Magnetic properties of Sohncke-type Pb(TiO)$Cu_4(PO_4)_4$ exposed by resonant x-ray Bragg diffraction

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The enantiomorphous (chiral) crystal class of Sohncke-type Pb(TiO)$Cu_4(PO_4)_4$ permits the rotation of the plane of polarization of light (optical activity). Copper ions participate in noncollinear antiferromagnetic order below a temperature ≈ 7 K, with magnetoelectric and piezomagnetic effects permitted. Crystal and magnetic symmetries of Pb(TiO)$Cu_4(PO_4)_4$ are fully incorporated in calculated resonant x-ray Bragg diffraction patterns that are successfully compared with existing limited experimental data [Misawa *et al.*, Phys. Rev. B **103**, 174409 (2021)]. Specifically, there is additional intensity of a Bragg spot (a chiral signature) from circular polarization (helicity) in the primary beam of x rays. The chiral signature is shown to arise from Cu axial magnetic dipoles, with the prospect of future experiments revealing interference between magnetic dipoles and (Templeton-Templeton) chargelike quadrupoles. An expression for the additional intensity used by Misawa *et al.* does not respect magnetic symmetry, and our symmetry-informed answer overturns their principal conclusions about chirality and magnetic order. Dirac quadrupoles and octupoles are potentially strong sources of diffraction when the reflection vector is parallel to the unique direction in the tetragonal lattice. Notably, a Dirac quadrupole is a parity- and time-odd atomic multipole unlike a multisite spin entity previously mentioned in the context of Pb(TiO)$Cu_4(PO_4)_4$ [Kimura *et al.*, Phys. Rev. B **97**, 134418 (2018)].

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I. INTRODUCTION

The structural symmetry of crystals permits optical activity (rotation of the plane of polarization of light) in only 15 of the 32 crystal classes. There are 11 enantiomorphous classes and four nonenantiomorphous classes [1–3]. The Sohncke-type structure of the compound Pb(TiO)$Cu_4(PO_4)_4$ of immediate interest belongs to the enantiomorphic crystal class 422 [4]. Copper ions form a noncentrosymmetric antiferromagnetic structure using the crystal class $4'22'$ below a Néel temperature ≈ 7 K [4]. Bulk magnetic properties include magnetoelectric (ME) and piezomagnetic (PM) effects. In more detail, a Landau free energy compatible with $4'22'$ includes nonlinear contributions in electric (E) and magnetic (H) fields. The latter are forbidden in crystal classes that contains anti-inversion ($\overline{1'}$), e.g., centrosymmetric compounds Cr_2O_3 (trigonal, magnetic crystal class $\overline{3}'m'$ [5]), GdB_4 (tetragonal, $4/m'm'm'$ [6]) and $Co_2V_2O_7$ (monoclinic, $2/m'$ [7]). Anti-inversion in the magnetic crystal class imposes PT-symmetry, and it protects x-ray diffraction patterns from circular polarization (helicity) in the primary beam. The protection is absent in the crystal class $4'22'$. We calculate the intensity circular polarization brings to a Bragg spot in the diffraction pattern, and refer to it as a chiral signature (ϒ) for Pb(TiO)$Cu_4(PO_4)_4$.

In our view, knowledge of the magnetic properties of Pb(TiO)$Cu_4(PO_4)_4$ is in disarray after publication of a faulty analysis of resonant x-ray Bragg diffraction patterns [8]. We revisit diffraction amplitudes for Pb(TiO)$Cu_4(PO_4)_4$ to argue our position. To this end, we use the established magnetic structure [4], and a theory of resonant x-ray Bragg diffraction derived with standard Racah algebra for atomic multipoles [9–11]. The theory is compatible with tried and tested sum rules in dichroic signals [12,13]. This desirable attribute is not fully realized in a phenomenological theory used by Misawa *et al.* [8] that contains free parameters and a constraint to cylindrical Cu site symmetry [14–17]. In consequence, diffraction amplitudes are not compatible with the full magnetic symmetry of Sohncke-type Pb(TiO)$Cu_4(PO_4)_4$ in which Cu ions use sites devoid of symmetry. Perils from using the theory in Ref. [14] with its cylindrical site symmetry are explicit in diffraction amplitudes calculated for terbium manganate [17]. Moreover, the particular application of the theory contains a nontrivial error [8]. According to our calculations, available diffraction data are not manifestations of crystal chirality (handedness) and magnetic quadrupole interference [4,8]. Returning to our elected theory, electronic multipoles therein can be estimated using an atomic wave function for the resonant ion [18–20], and simulations of electronic structure [21,22].

II. LATTICE AND MAGNETIC SYMMETRIES

The parent lattice for Pb(TiO)$Cu_4(PO_4)_4$ is $P42_12$ (tetragonal, No. 90, crystal class 422) [4]. Copper ions Cu^{2+} occupy

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general sites 8*g* devoid of symmetry, and coordinates $x \approx 0.267$, $y \approx 0.981$, $z \approx 0.401$ [4]. Inversion, mirror, improper rotations, and glide symmetries are absent in Sohncke lattices. A neutral screw axis 2_1 in $P42_12$ is achiral while the atomic structure around the axis is chiral [23]. (Of the 65 Sohncke lattices primitive ones are chiral and centered ones are not. Orthorhombic and lower symmetry lattices do not contain one of 11 enantiomorphous pairs and the related space groups are achiral.) Below a temperature ≈ 7 K, axial copper magnetic dipoles possess antiferromagnetic order described by the magnetic space group $P4'2_12'$ (No. 90.97, crystal class $4'22'$ [24]). We have established that this space group is equivalent to the irreducible representation Γ_2 deduced from an analysis of a magnetic neutron diffraction pattern [4]. The chemical and magnetic structures of $Pb(TiO)Cu_4(PO_4)_4$ are not centrosymmetric, not polar, and not compatible with ferromagnetism. Noncollinear magnetic order has a propagation vector = (0, 0, 0). Notably, the magnetic structure of an altermagnet possesses a zero propagation vector, but it is a collinear centrosymmetric antiferromagnet [25]. For such an altermagnet, a chiral signature and a PM effect are allowed, and a linear ME effect is forbidden [26].

III. RESONANT X-RAY BRAGG DIFFRACTION

X-ray diffraction patterns gathered on crystalline materials can contain Bragg spots that do not exist in patterns created by spheres of atomic charge located at points on the particular lattice. Their inherent weakness is offset by tuning the energy of primary x-rays from a synchrotron source to a specific atomic resonance [14–20]. The weak Bragg spots are not indexed by Miller indices for the lattice symmetry, i.e., they are space-group forbidden. Departures from spheres of atomic charge are usually labeled by components of an axial chargelike quadrupole (multipole rank = 2) that are invariant with respect to operations in the symmetry of sites occupied by the resonant ions (Neumann's principle [27,28]). Specifically, acentric sites such as those occupied by Cu ions in $Pb(TiO)Cu_4(PO_4)_4$ can harbor polar (parity-odd) multipoles that are chargelike (time-even) or magnetic (time-odd Dirac multipoles) [10,20,29,30].

States of x-ray polarization, Bragg angle θ, and the plane of scattering are shown in Fig. 1. A conventional labeling of linear photon polarization states places $\sigma = (0, 0, 1)$ and $\pi = (\cos(\theta), \sin(\theta), 0)$ perpendicular and parallel to the plane of scattering, respectively [10]. Secondary states are $\sigma' = \sigma$ and $\pi' = (\cos(\theta), -\sin(\theta), 0)$. The x-ray scattering length in the unrotated channel of polarization $\sigma'\ \sigma'$, say, is modeled by $(\sigma'\sigma)/D(E)$. In this instance, the resonant denominator is replaced by a sharp oscillator $D(E) = [E - \Delta + i\Gamma/2]/\Delta$ with the x-ray energy E in the near vicinity of an atomic resonance Δ of total width Γ, namely, $E \approx \Delta$ and $\Gamma << \Delta$. The cited energy-integrated scattering amplitude $(\sigma'\sigma)$, one of four amplitudes, is studied using standard tools and methods from atomic physics (Racah algebra) and crystallography [10,31]. A vast spectrum of virtual intermediate states makes the x-ray scattering length extremely complicated [19,20]. It can be truncated following closely steps in celebrated studies by Judd and Ofelt of optical absorption intensities of rare-earth ions [32,33]. An intermediate level of truncation used here reproduces sum rules for axial dichroic signals created by electric dipole - electric dipole (E1-E1) or electric quadrupole - electric quadrupole (E2-E2) absorption events [9,12,13]. The attendant calculation presented in Ref. [31] and Sec. 5.2 in Ref. [10] is lengthy and demanding. Here, we implement universal expressions for scattering amplitudes and reduce notation using $(\sigma'\sigma) \equiv F_{\sigma'\sigma}$, etc., for an amplitude $F_{\sigma'\sigma}$ listed by Scagnoli and Lovesey, Appendix C in Ref. [11]. A similar analysis exists for polar absorption events such as E1-E2 (Appendix D in Ref. [11]), and E1-M1 where M1 is the magnetic moment [34,35].

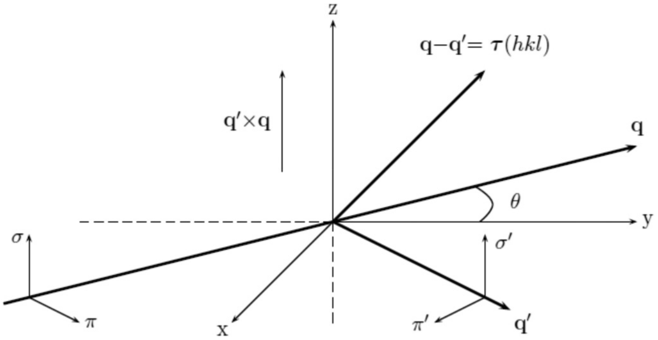

FIG. 1. Primary (σ, π) and secondary (σ', π') states of x-ray polarization. Corresponding wave vectors **q** and **q**′ subtend an angle 2θ. The Bragg condition for diffraction is met when $\mathbf{q} - \mathbf{q}'$ coincides with a reflection vector $\boldsymbol{\tau}(h, k, l)$. Lattice vectors (a, b, c) and the depicted Cartesian (x, y, z) coincide in the nominal setting of the crystal, and the beginning $\psi = 0$ of an azimuthal angle scan (rotation of the crystal by an angle ψ about the reflection vector).

Electronic degrees of freedom of Cu ions are encapsulated in spherical multipoles $\langle O^K_Q \rangle$, with rank K and (2K + 1) projections in the interval $-K \leqslant Q \leqslant K$. Cartesian and spherical components Q = 0, ±1 of a vector $\mathbf{n} = (a, b, c)$, for example, are related by $a = (n_{-1} - n_{+1})/\sqrt{2}$, $b = i(n_{-1} + n_{+1})/\sqrt{2}$, $c = n_0$. Complex conjugation of a multipole denoted by * is defined as $\langle O^K_Q \rangle^* = (-1)^Q \langle O^K_{-Q} \rangle$, meaning the diagonal multipole $\langle O^K_0 \rangle$ is purely real. The phase convention for real and imaginary parts labelled by single and double primes is $\langle O^K_Q \rangle = [\langle O^K_Q \rangle' + i\langle O^K_Q \rangle'']$. Whereupon, $\langle O^1_a \rangle = -\sqrt{2}\langle O^1_{+1} \rangle'$ and $\langle O^1_b \rangle = -\sqrt{2}\langle O^1_{+1} \rangle''$. For the most part, we follow Misawa *et al.* and implement an E1-E1 absorption event at the Cu L_3 absorption edge ($2p \rightarrow 3d$, $E \approx 930$ eV) [8]. The reduced matrix element of appropriate parity-even multipoles $\langle T^K_Q \rangle$ with K = 0, 1, 2 and a time signature $\sigma_\theta = (-1)^K$ appears in Sec. 5. 2 of Ref. [10]. Weaker parity-odd E1-E2 and E1-M1 absorption events occur at different energies [16].

IV. DIFFRACTION AMPLITUDES AND CHIRAL SIGNATURES

An electronic structure factor,

$$\Psi^K_Q = \left[\exp(i\kappa \cdot \mathbf{d})\langle O^K_Q \rangle_d\right], \tag{1}$$

specifies a Bragg diffraction pattern for a reflection vector $\boldsymbol{\kappa}$ defined by integer Miller indices (h, k, l). The implied sum in Eq. (1) is over 8g sites **d** used by Cu ions. See the Appendix for details concerning the calculation of Ψ^K_Q for $P4'2_12'$ (No.

90.97, crystal class 4′22′ [24]). Scattering amplitudes used here are derived directly from Ψ^K_Q and expressions listed by Scagnoli and Lovesey [11].

For a diffraction vector (0, 0, l) and a generic multipole $\langle \mathrm{O}^{\mathrm{K}}_{\mathrm{Q}} \rangle$ [24],

$$\Psi^{\mathrm{K}}_{\mathrm{Q}}(0,\ 0,\ l) = [1 + (-1)^{\mathrm{Q}} + 2\sigma_\theta \cos(\pi \mathrm{Q}/2)]\big[\gamma \langle \mathrm{O}^{\mathrm{K}}_{\mathrm{Q}} \rangle + \gamma^* (-1)^{\mathrm{K}} \langle \mathrm{O}^{\mathrm{K}}_{-\mathrm{Q}} \rangle\big], \tag{2}$$

with $\gamma = \exp(i2\pi l z)$. The first factor in Eq. (2) imposes $\Psi^K_Q(0, 0, l) = 0$ for odd Q. The structure factor is also zero for Q = 0 and an odd time-signature [magnetic $\sigma_\theta = -1$]. In consequence, axial magnetic dipoles $\langle \mathbf{T}^1 \rangle$ that are parity-even and time-odd, and anapoles that are parity- and time-odd do not participate in diffraction for a wave vector (0, 0, l). [A vector product (**R** × **S**) where **R** and **S** are electronic space (time-even and polar) and spin (time-odd and axial) variables, respectively, represents a spin anapole (Dirac dipole), for example.] Evidently, there are no forbidden reflections of the type (0, 0, l), and parity-even amplitudes $(\sigma'\sigma)$ and $(\pi'\pi)$ are dominated by charge (Thomson) scattering [10,11]. Even so, interesting information on the magnetic structure can reside in the channel with rotated polarization. The parity of $\langle \mathrm{O}^{\mathrm{K}}_{\mathrm{Q}} \rangle$ is absent in Eq. (2), and the electronic structure factor is valid for axial and polar absorption events. One finds $(\pi'\sigma) = 0$ for an E1-E1 event [11]. The amplitude for rotated polarization can be different from zero using Dirac multipoles, however. These multipoles for an E1-E2 event are denoted by $\langle \mathrm{G}^{\mathrm{K}}_{\mathrm{Q}} \rangle$ with K = 1–3, and $\langle \mathbf{G}^1 \rangle$ an aforementioned anapole [10,11,20]. Kimura *et al.* [4] invoke a magnetic quadrupole in their study of $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$ defined by multisite spins. This entity is unrelated to an atomic quadrupole $\langle \mathrm{G}^2_{\mathrm{Q}} \rangle$ in our theory of E1-E2 diffraction amplitudes [10,11,20]. The result

$$\begin{aligned}(\pi'\sigma)_{12} &\\ &= \surd(2/15)\cos^2(\theta)\big[\gamma' \cos(2\psi)\big\{\langle \mathrm{G}^2_{+2} \rangle' + 2\surd 2 \langle \mathrm{G}^3_{+2} \rangle''\big\} \\ &\quad + i\gamma'' \sin(2\psi)\big\{-\langle \mathrm{G}^2_{+2} \rangle'' + 2\surd 2 \langle \mathrm{G}^3_{+2} \rangle'\big\}\big],\end{aligned} \tag{3}$$

follows directly from expressions listed in Appendix D of Ref. [11] after setting $\sigma_\theta = -1$ and K = 2, 3 in Eq. (2). The crystal b axis is in the plane of scattering for $\psi = 0$. Subscripts 12 on the amplitude in Eq. (3) denote an E1-E2 absorption event. Intensity of a Bragg spot $|(\pi'\sigma)_{12}|^2$ is a fourfold periodic function of the azimuthal angle ψ, in keeping with (0, 0, l) parallel to the unique direction in the tetragonal structure. The intensity in question is absent in the paramagnetic phase of $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$, and we reiterate that an explicit calculation yields $(\pi'\sigma) = 0$ for an E1-E1 event and a diffraction vector (0, 0, l).

The conditions on Q in Eq. (2) are not universal for Sohncke-type lattices. For orthorhombic $\mathrm{P2_12_12_1}$ (No. 19) and cubic $\mathrm{P2_13}$ (No. 198), for example, the condition on Q is even $(l + Q)$ [36]. Space group No. 19 describes many molecular compounds. $\mathrm{NaClO_3}$ and $\mathrm{NaBrO_3}$ use the cubic No. 198 lattice, and possess the same chirality yet opposite senses of optical rotation.

The electronic structure factor for a reflection vector (h, 0, 0),

$$\begin{aligned}\Psi^{\mathrm{K}}_{\mathrm{Q}}(h,\ 0,\ 0) = {}& \langle \mathrm{O}^{\mathrm{K}}_{\mathrm{Q}} \rangle [\{\alpha + \alpha^*(-1)^{\mathrm{Q}}\} + \sigma_\theta (-1)^h \exp(-i\pi \mathrm{Q}/2)\{\beta + \beta^*(-1)^{\mathrm{Q}}\}] \\ &+ \langle \mathrm{O}^{\mathrm{K}}_{-\mathrm{Q}} \rangle (-1)^{h+K} [\{\alpha + \alpha^*(-1)^{\mathrm{Q}}\} + \sigma_\theta (-1)^h \exp(i\pi \mathrm{Q}/2)\{\beta + \beta^*(-1)^{\mathrm{Q}}\}],\end{aligned} \tag{4}$$

possesses space group forbidden reflections, i.e., $\Psi^{\mathrm{K}}_0(h, 0, 0) = 0$ for even K, $\sigma_\theta = +1$, and odd h. Spatial phase factors $\alpha = \exp(i2\pi h\mathrm{x})$ and $\beta = \exp(i2\pi h\mathrm{y})$.

In practice, our chiral signature Υ is the measured difference in intensities of a Bragg spot observed with oppositely handed primary x rays. Thus, Υ and XMCD signals are alike with regard to polarization requirements. For (h, 0, 0) with odd h and an E1-E1 [$\sigma_\theta = (-1)^{\mathrm{K}}$] absorption event

$$\begin{aligned}\Upsilon(h,\ 0,\ 0) &= [(\pi'\pi)^*(\pi'\sigma)]'' \\ &= (1/\surd 2)\cos(\theta)\sin(2\theta)\big[-\mathrm{A_0A_1} + 2\sin(2\psi)\big\{\mathrm{A_0}(\alpha' + \beta')\langle \mathrm{T}^2_{+2} \rangle'' - \mathrm{A_1}\big(\alpha''\langle \mathrm{T}^2_{+1} \rangle' - \beta''\langle \mathrm{T}^2_{+1} \rangle''\big)\big\}\big].\end{aligned} \tag{5}$$

The definition of Υ anticipates $(\sigma'\sigma) = 0$, and $(\pi'\pi)^*$ is the complex conjugate of $(\pi'\pi)$. Axial magnetic dipoles in Eq. (5) are $\mathrm{A_0} = [4(\alpha' + \beta')\langle \mathrm{T}^1_{\mathrm{c}} \rangle]$ and $A_1 = [2\surd 2(\alpha''\langle \mathrm{T}^1_{\mathrm{b}} \rangle - \beta''\langle \mathrm{T}^1_{\mathrm{a}} \rangle)]$. The crystal c axis is normal to the plane of scattering at the start of the azimuthal angle $\psi = 0$. Parity-even E1-E1 diffraction amplitudes for (h, 0, 0) and odd h are

$$\begin{aligned}&(\sigma'\sigma) = 0,\ (\pi'\pi) = \sin(2\theta)[(i/\surd 2)\cos(\psi)\mathrm{A_0} + \sin(\psi)\mathrm{A_1}], \\ &(\pi'\sigma) = \cos(\theta)[-(i/\surd 2)\sin(\psi)\mathrm{A_0} + \cos(\psi)\mathrm{A_1} - \cos(\psi)\mathrm{B_1} + i\sin(\psi)\mathrm{B_2}].\end{aligned} \tag{6}$$

Chargelike quadrupoles (nonmagnetic Templeton-Templeton multipoles) are $\mathrm{B_1} = [4i\{\alpha''\langle T^2_{+1} \rangle' - \beta''\langle T^2_{+1} \rangle''\}]$ and $B_2 = [4i(\alpha' + \beta')\langle T^2_{+2} \rangle'']$. Rotated amplitudes $(\pi'\sigma)$ and $(\sigma'\pi)$ are related by a change in sign of the magnetic dipoles.

Misawa *et al.* [8] report Bragg spot intensities and simulation data [22] for a reflection vector (1, 0, 0) and an azimuthal angle $\psi = 0$. Notably, they observe a chiral signature in the magnetic phase of $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$ with a sample temperature = 6 K (Néel temperature ≈ 7 K). According to Eq. (5) the chiral signature $\Upsilon(1, 0, 0)$ at $\psi = 0$ is a product of magnetic dipoles. The corresponding expression for the chiral signature offered by Misawa *et al.* [8] violates magnetic symmetry and it is fundamentally different from Eq. (5). For simplicity, compare Eq. (19) for the chiral signature in Ref. [8] with the value of $\Upsilon(h, 0, 0)$ for $\psi = 0$. The latter is proportional to a product of axial dipoles $\mathrm{A_0} \propto \langle T^1_{\mathrm{c}} \rangle$ and

A_1. By contrast, Eq. (19) in Ref. [8] includes the product of $\langle T_c^1 \rangle$ and a Templeton-Templeton quadrupole denoted F_2 in Eq. (8) in [8]. Correction of the chiral signature destroys the claim to have observed interference between a magnetic dipole and a nonmagnetic quadrupole [Templeton-Templeton or anisotropy of the susceptibility tensor (ATS) scattering], and negates evidence for chirality and magnetic quadrupole order in $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$ Misawa *et al.* [8]. An error in the algebra for their chiral signature leads to an erroneous factor $\cos(2\psi)$ multiplying the product of dipoles. Moving to the paramagnetic phase and axial dipoles $\mathrm{A}_0 = \mathrm{A}_1 = 0$, experimental data and simulation results displayed in Fig. 2(d) in Ref. [8] are consistent with $|(\pi'\sigma)|^2$ in Eq. (6) if quadrupoles therein satisfy $|B_1| >> |B_2|$. Misawa *et al.* [8] arrive at a similar conclusion.

Hexagonal $\mathrm{P6_3 2'2'}$ (No. 182.183, $62'2'$) is an example of a magnetic Sohncke-type structure that possesses a chiral signature akin to Eq. (5) using higher-order multipoles. For a hexagonal lattice an E2-E2 event [$\sigma_\theta = (-1)^{\mathrm{K}}$] is needed, because projections on multipoles $\langle \mathrm{T}^{\mathrm{K}}_{\mathrm{Q}} \rangle$ for a reflection vector $(0, 0, l)$ with odd l are restricted to $\mathrm{Q} = \pm 3$. The corresponding chiral signature is a sum of octupoles $[\langle T^3_{+3} \rangle' \langle T^3_{+3} \rangle'']$ and a product of octupoles and hexadecapoles ($\mathrm{K} = 4$). Notably, magnetic crystal classes $4'22'$ used for $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$ and $62'2'$ possess identical Landau free energies $\approx$ [EH + EHH + HEE].

V. CONCLUSIONS

In summary, we have investigated the magnetic properties of Sohncke-type $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$ using scattering amplitudes for resonant x-ray Bragg diffraction by the 3d-transition metal ion [10,23]. Our symmetry-informed results use the magnetic space group $\mathrm{P4'2_1 2'}$ (No. 90.97, magnetic crystal class $4'22'$ [24]) inferred from published neutron diffraction patterns (Supplemental Material for Ref. [4]). Regarding the theory of resonant x-ray diffraction, the spectrum of virtual intermediate states in the photon scattering length is truncated using the method pioneered by Judd and Ofelt for optical absorption intensities of rare-earth ions [31,32,33,37]. Sum-rules for parity-even dichroic signals are completely accounted for in the electronic multipoles of the resonant ions [10,12,13].

A predicted magnetic chiral signature Eq. (5) accords with limited diffraction patterns using handed (helical) x rays [8]. Future measurements can test changes to the signature with rotation of the crystal about the reflection vector (an azimuthal angle scan) and thereby pronounce on the worthiness of the magnetic space group $\mathrm{P4'2_1 2'}$ for $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$. Measured and calculated paramagnetic diffraction agree when one set of quadrupoles dominate. According to a calculation of the amplitude in the rotated channel of photon polarization [denoted $(\pi'\sigma)$ in Fig. 1], there is no diffraction enhanced by an electric dipole– electric dipole (E1-E1) event for a reflection vector parallel to the unique direction of the tetragonal structure. Diffraction by Dirac multipoles is allowed for this special reflection vector, however, and we predict intensity expected from the polar electric dipole - electric quadrupole (E1-E2) absorption event. Dirac multipoles are local and single-site (parity- and time-odd) unlike a multisite spin entity mentioned in the context of $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$, cf. line 7 on p. 2 in Ref. [4].

Our diffraction patterns for an E1-E1 event overturn conclusions presented by Misawa *et al.*; specifically, the claim in the title of their paper to have evidence of chirality and magnetic quadrupole order in $\mathrm{Pb(TiO)Cu_4(PO_4)_4}$ is unfounded. In Sec. IV.F of their paper, Misawa *et al.* [8] submit that their measured magnetoelectric-cooling effect on circular dichroism is linked to magnetic quadrupole order. To this end, the authors appeal to interference in diffraction between axial magnetic dipoles and a Templeton-Templeton quadrupole (ATS scattering), alongside a nebulous magnetic quadrupole defined by multisite spins [4]. It is an artefact of diffraction amplitudes that are manufactured and unfaithful to magnetic symmetry; see Sec. IV.C and Eq. (17) therein [8]. No such interference exists in diffraction amplitudes for magnetic space group $\mathrm{P4'2_1 2'}$ inferred from magnetic neutron Bragg diffraction [4]. A direct connection between the atomic multipole view used in the present study and the extended multipole view used by Misawa *et al.* [8] is beyond the scope of the present study.

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APPENDIX: ELECTRONIC STRUCTURE FACTOR

General sites 8g used by copper ions in tetragonal $\mathrm{P4'2_1 2'}$ (No. 90.97) are devoid of symmetry. In a unit cell they are related by translations, and rotations and antirotations referred to Cartesian coordinates (x, y, z) with the z axis aligned with crystal c axis. Specifically [24], $4'^{\pm}_z = \sigma_\theta\, 4^{\pm}_z$, 2_x, 2_y, 2_z, $2'_{x+y}$, $2'_{x-y}$, with, for example, $2_{x+y}(\mathrm{x, y, z}) = (\mathrm{y, x, -z})$ and $2'_{x+y}$ $\langle \mathrm{O}^{\mathrm{K}}_{\mathrm{Q}} \rangle = \sigma_\theta (-1)^{\mathrm{K}} \exp(i\pi \mathrm{Q}/2)\, \langle \mathrm{O}^{\mathrm{K}}_{-\mathrm{Q}} \rangle$. The electronic structure factor $\Psi^K_Q(\mathrm{P4'2_1 2'})$ is a sum of four $\langle \mathrm{O}^{\mathrm{K}}_{\mathrm{Q}} \rangle$ and four $\langle \mathrm{O}^{\mathrm{K}}_{-\mathrm{Q}} \rangle$ with coefficients that depend on Miller indices and general coordinates listed in Sec. II. Equations (2) and (4) apply to reflection vectors $(0, 0, l)$ and $(h, 0, 0)$, respectively.

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