Resonant x-ray Bragg diffraction from orbital moments in vanadium sesquioxide (V_2O_3) and haematite (α-Fe_2O_3)

LETTER TO THE EDITOR

Resonant x-ray Bragg diffraction from orbital moments in vanadium sesquioxide (V_2O_3) and haematite (α –Fe_2O_3)

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Abstract. Resonant x-ray diffraction from V_2O_3 which has been observed at charge-forbidden reflections ($h + k + l$ odd) is here attributed to orbital moments of the vanadium ion. Furthermore, it is argued that the contribution to intensity as a function of x-ray energy seen in the experiment on the low energy side of the electric dipole (E1) resonance is due to an electric quadrupole (E2) resonance. The absence of the E1 resonance for h odd, and appearance of the E2 resonance at h odd and h even is accounted for in the calculated structure factor. For h odd the structure factor is proportional to the octupole moment of the vanadium ion, which is estimated to have a magnitude similar to that of the orbital angular momentum. In the case of E2 resonant x- ray Bragg diffraction from haematite the calculated structure factor contains three orbital moments, two of odd rank and one of even rank. The calculated polarization dependence and azimuthal-angle scans are in complete accord with experimental findings. The contribution of even and odd rank moments is shown to make scattering depend on circular polarization.

In 3d transition-metal compounds orbital moments are induced by the spin–orbit coupling and they contribute to many properties, including anisotropy, magnetoelastic relaxation and canted antiferromagnetism. Over the past few years, investigations of 3d oxides, especially perovskite-type manganites, have shown that the configuration of orbital moments plays a vital role in their properties, e.g. colossal magnetoresistance. Fortunately, orbital moments are significant in the diffraction of x-rays, because of the $\boldsymbol{A} \cdot \boldsymbol{p}$ interaction between photons and electrons. Their contribution to scattering is not tied to spin moments in the sample, unlike the usual situation encountered in neutron scattering, which is from magnetic moments. An extreme case is scattering enhanced by a resonance at the K edge and an electric quadrupole (E2) event, for then scattering is totally from orbital moments of the 3d valence shell, to a very good approximation.

We use this property in a unified explanation of resonant x-ray Bragg diffraction from vanadium sesquioxide (V_2O_3) [1] and haematite (α–Fe_2O_3) [2] observed at charge-forbidden reflections. In addition to the mean value of the orbital angular momentum, $\langle \boldsymbol{L} \rangle$, an orbital moment of rank one, unique contributions to scattering are made by orbital moments of rank $K > 1$, each having $(2K + 1)$ components. With V_2O_3 one observes $K = 3$ (the octupole moment = $\boldsymbol{\Lambda}$) and in scattering from haematite one observes both $K = 3$ and $K = 4$ (the hexadecapole moment = $\boldsymbol{\Upsilon}$). The maximum number of components of $\langle \boldsymbol{\Lambda} \rangle$ and $\langle \boldsymbol{\Upsilon} \rangle$ different from zero is set by the point-group symmetry of the site occupied by the resonant ion. For the compounds of interest here the principal symmetry is D_{3d}, and possible non-zero components are $\langle \Lambda_0 \rangle$, $\langle \Lambda_{\pm3} \rangle$, $\langle \Upsilon_0 \rangle$ and $\langle \Upsilon_{\pm3} \rangle$. The magnitude of these components can be similar to that of $\langle \boldsymbol{L} \rangle$.

The offered interpretation uses a model for the resonant scattering-length in which the resonant denominator and the matrix elements are decoupled, and the matrix elements are

summed over the quantum labels of the intermediate states that contribute to the resonance in question. With the x-ray energy, E, almost matched to the resonance energy, Δ, the scattering length is proportional to

$$\frac{F(\boldsymbol{\tau})}{(E - \Delta + \mathrm{i}\Gamma/2)} \tag{1}$$

where Γ is the width of the resonance. In (1), $F(\boldsymbol{\tau})$ is a unit cell structure factor evaluated for the reciprocal lattice vector $\boldsymbol{\tau}$. With use of an atomic model for the resonant ion, $F(\boldsymbol{\tau})$ is calculated without approximation [3, 4]. One has

$$F(\boldsymbol{\tau}) = \sum_{\boldsymbol{d}} \langle Z(\boldsymbol{d}) \rangle \exp(\mathrm{i}\boldsymbol{d} \cdot \boldsymbol{\tau}) \tag{2}$$

where the sum is over the positions of ions in the magnetic unit cell. For an E2 event, $\langle Z(\boldsymbol{d}) \rangle$ is the sum of five scalar products

$$\langle Z(\boldsymbol{d}) \rangle = \sum_{K=0}^{4} (2K + 1)^{1/2} \boldsymbol{H}^{(K)} \cdot \langle \boldsymbol{T}^{(K)}(\boldsymbol{d}) \rangle \tag{3}$$

in which the spherical tensor $\boldsymbol{H}^{(K)}$ is determined by the conditions of the primary and secondary beams, and $\langle \boldsymbol{T}^{(K)} \rangle$ is proportional to an orbital moment of the 3d valence shell, e.g. $\langle \boldsymbol{T}^{(1)} \rangle = \langle \boldsymbol{L} \rangle /\sqrt{30}$, $\langle \boldsymbol{T}^{(3)} \rangle = \langle \boldsymbol{\Lambda} \rangle /(3\sqrt{70})$ and $\langle \boldsymbol{T}^{(4)} \rangle = \langle \boldsymbol{\Upsilon} \rangle/(18\sqrt{70})$. (For an electric dipole (E1) event $K = 0$, 1 and 2.)

Physical properties of $\langle T_m^{(K)} \rangle$, $-K \leqslant m \leqslant K$, are revealed in their transformation properties. We will use a rotation by π about the principal axis, z, under which $\langle T_m^{(K)} \rangle \to (-1)^m \langle T_m^{(K)} \rangle$, and reversal of the direction of time, under which $\langle T_m^{(K)} \rangle \to (-1)^{K+m} \langle T_{-m}^{(K)} \rangle$. The latter transformation applies to magnetic moments whose axes (x, y, z) are related through a rotation by π about the y-axis, i.e. moments antiferromagnetically aligned with respect to each other.

Below its Néel temperature V_2O_3 has a monoclinic structure, derived from a trigonal structure in the paramagnetic and metallic phase. The vanadium moments form ferromagnetic sheets and moments in neighbouring sheets are oppositely aligned. Figure 1 includes our construction of the magnetic unit cell, which contains eight vanadium ions. Bragg reflections $(h\,k\,l)$ with $h + k + l$ odd are charge forbidden. Taking account of the configuration of magnetic moments, and the rotation by $180°$ of the chemical environment of ions labelled 1, 2, 5 and 6 relative to ions 3, 4, 7 and 8, we find the unit cell structure factor for charge-forbidden reflections is derived from

$$2 \left\{ \cos\phi + (-1)^{h+m} \cos(\phi - \varepsilon) \right\} \left\{ 1 - (-1)^K \right\} \langle T_m^{(K)} \rangle. \tag{4}$$

The two positional phases are $\phi = 2\pi(xh + yk + zl)$ and $\varepsilon = 4\pi yk$. The x and z position parameters of the vanadium ions are large compared to $y \approx 0.002$ [5], and strong Bragg reflections have $h + m$ even.

The structural phase transition in V_2O_3 which accompanies the onset of long-range magnetic order leaves the oxygen–vanadium distances essentially equal [5], and physical properties of the cations are bound by the requirement of the principal element of symmetry, D_{3d}. So, the allowed values of the projection m are 0 and ± 3. Tensors with $K = 0$, 1 and 2 are diagonal ($m = 0$) and tensors with $K = 3$ and 4, exclusive to E2 events, contain $m = 0$ and ± 3.

According to (4), a strong reflection with h even contains m even and, therefore, the unit cell structure factor is built from diagonal tensors. Of these, tensors of even rank cancel out, as expected for a charge-forbidden structure factor. We conclude that for h even the structure
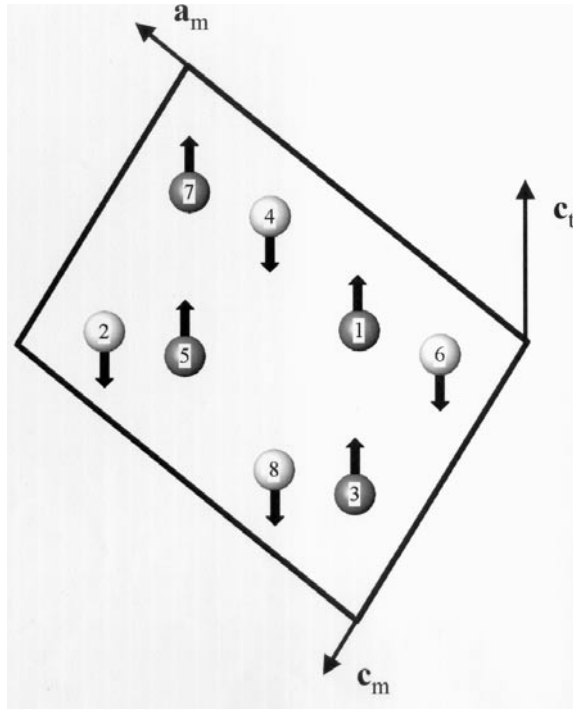
Figure 1. The magnetic structure and monoclinic unit cell of the ordered state of V_2O_3 [5, 6]. The monoclinic axis b_m is perpendicular to the paper, and the moments lie in the a_m–c_m plane.

factor is built from $\langle L_0 \rangle$ and $\langle \Lambda_0 \rangle$, and E1 and E2 absorption events participate. Data for the diffraction intensity as a function of E and $\tau = (221)$ are consistent with this finding [1]. However, in the accompanying text the authors maintain that the relatively weak intensity at $E = 5.464$ keV is not caused by an E2 event, as we would have it. As we will now see, their data for $\tau = (111)$ is compelling evidence in favour of our interpretation.

From (4), a strong reflection with h odd contains m odd, namely $m = \pm 3$, and this can only arise from an E2 event. Intensity as a function of E and $\tau = (111)$ displays one peak at the same energy $E = 5.464$ keV as the low energy peak seen with $\tau = (221)$. We conclude that, at this energy diffraction is due to an E2 event, and for h odd the structure factor is proportional to the octupole moment. The result (4) leads to

$$F(111) \propto \tfrac{2}{3} \left(\tfrac{2}{5} \right)^{1/2} \{ \cos \phi + \cos (\phi - \varepsilon) \} \langle \Lambda_{+3} \rangle . \tag{5}$$

Using $\langle L_0 \rangle = -0.5$ [1] we find $|\langle \Lambda_{+3} \rangle| \approx 1.6$. The reported polarization analysis and azimuthal angle dependence of the (111) intensity reveals little about the local environment of a resonant (vanadium) ion because the principal axes are not arranged relative to the plane of scattering in a simple way (the angles between $\tau = (111)$ and the principal axes are $50.37°$, $42.57°$ and $103.03°$).

This is not so in an elegant experiment on haematite [2] using enhancement from an E2 event in absorption by iron ions; the trigonal axis of the rhombohedral cell passes through the four resonant (ferric) ions and it is aligned with τ. An azimuthal angle scan is rotation by ψ about τ. Below the Néel temperature magnetic moments have the configuration $+ - -+$, and above the Morin temperature they are contained in the basal plane. Canting of the moments out of the plane is caused by a Dzyaloshinsky–Moriya interaction, the strength of which
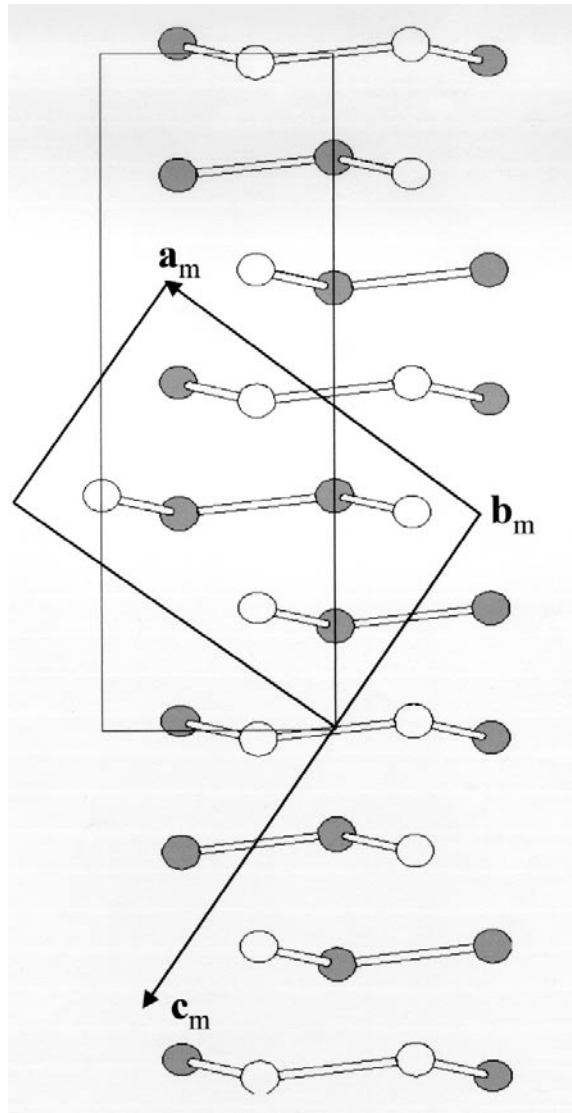
Figure 1. (Continued.)

lies along the trigonal axis [7, 8]. At lower temperatures the quantization and trigonal axes coincide. There is a rotation by $180°$ about the trigonal axis between ions with opposite moment directions; two such ions are described in the theory by $\langle T_m^{(K)} \rangle$ and $(-1)^K \langle T_{-m}^{(K)} \rangle$.

The unit cell structure factor for a charge-forbidden reflection (rhombohedral cell and $h + k + l$ odd) is derived from

$$2\mathrm{i} \sin\phi \langle T_m^{(K)} \rangle \left\{ 1 - (-1)^{K+m} \right\} \tag{6}$$

where $\phi = 2\pi z(h + k + l)$ and the position parameter $z = 0.105$. For $m = 0$ the structure factor is possibly different from zero for K odd, whereas for $m = \pm 3$ one must have $K = 4$ [3].

In order to describe the azimuthal angle dependence of the diffraction intensity (6) is first transformed to the axes of the experimental geometry, in which $H^{(K)}$ is defined, and then rotated by ψ about τ. The value of the structure factor depends on polarization in the primary and secondary beams, and this information is contained in $H^{(K)}$. Denoting the orthogonal linear polarizations as σ and π, with σ perpendicular to the plane of scattering, the structure factors for a charge-forbidden reflection and an E2 event are as follows; $F_{\sigma'\sigma}(\tau) = F_{\pi'\pi}(\tau) = 0$ and $F_{\pi'\sigma}(\tau) = F_{\sigma'\pi}(\tau)$ with

$$F_{\pi'\sigma}(\tau) = \tfrac{1}{5}\sin\phi \times \left\{ \langle L_0 \rangle \sin 3\theta + \tfrac{1}{3}\langle \Lambda_0 \rangle \sin\theta (3\sin^2\theta - 1) \right.$$
$$\left. + \tfrac{i}{6}\left(\tfrac{5}{7}\right)^{1/2} \langle \Upsilon_{+3} \rangle \cos^3\theta \sin 3\psi \right\}. \tag{7}$$

Here, θ is the Bragg angle. These theoretical findings are consistent with observations on haematite obtained with $\tau =$ (111) [2].

Intensity observed in the unrotated channel $\sigma'\sigma$ is completely accounted for in terms of leakage (the primary σ polarization is 93%) [2] and thus the observation is consistent with $F_{\sigma'\sigma}(\tau) = 0$. Intensity in the rotated channel $\pi'\sigma$ is different from zero and not contaminated by leakage. Our finding ascribes this intensity to three orbital moments of rank $K = 1$, 3 and 4. The hexadecapole is responsible for the observed six-fold periodicity with respect to ψ [2], and the order stems from the three-fold rotation axis passing through the four ferric ions in the rhombohedral unit cell. The 90° phase shift between contributions to $F_{\pi\sigma}(\tau)$ from diagonal moments and $\langle \Upsilon_{+3} \rangle$ merits comment. First, it reflects the fact that the diagonal moments are of odd rank and axial-like quantities, while $\langle \Upsilon_{+3} \rangle$ is a component of an even-rank moment and a polar-like quantity. Secondly, the phase shift does not make scattering sensitive to circular polarization in the primary beam, or create circular polarization in the secondary beam, because $F_{\sigma'\sigma}(\tau)$ and $F_{\pi'\pi}(\tau)$ are both zero. Lastly, the phase shift is absent if the configuration of moments is $++--$. Hence, the observed variation with ψ supports the moment configuration $+--+$ used in the calculation leading to (7).

As noted at the end of our discussion of V_2O_3, structure factors depend on the orientation of the crystal relative to the experimental geometry. By way of an illustration, consider haematite with the trigonal axis inclined to the plane of scattering such that with $\psi = 0$ the axis is perpendicular to the plane, and with $\psi = \pi/2$ the axis is in the plane and perpendicular to τ. In this orientation both $F_{\sigma'\sigma}(\tau)$ and $F_{\pi'\sigma}(\tau)$ can be different from zero and scattering is made sensitive to circular polarization. One finds, for example

$$F_{\sigma'\sigma}(\tau) = -\tfrac{1}{5}\sin\phi \sin 2\theta \cos\psi \left\{ \langle L_0 \rangle + \langle \Lambda_0 \rangle \left(1 - \tfrac{5}{3}\cos^2\psi\right) \right\} \tag{8}$$

which vanishes for $\psi = \pi/2$, as might be expected. Circular polarization in the primary beam introduces to the resonant cross-section a term whose weight is proportional to

$$-P_2 \sin\theta (\cos\theta \cos\psi \sin\phi)^2 \langle \Upsilon_{+3} \rangle (3(\sin\psi \cos\theta)^2 - 1)$$
$$\times \left\{ \langle L_0 \rangle \left(5 - 8\cos^2\theta\right) + 2\langle \Lambda_0 \rangle \cos^2\theta\left(1 - \tfrac{5}{3}\cos^2\psi\right) \right\} \tag{9}$$

where P_2 is the mean helicity in the beam. Note that the weight vanishes for $\psi = \pi/2$, and it is proportional to the hexadecapole. Periodicity with respect to ψ created by the three-fold axis is not present in (8) and (9). The expression (9) is appropriate for the moment configuration $+--+$. For the configuration $++--$ the corresponding expression is zero and scattering is independent of circular polarization.

The orbital moment $\langle L_0 \rangle$ is proportional to the strength of the Dzyaloshinsky–Moriya interaction, which produces a small moment-canting effect, and weak ferromagnetism. In equation (7) for $F_{\pi'\sigma}(\tau)$ the dependence on θ is such that for small θ the structure factor is essentially independent of the octupole ($\theta = 10.96°$ for $\tau =$ (111)). In Moriya's calculation [7] the orbital moments in haematite are created by off-diagonal components in the combined

action of the spin–orbit coupling and the exchange interaction, and as such they might have small values. (It is possible that the signals observed from haematite are due in part to scattering processes absent in (1) and (3) through decoupling the matrix elements and resonant energy denominator [3]. In this event, the fundamental features of the structure factor will be as described.)

To conclude, we have successfully interpreted two resonant x-ray diffraction experiments on 3d-transition metal compounds using one theoretical framework. Common features of note include use of an electric quadrupole (E2) absorption event and the investigation of charge-forbidden Bragg reflections; taken together, these particular features mean access to interesting and subtle properties of the orbital magnetism. With regard to V_2O_3 there are two key differences between the proposed interpretation and the original one [1]. First, a contribution by the E2 event is here admitted, and found to be responsible for a significant item of the diffraction pattern associated with orbital ordering. Secondly, our theoretical framework includes orbital moments of odd rank. Such moments are absent in the more crude approximation that underpins the original investigation, which is not capable of predicting the octupole moment at the heart of our structure factor. In the case of haematite one of our results points to the possibility of magnetic contributions to scattering induced by circular polarization in the primary beam.

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