Melting of chiral order in terbium manganate (TbMnO$_3$) observed with resonant x-ray Bragg diffraction

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Abstract
Resonant Bragg diffraction of soft, circularly polarized x-rays has been used to observe directly the temperature dependence of chiral-order melting in a motif of Mn ions in terbium manganate. The underlying mechanism uses the $b$-axis component of a cycloid, which vanishes outside the polar phase. Melting is witnessed by the first and second harmonics of a cycloid, and we explain why the observed temperature dependence differs in the two harmonics. Conclusions follow from an exact treatment of diffraction by using atomic multipoles in a circular cycloid, since a standard treatment of the diffraction, based on a single material-vector identified with the magnetic dipole, does not reproduce correctly observations at the second harmonic.

1. Introduction
An electronic state in which charge and magnetic polarizations coexist has been at the centre of materials science in the past decade. More work is needed to fully understand the phenomenon of multiferroicity, and to develop practical applications, notably controlling charges by applied magnetic fields and spins by applied voltages.

Two different mechanisms seem able to generate magnetically induced polarization. First, exchange-striction appearing in nearly collinear spin structures [1, 2]. The coexistence of ferromagnetic and antiferromagnetic spin coupling introduces frustration in the system that is partially released by shifting the magnetic ions. Ions with antiparallel spins get closer, while ions having parallel spins are moved further apart. Such is the case of hexagonal HoMnO$_3$ [3] or orthorhombic RMn$_2$O$_5$ ($R = $ Tb, Ho, Dy) [4–6]. Secondly, a magneto-electric effect can arise from the Dzyaloshinskii–Moriya interaction [7, 8]. The D–M interaction favours orthogonal spins, and it may induce canting of nominally parallel spins deprived of inversion symmetry. In a magnetically induced multiferroic, such as TbMnO$_3$, the presence of a chiral magnetic structure induces polarization by shifting the oxygen atoms [9, 10].

The latter mechanism has generated debate in the community, specifically on the role of the ionic displacements. Katsura et al first argued that a novel mechanism, based on a spin super-current $\approx S_1 \times S_2$, was the source of the magneto-electric effect [11]. In this approach, the magneto-electric coupling is entirely arising from the non-collinear spin...
structure, without the need to invoke structural distortion that would break inversion symmetry (pure electronic contribution to electric polarization). Further theoretical work insisted on lattice distortions, and concluded that they should play a pivotal role in the physics of such materials [12, 13]. Experimentally the lattice distortions, if any, are minute and only recently with an elegant and sophisticated experiment Walker et al. have shown that there are indeed lattice distortions in the polar phase of TbMnO₃, even if only of few femto-metres for the Tb ions [14]. Malashevich and Vanderbilt [15] argue that the pure electronic contribution suffers an accidental cancellation due to the rotation of the Mn–O octahedral, but it is a relevant player for other phases or other multiferroics. In light of the current debate, it is valuable to observe directly changes occurring in the electronic density at the onset of the multiferroic phase.

In section 2, we describe the experimental method, resonant x-ray Bragg diffraction. To unambiguously detect and study chiral properties of TbMnO₃ we exploit circular polarization in the primary beam of x-rays, and measure intensities of satellite reflections. In addition, our communication reports corresponding results observed with linear polarization. Figure 1 depicts states of polarization and the plane of scattering. Intensities have been gathered with changes to the orientation (azimuthal angle) and temperature of the sample.

The established magnetic structure for the multiferroic phase of TbMnO₃ is consistent with our data for the first harmonic, section 3 [10, 14, 16]. We report equal amounts of data on the first and second harmonics of the Mn chiral order, which appear concomitantly with the magnetic order at 42 K and persists also in the polar phase appearing at 27 K. Thereafter, in section 4, we develop a complete, atomic theory of diffraction by a circular cycloid, and prove its correctness for intensities at the first and second harmonics, by rigorous tests against our data collected as a function of the azimuthal angle in section 5. Melting of chiral order is the main topic in section 6. Conclusions are gathered in section 7.

2. Sample preparation and experimental method

A TbMnO₃ single crystal was grown by the floating-zone technique using a four mirror image furnace. The starting materials for the preparation of feed rods for the floating-zone crystal growth were Tb₂O₃ and MnO (99.99% purity) obtained from Alfa Aesar. Stoichiometric amounts of raw materials were thoroughly ground together and then synthesized at 1200°C for 20 h in air with an intermediate grinding after 10 h. The powder was then compacted into a rod (typically 6 mm in diameter and 80 mm long), and sintered in a box furnace at 1450°C for 8 h in air. Large, stoichiometric and crack-free crystals were grown at 0.5 mm h⁻¹ with rotation rate of 15 rpm for the growing crystal and 0 rpm for the feed rod under static argon. A sample was subsequently cut with facets parallel to the crystallographic axes and mounted on a sample holder with the b-axis perpendicular to the sample holder surface. The sample was not poled during the experiment, but it was undergoing poling in tests prior to beam-time. Analysis of data took into account presence of in-balance in domain population.

Experiments were performed with the RESOXS chamber [17] at the X11MA beamline [18] of the Swiss Light Source. Twin Apple undulators provide linear, horizontal, π and vertical, σ, and circularly, right and left, polarized x-rays with a polarization rate close to 100%, cf. figure 1. The sample was attached to the cold finger of an He flow cryostat with a base temperature of 10 K. Azimuthal scans were achieved by rotation of the single crystal, with an accuracy of approximately ±5°.

Angular anisotropy in electronic structure can produce structurally forbidden Bragg reflections. Such is the case with dysprosium borocarbide, for example, and weak space-group forbidden reflections observed in Thomson scattering are reported by Adachi et al. [19]. A resonant event in diffraction produces a helpful enhancement of intensity. In addition, resonant diffraction can rotate primary polarization, and thus depend on photon helicity, whereas Thomson scattering is diagonal in polarization states. Absence of translation symmetry also generates space-group forbidden reflections, or satellite reflections. Intensities we report in resonant Bragg diffraction by TbMnO₃ are consequences of departures from spherical symmetry in electronic structure and, also, the absence of translation symmetry in a chiral structure. In accompanying calculations of the scattering length the very same symmetry considerations are placed at the forefront. Energy profiles are those for oscillators, consistent with the fast-collision approximation and angular isotropy of the core state [20–23].

A theory of resonant x-ray Bragg diffraction is laid out by Dmitrienko [24], and Templeton and Templeton report the first relevant data, e.g., tetragonal K₂PtCl₄ (P4/mmm-type) and sodium bromate (P2₁2₁2₁-3-type) [25]. Formulations of resonant diffraction found in the cited papers use classical optics and physical properties of crystals with Cartesian tensors, as in the treatise by Nye [26], and no attempt is made at calculating an energy profile. Components of the tensors permitted by crystal symmetry are phenomenological
Figure 2. Polarization analysis at the Mn $L_2$-edge. Open (black) circles represent intensities collected in the $\pi'$-$\pi$ channel, closed (blue) squares in the $\sigma'$-$\sigma$ channel. Closed (red) diamonds and closed (green) triangles represent intensities in the rotated channels, $\sigma'$-$\pi$ and $\pi'$-$\sigma$, respectively. Data were collected at two different azimuthal angles and at two satellite reflections. (A) $(0, \tau, 0)$ with $\psi = 180^\circ$ (B) $(0, 2\tau, 0)$ with $\psi = 180^\circ$. (C) $(0, \tau, 0)$ with $\psi = 90^\circ$. (D) $(0, 2\tau, 0)$ with $\psi = 90^\circ$. Data are shifted for clarity.

quantities that depend on wavelength, and with no operational definition they cannot be related to material properties. An atomic theory appeared shortly afterwards [20] in response to data for resonant Bragg diffraction by an incommensurate magnetic motif (full reports of experiments on magnetically ordered holmium, a spiral antiferromagnet, are found in [27, 28]). Hannon et al [20] show that, electronic multipole events in x-ray diffraction provide sensitivity to magnetic properties of a material, an eye-opening revelation at the time of publication that is taken for granted today. For the sake of demonstration, Hannon et al tackle the formidable task of describing electronic structure at an atomic level of detail by imposing cylindrical symmetry, in which dipole and quadrupole contributions to scattering by a resonant ion are all generated from a single material-vector, $z$, assigned to a magnetic dipole. In consequence, their x-ray scattering length is not universally applicable, unlike Dmitrienko’s symmetry-based formulation of resonant Bragg diffraction by non-magnetic electronic structure [24]. Neither Dmitrienko [24] or Hannon et al [20] calculate energy profiles, which are mere factors in contributions to the scattering length labelled by electronic symmetry. Haverkort et al [29] estimate the factors in scattering lengths constructed with Cartesian tensors, in the footsteps of Dmitrienko [24] and Hannon et al [20], for various symmetries, using a multiplet crystal-field approach to electronic structure. Simulations by Cricchio et al [30] of hidden order in URu$_2$Si$_2$ using density-function theory for itinerant electrons are analysed in terms of spherical tensors that are employed by us. Such simulations make possible an estimate of the absolute value of the scattering length, while we settle for ratios of contributions inferred from our data. Reviews of many applications of resonant x-ray Bragg diffraction, and advances in formulations, include [23, 31, 32].

3. Observations with linear polarization

The approximate, simple scattering length deployed by Hannon et al [20] says that first-order and second-order satellites, respectively, are linear and quadratic in the material-vector, or stick, $z$, assigned to each resonant ion. A vector $(0, f_b, f_c)$ is consistent with the established motif of Mn ions in terbium manganate, with components of a circular cycloid in the $b$–$c$ plane [10, 33, 34], and predictions for the first harmonic $(0, \tau, 0)$ from a stick-model. Our data are displayed in figure 2. In particular, there is no intensity at an azimuthal angle $\psi = 180^\circ$ ($a$- and $b$-axis in the plane of diffraction) in the $\sigma'$-$\sigma$ channel, because it is proportional to $f_c^2$, and no intensity in the $\sigma'$-$\sigma$ and $\pi'$-$\pi$ channels at $\psi = 90^\circ$ ($b$- and $c$-axis in the plane of diffraction), where diffraction in the $\pi'$-$\pi$ channel is proportional to $(f_b^2 \cos^2 \theta - f_c^2 \sin^2 \theta)$ and the Bragg angle, $\theta$, is depicted in figure 1. Diffraction in the $\sigma'$-$\sigma$ channel is predicted to be identically zero at $\psi = 90^\circ$, and our data (panel D in figure 2) shows the prediction is wrong for the second harmonic $(0, 2\tau, 0)$, while it is correct
for the first harmonic. To explain this finding we use an exact calculation of diffraction by a circular cycloid, leaving behind the restriction to cylindrical symmetry in the stick-model while retaining a simple energy profile.

4. Diffraction by a circular cycloid

Five years after Hannon et al [20] communicated their ground-breaking insight they published a brief account of a full atomic theory of resonant x-ray diffraction [21], complete with the fast-collision approximation and concomitant explicit dependence on the x-ray energy of the stick-model. Electronic degrees of freedom are encapsulated in irreducible, spherical multipoles, which cannot be represented by a material-vector, in the general case [35]. Our notation for a spherical multipole is $(T^K_Q)$, with a complex conjugate $(T^K_Q)^* = (-1)^Q(T^K_{-Q})$, where the positive integer $K$ is the rank and $Q$ the projection, which satisfies $-K \leq Q \leq K$ [23, 36]. Angular brackets (...) denote the time-average of the enclosed quantum-mechanical operator, i.e., a multipole is a property of the electronic ground-state. Angular anisotropy in electronic structure is quantified by $K$ and $Q$, and $K = 0$ (scalar, adds to simple charge scattering), $K = 1$ (dipole) and $K = 2$ (quadrupole) for an E1–E1 event under consideration, and the time signature of parity-even multipoles is $(-1)^K$.

Thermodynamic properties of multipoles serve to contrast the stick-model and spherical multipoles. One can make the identification $z = (x, y, z) \propto (T^1_0)$, and the dipole $(T^1_0)$ is known, from work on sum-rules for dichroic signals, to be a linear combination of spin, $(S)$, orbital moment, $(L)$, and a dipole that expresses magnetic anisotropy [37]. As for the thermodynamic properties of $(T^1_0)$ it might reasonably scale with the total angular momentum, $(J)$. Analogously, a quadrupole $(T^2_0)$ might scale with $[3(J(J+2) - J(J+1))]$, which vanishes in the absence of magnetic correlations and, also, when $J = 1/2$ (a decomposition of $(T^2_0)$ into standard operators is available [38]). In the stick-model the corresponding quantity for the quadrupole is $z^2 \propto (J_z)^2$. To illustrate likely differences in temperature dependences of quadrupole entities, figure 3 displays normalized values of $(J_J)^2$ and $[3(J(J+2) - J(J+1))]$ as a function of temperature and $J$. Results are derived from an isotropic Heisenberg model treated with the molecular-field approximation [22].

An exact formulation of diffraction by an ideal circular cycloid with moment rotation in the $y$-$z$ plane is given in previous work on ThMnO$_4$ [39], and here we make the first full use of results to build a wholly satisfactory interpretation of our new data on the second harmonic. The super-cell length $L = (2n + 1)a$ where $a$ is a lattice spacing and $n$ an integer. The integer $f$ measures the wavevector in units of the fraction $(2\pi/\alpha)(a/L) = 2\pi/(L(2n + 1))$, while the turn angle $= 2\pi/(2n + 1)$. Multipoles for the super-cell are denoted by $(C^K_Q)$ and some expressions for $K = 1$ and 2 are listed in table 1. A few properties of $(C^K_0)$ are more or less obvious, e.g., $(C^K_1) = 0$ for the second harmonic, $f = 2$, agrees with the stick-model, and a $90^\circ$ phase shift between $y$- and $z$-dipoles in the ideal $y$-$z$ cycloid, $(C^K_{-1}) = -i(C^K_1)$. General results, and specific results for the ideal $y$-$z$ cycloid, include: (i) Non-zero multipoles obey the identity for rotation by $180^\circ$ about the axis normal to the plane of the cycloid, $C_{2\pi}(C^K_Q) = (-1)^K(C^K_{-Q})$. (ii) Using the identity $C_{2\pi}(C^K_Q) = (-1)^Q(C^K_{-Q})$ one finds $(C^K_{-Q}) = (-1)^Q(-1)^K(C^K_{-Q})$. (iii) $(C^K_1) \propto (C^K_{1+1} - C^K_{1-1}) = 0$ because $(C^K_0) = 0$ for $f > 1$ and $(C^K_{1+1}) = (C^K_{1-1})$ for $f = 1$. In the general case (iv) for given $f$ and $K$ all $(C^K_Q)$ are proportional to one another. Scaling coefficients are complex and depend on both the magnitude

| Table 1. Multipoles with $K = 1$ and 2 for the first ($f = 1$) and second ($f = 2$) harmonic of a circular cycloid with moment rotation in the $y$-$z$ plane. Results are generated from an expression given by Scagnoli and Lovesey [39]. (Note that in equation (F4) the sign in front of the second double sum is incorrect and it should be a minus sign.) |
|---|
| $f = 1$, $(C^1_0) = (1/2)[(T^1_0) - i(T^1_1)]$ with $(T^1_1) = i(T^1_{-1} + T^1_{+1})/\sqrt{2}$, $(C^1_{+1}) = (C^1_{-1}) = (C^1_0)/\sqrt{2}$. $(C^2_0) = 0$, $(C^2_{+1}) = -(C^2_{-1}) = (1/4)[(T^2_{+1} - T^2_{-1}) + (T^2_{+2} + T^2_{-2})]$. $(C^2_{+2}) = -(C^2_{-2}) = (C^2_{+1})$. $f = 2$, $(C^1_0) = (C^1_{+1}) = (C^1_{-1}) = 0$. $(C^2_0) = (1/4)\sqrt{3(2)}(T^2_{+1} + T^2_{-1}) + (1/8)\sqrt{3(2)}(T^2_{+2} + T^2_{-2}) + (3/8)(T^2_0)$. $(C^2_{+1}) = (C^2_{-1}) = \sqrt{2}/3(C^0_0)$. $(C^2_{+2}) = (C^2_{-2}) = (1/2)(C^2_{+1})$. |

Figure 3. Values of the normalized quantities $(J_J)^2/J^2$ (shown with black lines) and $(3(J(J)^2) - J(J+1))/(J(J+1))$ (shown in red) as a function of reduced temperature $T/T_c$, and $J$. Results are derived from an isotropic Heisenberg model treated with the molecular-field approximation. Expressions for these quantities are found in [22].
and sign of the projection \( Q \). (v) \( (C^0_Q) \) does not depend on \( \alpha \).

(vi) \( (C^K_Q) \) is not Hermitian. (vii) \( (C^K_{Q'}) = 0 \) for \( K < f \).

For the purpose of calculating unit-cell structure factors, \( A_k \), it is always convenient to construct linear combinations of multipoles that are even \( (A_k Q) \) and odd \( (B_k Q) \) functions of the projection, \( Q \) [39] and,

\[
A_{K,Q} = A_{K,-Q} = \frac{1}{2} [\exp(-iQ\alpha)\Psi_{k,Q} + \exp(iQ\alpha)\Psi_{-k,-Q}],
\]

\[
B_{K,Q} = -B_{K,-Q} = \frac{1}{2} [\exp(-iQ\alpha)\Psi_{k,Q} - \exp(iQ\alpha)\Psi_{-k,-Q}].
\] (1)

with \( \alpha = 90^\circ \) for a Bragg wavevector parallel to the crystal \( b \)-axis, cf figure 1. For a commensurate motif of multipoles, elements of symmetry in the space group will dictate the make-up of the electronic structure factor \( \Psi_{k,Q} \) in (1).

To construct a minimal model of a cycloid existing in TbMnO\(_3\) we seek guidance from the space group \( Pbnn \) in which Mn ions occupy sites 4b (standard setting \( \text{Pnnm} \), \#62 [39]) to derive the identity,

\[
\Psi_{k,Q} = \{1 + C_{2x} + \exp(i\beta)[C_{2x} + C_{2y}]/2\} (C^0_Q).
\] (2)

Here, \( \beta \) is the fractional wavevector and \( C_{2y} \) denotes the operation of rotation by 180° about the \( y \)-axis. To make use of this expression we have to determine quantities \( C_{2x}(C^0_Q) \) and \( C_{2y}(C^0_Q) \) for \( K = 1 \) and 2, while \( C_{2x}(C^0_Q) = (-1)^9(C^0_Q) \) for the \( y-z \) cycloid. Using specific results in table 1, we find \( \Psi_{k,Q} \) proportional to \( (1 - \exp(i\beta)) \) for \( f = 1 \), where \( \beta = \pi \tau \equiv 51^\circ \).

Because the spatial phase factor is common to all multipoles it cancels out in ratios, which all that can be inferred from diffraction data. With \( f = 2 \), operations \( C_{2x}(C^2_Q) \) and \( C_{2y}(C^2_Q) \) have the effect of creating the complex conjugate of \( (C^0_Q) \). In consequence, \( \Psi_{k,Q} = 2(1 + \exp(2i\beta))Re \cdot (C^2_Q) \) leading to the conclusion that real parts of \( (C^2_Q) \) contribute to scattering with \( f = 2 \).

In light of these findings we equate \( \Psi_{k,Q} \) and \( (C^k_Q) \) in (1), and the expressions,

\[
A_{k,Q} = (C^k_Q)(\exp(-iQ\alpha) + \exp(iQ\alpha)(-1)^{K+f}/2),
\]

\[
B_{k,Q} = (C^0_Q)(\exp(-iQ\alpha) - \exp(iQ\alpha)(-1)^{K+f}/2),
\] (3)

with \( \alpha = 90^\circ \) define our minimal model of a circular cycloid for Mn ions in terbium manganate.

\(-0, \tau, 0 \) and \( f = 1 \); allowed contributions are found to be,

\[
A_{1,0} = (C^1_0), \quad A_{2,1} = -(C^2_1),
\]

\[
B_{1,1} = -(C^1_1) \quad \text{and} \quad B_{2,2} = -(C^2_2).
\] (4)

The dipole \( (C^1_0) \equiv (C^1_z) = (1/2)[(T^0)_{y} - i(T^1_y)] \) and \( (C^2_1) \equiv (C^2_{x+y}) \) can be complex. Previously, we noted the identities \( (C^1_z) = 0 \) and \( (C^1_z) = -(C^1_y) \) for the \( y-z \) cycloid. We use \( A_{1,0} \) to normalize multipoles inferred from data, table 2. The quantity \( r = iB_{1,1}/A_{1,0} \) is proportional to \( (C^1_y)/(C^1_z) \) and it is purely real for the ideal cycloid. We anticipate that quadrupole contributions are small. For \( (C^2_{x+y}) \) is composed of charge fluctuations normal to the \( y-z \) plane that are absent in the stick-model with \( (x) = 0 \). Specifically,

\[
(C^2_{x+y}) = (i(xy) - (xz))/\sqrt{6}, \quad \text{where} \ (\alpha \beta) \ \text{is a standard, purely real Cartesian quadrupole and} \ (\alpha \beta) \Rightarrow (\alpha \beta) \ \text{in the stick-model}.
\]

Unit-cell structure factors for an \( E1-E1 \) event have the property that \( F_{\sigma'\sigma} \) and \( F_{\pi'\pi} \) do not depend on \( B_k,Q \). We find \( (f = 1) \),

\[
F_{\sigma'\sigma} = -i \sin(2\psi)A_{1,1},
\]

\[
F_{\pi'\pi} = (i/\sqrt{2}) \sin \theta \cos(\psi)A_{1,0} - i \sin^2 \theta \sin(2\psi)A_{1,1},
\]

\[
F_{\sigma'\pi} = (i/\sqrt{2}) \cos \theta \sin(\psi)A_{1,0} + i \sin \theta B_{1,1}
\]

\[
- \sin \theta \cos(2\psi)A_{1,1} + i \cos \theta \sin(\psi)B_{2,2}.
\] (5)

A result for \( F_{\sigma'\pi} \) is derived from \( F_{\pi'\pi} \) by the change of sign to both \( A_k \). Quadrupoles in (5) contribute Templeton and Templeton scattering by a cycloid [25]. These contributions are omitted by Jiang et al [10] without supporting evidence.

\(-0, 2\tau, 0 \) and \( f = 2 \); Recall that \( (C^3_z) = 0 \), and allowed contributions are,

\[
A_{2,0} = (C^2_0), \quad A_{2,2} = -(C^2_{2z}),
\]

\[
B_{2,1} = -i(C^2_1).
\] (6)

The quadrupole \( (C^2_0) = (3(zz) + (x^2 - y^2) - 4i(yz))/8 \) is complex, while ratios of multipoles are purely real, with \( (C^2_{x+y})/(C^2_0) = \sqrt{2}/3 \) and \( (C^2_{x+y})/(C^2_0) = \sqrt{1}/6 \). If we make \( A_{2,0} = (C^2_0) \) a common factor, \( F_{\pi'\pi} \) and \( F_{\sigma'\pi} \) are expected to be purely real. On the other hand, we anticipate \( B_{1,1}/A_{2,0} \) is purely imaginary and thus \( F_{\sigma'\pi} \) contains an imaginary component (the sign of \( B_{1,1} \) is not available from the intensity, \( |F_{\pi'\pi}|^2 \)). This is not allowed in the stick-model, with \( A_{2,0} = (3(z^2) - 1)/\sqrt{6}, A_{2,2} = (y^2)/2, B_{2,1} = -i(y(z), \text{and}
\]

\[
A_{2,1} = B_{2,2} = 0.
\]

For the second harmonic \( (f = 2) \),

\[
F_{\pi'\pi} = (1/2 \cos(2\psi)\sqrt{3}/2)A_{2,0} + A_{2,2}
\]

\[
- (1/2)A_{2,2} - \sqrt{1/6}A_{2,0},
\]

\[
F_{\pi'\pi} = (1/2)\sin^2 \theta \cos(2\psi)\sqrt{3}/2A_{2,0} + A_{2,2}
\]

\[
+ (1/2)(1 + \cos^2 \theta)A_{2,2} - \sqrt{1/6}A_{2,0},
\] (7)

\[
F_{\pi'\pi} = -(1/2)\sin \theta \cos(2\psi)\sqrt{3}/2A_{2,0} + A_{2,2}
\]

\[
- \cos \theta \cos(\psi)B_{2,1},
\]

and \( F_{\sigma'\pi} \) is derived from \( F_{\pi'\pi} \) by the change of sign to both \( A_k \). In contrast to a prediction from the stick-model noted in section 3, at the second harmonic \( F_{\pi'\pi} \) can be different from zero at \( \psi = 90^\circ \). This finding is in accord with data in figure 2.

5. Azimuthal-angle scans

\(-0, \tau, 0 \) Data are displayed in figure 4. They are compared to predictions for the \( f = 1 \) circular cycloid with structure

\begin{tabular}{|c|c|c|c|c|}
\hline
& \( A_{1,0} \) & \( B_{1,1} \) & \( B_{2,1} \) & \( A_{2,0} \) & \( A_{2,2} \) \\
\hline
\( (0, \tau, 0) \) & 1 & 0 & -0.45 & 0.71 & 1.0 & 0.06 \\
\hline
\end{tabular}

Table 2. Inferred values of multipole contributions (5) and (7). Values of \( A_{k,Q} \) and \( B_{k,Q} \) for 10 K.
6. Observations with circular polarization

- $(0, \tau, 0)$ Dependence of the diffracted intensity as a function of circular polarization (helicity), $P_2$, is proportional to factors (5). Expressions for intensities in terms of structure factors, including circular polarization in the primary beam, can be found in [40]. Equation (8) is a specific example.

One can show that, $\Psi_{1,0}$ and $\Psi_{2,\mp 1}$ are proportional to $(T^{1}_{0})$, which is purely real, and $(T^{2}_{2} - T^{3}_{1}) \propto i(\alpha \beta)$, respectively. We have argued the case for the quadrupole $(\alpha \beta)$ to be small, which means $A_{2,1} \approx B_{2,2} \approx 0$ and $F_{P_{2} \sigma} \approx 0$. The ideal circular cycloid yields $t = iB_{1,1}/A_{1,0} = 0.71$. Table 2 contains a value of $B_{1,1}/A_{1,0}$ inferred from a fit to data collected at 10 K, by when it has softened and amounts to 63% of its ideal value.

- $(0, 2\tau, 0)$ Data are displayed in figure 5, together with fits to intensities derived with expressions (7). Inferred values of $A_{2,2}/A_{2,0}$ and $B_{2,1}/A_{2,0}$ in table 2 agree with predictions based on a circular cycloid, given in section 4, with the magnitude of $A_{2,2}$ small compared to $|B_{2,1}|$ and a phase difference of 90° between the two contributions. In light of the conclusion drawn in section 6, reduction at 10 K of $B_{2,1}/A_{2,0}$ to 87% of its magnitude in the ideal cycloid is consistent with (i) a partially melted cycloid and (ii) a dependence of intensity on temperature that is different for first and second harmonics. Figure 6 illustrates further the limitation of the stick-model. The azimuthal-angle dependence of the $(0, 2\tau, 0)$ reflection is strongly dependent on the energy of the incident x-rays and terms quadratic in $f_0, f_2$ in the stick-model are not compatible with such complex dependence.

6. Observations with circular polarization

- $(0, \tau, 0)$ Dependence of the primary x-rays (653 eV) corresponds to the Mn L$_2$-edge. Top panel: dependence measured as a function of the circular polarization (helicity) of the incident x-rays: normalized intensities $I_{L}/(I_{L} + I_{R})$ and $I_{R}/(I_{L} + I_{R})$. Lower panel: dependence measured with linearly polarized x-rays: normalized intensities $I_{L}/(I_{L} + I_{R})$ and $I_{R}/(I_{L} + I_{R})$. Continuous lines are fits to intensities derived from (5). For completeness, dashed lines represent the intensities $I_{L}$ and $I_{R}$ calculated from (5).

- $(0, 2\tau, 0)$ Dependence measured with linearly polarized incident x-rays: $I_{L}$ and $I_{R}$ normalized by their sum, as in figure 4. Lower panel: dependence measured with linearly polarized incident x-rays: $I_{L}$ and $I_{R}$ normalized by their sum, as in figure 4. Continuous lines are fits to intensities derived from (7).

- $(0, \tau, 0)$ Reflection at $\psi = 87°$. This behaviour amounts to

$$I = \sin^2\theta[\cos^2\phi + \frac{2}{\sqrt{2}}P_{2}\cos\theta],$$

for $\psi = 180°$. According to data in figure 7, $I \propto (C_{11}^{1} \cdot C_{11}^{1})/|C_{11}^{1} |$. This behaviour amounts to
consistent with the diffraction pattern of a cycloid. Melting of chiral order in the Mn motif is observed in our data at both the first and second harmonics of the cycloid.

We use exact results for diffraction by multipoles (of arbitrary rank) in a circular cycloid to build a minimal model of diffraction by the Mn motif. All previous discussions in the literature, of diffraction by multipoles in a circular cycloid, omit full angular anisotropy by using from the outset trivial stick-representations, e. g., a second-rank multipole (quadrupole) is represented by a product of two sticks. We are forced to consider the exact case because the stick-model does not account for the second harmonic of diffraction by TbMnO$_3$. Specifically, at the second harmonic intensity is observed in an unrotated channel of polarization, $\sigma^\prime\sigma$, for which the stick-model predicts a null result. In addition, it is shown that intensity in the rotated channel, $\pi^\prime\sigma$, possesses an azimuthal-angle dependence not allowed in the stick-model. In general, the first harmonic of diffraction by a cycloid can have contributions from quadrupoles. The quadrupoles permit Templeton and Templeton scattering absent when constituent quadrupoles are reduced to products of sticks.

We hope our work motivates ab initio simulations of the energy dependence of the second harmonic as it could shed light on the modification of electronic structure occurring at the onset of the polar phase.

7. Conclusions

Chiral order in a material is unambiguously detected by a probe with a matching characteristic, and we have used circularly polarized x-rays to detect such order in a single crystal of terbium manganate (TbMnO$_3$). Likewise, tuning the energy of x-rays to an atomic resonance of a manganese ion, the Mn $L_{2,3}$-edges, means these ions and no others participate in the chiral order. Diffraction as a function of rotation about the Bragg wavevector—an azimuthal-angle scan—is entirely

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