langle \mathbf{Q}_\perp \rangle$
$(102)_m$	0.007	0	0.084
$(120)_m$	0.002	0.027	0.004
$(122)_m$	0.011	0.063	-0.036
$(320)_m$	0.022	-0.118	-0.016
$(140)_m$	0.001	0.021	0.002
$(340)_m$	0.017	-0.091	-0.016

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Figure 1

Positions of the eight V ions in the monoclinic cell adopted by V_2O_3 below the Néel temperature, together with the configuration of their moments in the plane spanned by \mathbf{a}_m and \mathbf{c}_m . The monoclinic Bragg wavevector $\boldsymbol{\tau}_m = (20\bar{2})_m$ is parallel to the trigonal axis \mathbf{c}_h , and \mathbf{b}_m is normal to the plane of the diagram and parallel to \mathbf{a}_h [11].

Figure 2

The figure illustrates the sites and magnetic configuration of the four Dy ions in the magnetic unit-cell of DyB_2C_2 . The axis of quantization of the ion labelled 1 lies in the $a - b$ plane, normal to the twofold axis of rotation symmetry, and it subtends an angle ϕ with the a -axis: namely, it is the vector $(\cos\phi, \sin\phi, 0)$. Corresponding axes for Dy ions labelled 2, 3 and 4, respectively, are $(-\sin\phi, -\cos\phi, 0)$, $(-\sin\phi, \cos\phi, 0)$ and $(\cos\phi, -\sin\phi, 0)$. Below the magnetic critical temperature T_c the net moment is directed along the a -axis and it vanishes for $\phi = 45^\circ$.