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Calculated chiral and magneto-electric dichroic signals for copper metaborate (CuB$_2$O$_4$) in an applied magnetic field

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Abstract

Expressions for dichroic signals in terms of electron multipoles have been used to analyse optical data gathered on a crystal of copper metaborate in the presence of a magnetic field. Calculated signals comply with the established crystal and magnetic structures of CuB$_2$O$_4$, and respect the global symmetries of parity-even and parity-odd dichroic signals in full. We have success in describing five different experiments in total. The claim by Saito et al (2008 Phys. Rev. Lett. 101 117402) that they observe magnetic control of crystal chirality in one of their five experiments is challenged.

1. Introduction

We examine the recent claim by Saito et al [1] that a magnetic field can control the chirality of a crystal. This is counterintuitive because a magnetic field does not couple to chirality, a pseudo-scalar electron variable, and a magnetic field does not resolve an enantiomorph from a racemic mixture. While an electric field can change the electronic structure of a material an applied magnetic field cannot effect this change, unless the magnetic field is strong enough to threaten the integrity of the material. Thus, alleged control of chirality in a crystal that supports long-range magnetic order by application of a modest static magnetic field [1] is at odds with established wisdom.

Evidence for the claim is an apparent dependence of a dichroic signal, measured with a crystal of copper metaborate (CuB$_2$O$_4$), on an external magnetic field; for fields applied parallel to the crystal $a$-axis and the $b$-axis the signal in question has equal magnitude and opposite sign [1]. The authors assume that this signal is exclusively natural circular dichroism (NCD) created by an E1–M1 absorption event, which indeed contains the chirality, or enantiomorphism, of the material. If different from zero, NCD is equal in magnitude and opposite in sign for structures related by a mirror operation, i.e., an enantiomorphic space-group pair. An examination we report, of all dichroic signals allowed for copper metaborate in the presence of a magnetic field, shows the claim by Saito et al [1] is not correct. Instead, linear dichroism (LD), from the electron variable responsible for Templeton and Templeton scattering in x-ray diffraction, is a most likely source of the observed signal.

The crux of our rebuttal of the claim by Saito et al [1] starts with the fact that NCD relates to a ground state, time-even and polar property of electrons, which does not depend on the polarity of a magnetic field, added to the following findings applicable to CuB$_2$O$_4$. Our calculations show that copper metaborate subject to a magnetic field in the $a$–$b$ plane is described by an orthorhombic point-group, whereas the eleven enantiomorphic space-group pairs do not include an orthorhombic structure. Furthermore, the point-group appropriate to a field along the $a$-axis ($b$-axis) of copper metaborate is $222'$ ($22'$), or $22'$,$22'$. Since the operation of time reversal (denoted by a prime) does not change electron properties in NCD calculated values of this signal for $222$ and magnetic $22'$,$22'$, point-groups are the same. Crystals belonging to class $222$ allow NCD and they can exist in two different forms which are mirror images of one another. A magnetic field cannot execute a transition of one form to its mirror image because a magnetic field does not couple to chirality, which is the relevant order-parameter for such a transition.
At room temperature, copper metaborate has the tetragonal structure described by space-group #122 and point-group $D_{2d}$. Néert et al [2] have studied structural and dielectric properties of the material. In zero magnetic fields, they find no evidence of a structural phase-transition with the onset of long-range magnetic order at 21 K, and identical temperature behaviour of the dielectric constants along $a$- and $b$-axes. Absence of dielectric anomalies implies that electric polarization is zero in the paramagnetic and ferromagnetic phases. Ferroelectricity in $D_{2d}$ is forbidden, while optical activity is allowed even though it is not an enantiomorphic point-group.

Petarkovskii et al [3] made a complete characterization of magnetic properties of copper metaborate. Specific heat and susceptibility data demonstrate two magnetic phase-transitions at 21 and 10 K. From magnetization measurements, copper metaborate is a weak ferromagnet in the interval of temperatures bracketed by 21 and 10 K. Later work [4], with neutron diffraction, showed a commensurate canted antiferromagnetic motif.

2. Point-groups

Because dichroic signals are bulk quantities, they are subject to selection rules in the point-group. The point-group of a crystal in a magnetic field is the intersection of the grey group, created by addition of time reversal to the non-magnetic point-group ($D_{2d}$), and the point-group of the magnetic field. One finds: (I) field parallel to $[1, 0, 0]$ point-group $22^2$; (II) field parallel to $[0, 1, 0]$ point-group $2'22'$; (III) field parallel to $[1, 1, 0]$ point-group $m'm'm'$; (IV) field parallel to $[1, 1, 0]$ point-group $m'm'm'$. The point-group is specified in crystal axes $[1, 0, 0], [0, 1, 0], [0, 0, 1]$ when the field is along a cell edge. Different axes are used for the point-group when the field is parallel to a diagonal in the $a$–$b$ plane, namely, $[1, 1, 0], [1, 1, 0], [0, 0, 1]$. The four point-groups are orthorhombic. 222 is enantiomorphic and allows optical activity, and ferroelectricity is possible in 222 while ferroelectricity is forbidden. $m'm'm'$ is one of four point-groups that are not enantiomorphic but allow optical activity. The point-group $m'm'm'$ may exhibit ferroelectricity and ferroelectricity, with the polar moment parallel to the $c$-axis.

3. Dichroic signals

Dichroic signals can be expressed in terms ground-state properties of the electrons called atomic multipoles, which have a rank $K$ with $K = 0$ (scalar or monopole), $K = 1$ (dipole), $K = 2$ (quadrupole), etc. A parity-even multipole is unchanged by inversion, $I$, whereas the inversion operation changes the sign of parity-odd multipoles. A parity-even multipole of rank $K$ subjected to time reversal, $\theta$, acquires a factor $(-1)^K$, whereas the parity-odd, time-even multipole (ungerade) is unchanged by $\theta$ and the parity-odd, time-odd multipole (gerade) acquires a factor $-1$. Thus a Gerade multipole is unchanged by the compound operation $I \theta$, which is why a Gerade multipole is labelled a magneto-electric multipole. An Ungerade multipole is a polar multipole. Notable are polar and magneto-electric multipoles of even rank because they behave as pseudo-tensors. In particular, the polar monopole is a measure of chirality, and the magneto-electric monopole is analogous to magnetic charge.

Equivalent operators for the spherical tensors associated with parity-odd multipoles can be constructed from the position operator, $R$, and the magnetic moment operator, $\mu = L + 2S$. For example, equivalent operators for the polar monopole (chirality) and dipole ($K = 1$) are a scalar ($\Omega \cdot \mu$) and $R$, respectively, where $\Omega = (\mu \times R - R \times \mu)$ is an anapole operator, which is both time-odd and parity-odd. Magneto-electric monopole (magnetic charge) and dipole operators can be represented by $(\mu \cdot R)$ and $\Omega$, respectively.

Central in expressions for dichroic signals is the structure factor $\Psi_{K,Q}(j)$ where $Q$ is the projection ($-K \leq Q \leq K$), and $j$ labels the multipole type, namely, parity-even, polar or magneto-electric. The structure factor is a sum over sites in the unit cell used by ions, which contribute appropriate multipoles to $\Psi_{K,Q}(j)$, and it embodies all symmetries of the cell. For future use, note that rotation of the crystal through an angle $\psi$ about the $c$-axis introduces a factor $\exp(i\psi Q)$ to $\Psi_{K,Q}(j)$.

Lovesey et al [5] and Collins et al [6] provide expressions for dichroic signals used here. The expressions record the dependence of signals on polarization in the beam of light and the angular dependence. Evaluated for any material, our expressions for dichroic signals are purely real. Properties emanating from the real part of the refractive index, birefringent dispersion and optical rotatory dispersion, Faraday rotation and the quadratic magneto-optic (Cotton–Mouton) effect are not calculated.

Selection rules on signals arise from radial and angular matrix elements that are not explicitly displayed [5, 6]. We note that the M1 operator is the magnetic moment and not, as often stated, solely orbital angular momentum.) In common with all parity-odd absorption events, a necessary condition for non-zero E1–M1 is that the equilibrium state of the resonant ion is a mixture of states of even and odd parity. A number of mechanisms, including, odd-order components of the electric crystal-potential, configuration interactions, and covalent bonding generate such mixed states. Additionally, the equilibrium state must contain an orbital with the same angular momentum as the intermediate state from which an electron is photo-ejected, since the magnetic moment operator does not connect states with different orbital angular momentum, and the orbitals in question must have non-zero overlap, e.g., orbitals within one atomic shell and orbitals centred on different sites in the crystal.

Both E1–E2 and E1–M1 dichroic signals possess the global symmetries that are evident in the following expressions. One point of detail in which the two parity-odd signals differ is the rank of contributing tensors; $K = 0, 1$, and 2 for E1–M1 while $K = 1, 2$, and 3 for E1–E2. In the following, we consider an E1–M1 resonant event to be the most likely source of a parity-odd contribution to optical dichroic signals. The Cu d–d resonant process in CuB2O4 proposed by Saito et al [7], Saito et al [1] and Arima [8] as the source of their dichroic signals does not satisfy conditions necessary for a non-zero E1–M1 event.
Polarization is in terms of Stokes parameters; $P_z$ is helicity (a pseudo-scalar) and $P_3$ linear polarization. The coordinate system $(x, y, z)$ for the experiment has the wavevector, $q$, parallel to the $z$-axis and linear polarization $P_3 = +1$ (often labelled $\sigma$-polarization) parallel to the $x$-axis. Orthonormal crystal axes $(a, b, c)$ nominally coincide with $(x, y, z)$.

Two dichroic signals are created by a parity-even absorption event, namely, linear dichroism (LD) and magnetic circular dichroism (MCD). Associated parity-even multipoles are labelled $t$. For the E1–E1 event, $\text{LD} = P_3(\Psi_{2,2}(t) + \Psi_{2,-2}(t))$, and $\text{MCD} = n P_3 \Psi_{1,0}(t)$, where $n = q_z/|q|$. Quadrupoles in LD are also responsible for Templeton and Templeton scattering, while MCD is related to the ferromagnetic component in the distribution of magnetization.

Parity-odd absorption creates three signals, natural circular dichroism (NCD), magnetic chiral dichroism ($\text{M}_D$) and non-reciprocal linear dichroism (NRLD). Multipoles labelled $u$ (Ungerade) are parity-odd and time-even, and multipoles labelled $g$ (Gerade) are parity-even and time-odd. For the E1–M1 event, $\text{NCD} = P_3(\sqrt{2}\Psi_{0,0}(u) - \Psi_{2,0}(u))$, $\text{M}_D = n \Psi_{1,0}(g)$, and $\text{NRLD} = i n P_3(\Psi_{2,-2}(g) - \Psi_{2,2}(g))$.

NCD and the chirality of the crystal are related, and those not belonging to the enantiomorphic crystal class show no NCD signal. Anapoles contribute $\text{M}_D$. A motif of parity-odd and time-odd quadrupoles generates NRLD. Arima [8] and Kubota et al [9] call the sum of $\text{M}_D$ and NRLD, the two signals related to magneto-electric multipoles, directional dichroism.

The five expressions for dichroic signals given above apply to $q$ parallel to the $c$-axis and $\sigma$-polarization along the $a$-axis. NCD has cylindrical symmetry and it does not change with rotation of the crystal about the beam. This property of NCD is required by its dependence on circular polarization, which has cylindrical symmetry about the beam.

To analyse all data reported by Saito et al [1, 7] we also need expressions appropriate for light propagating along the $b$-axis and $[\bar{1}, 1, 0]$.

One finds for $q || [0, 1, 0]$ and $\sigma$-polarization $[1, 0, 0]$, $\Psi_{1,0} \rightarrow i(\Psi_{1,1} + \Psi_{1,-1})/\sqrt{2}$, and $i(\Psi_{2,-2}(g) - \Psi_{2,2}(g)) \rightarrow -(\Psi_{2,-1}(g) - \Psi_{2,1}(g))$.

With $q || [\bar{1}, 1, 0]$ and $\sigma$-polarization $[1, 1, 0]$, $\Psi_{1,0} \rightarrow \{ \exp(i\pi/4)\Psi_{1,1} - \exp(-i\pi/4)\Psi_{1,-1} \}/\sqrt{2}$, and

\[
i(\Psi_{2,-2}(g) - \Psi_{2,2}(g)) \rightarrow -(\Psi_{2,-1}(g) - \Psi_{2,1}(g)).
\]

Expressions for $\Psi_{1,0}$ find application to both MCD and $\text{M}_D$ with multipoles labelled $t$ and $g$, respectively.

4. Parity-even multipoles

The structure factor $\Psi_{K,Q}(t)$ has $K + Q$ even for all point-groups of interest here since they contain the operation $2 = \theta C_2: [0, 0, 1]$. Thus time-odd (even) multipoles have $Q$ odd (even). It is straightforward to show that, $\Psi_{K,-Q}(t) = -(1)^Q \Psi_{K,Q}(t)$ for (I) and $\Psi_{K,-Q}(t) = \Psi_{K,Q}(t)$ for (II). Turning to magnetic fields along diagonals in the $a$–$b$ plane, $\Psi_{K,-Q}(t) = \exp(iQ\pi/2)\Psi_{K,Q}(t)$ for (III) and $\Psi_{K,-Q}(t) = \exp(-iQ\pi/2)\Psi_{K,Q}(t) = -(1)^K \exp(iQ\pi/2)\Psi_{K,Q}(t)$ for (IV).

5. Polar multipoles

Because a polar multipole is time-even, and independent of the polarity of an applied magnetic field, we need to consider point-group 222 for (I) and (II), and point-group $mm2$ for (III) and (IV). In both, invariance with respect to $2 = C_2:[0, 0, 1]$ makes $Q$ even. We find $\Psi_{K,-Q}(u) = -(1)^K \Psi_{K,Q}(u)$ for 222 and $\Psi_{K,-Q}(u) = -(1)^K \exp(iQ\pi/2)\Psi_{K,Q}(u)$ for $mm2$. From these results it follows that, $K$ is restricted to even integers when $Q = 0$.

6. Magneto-electric multipoles

For a magneto-electric multipole to be invariant with respect to $2^*$, which appears in all point-groups of interest, it is necessary that $Q$ is an odd integer. With the applied field along a cell edge, $\Psi_{K,-Q}(g) = -(1)^K \Psi_{K,Q}(g)$ for (I) and $\Psi_{K,-Q}(g) = -(1)^K \Psi_{K,Q}(g)$ for (II). Lastly, $\Psi_{K,-Q}(g) = -(1)^K \exp(iQ\pi/2)\Psi_{K,Q}(g)$ for (III) and $\Psi_{K,-Q}(g) = -(1)^K \exp(-iQ\pi/2)\Psi_{K,Q}(g) = -(1)^K \exp(iQ\pi/2)\Psi_{K,Q}(g)$ for (IV).

7. Analysis of data

We use the foregoing results in an analysis of dichroic signals measured with the copper metaborate sample held at 15 K, and we begin with data published by Saito et al [7].

Figure 2 of this paper reports data gathered with a field–difference method. (The field strength 500 Oe exceeds the coercive field $\approx 300$ Oe [2].) Thus observed signals are time-odd and the candidates are MCD, $\text{M}_D$ and NRLD. The signal is NRLD if polarization of the light is 100% linear, and it is allowed with $q || [1, 1, 0]$ and (III) in accord with data displayed in figure 2a. Rotation of the crystal by 180° about $q$ does not change the sign of NRLD, because it is composed of structure factors with projections ±2. However, rotation reverses alignment of the crystal with the applied magnetic field. The NRLD signal duly changes sign, since it is time-odd.
which is observed. We conclude that figure 2a is observation of NRLD.

This conclusion is in total accord with the null result in figure 2b, because NRLD is forbidden with \( \mathbf{q} \parallel [0,1,0] \) and (I).

We turn next to data reported by Saito et al [1]. Panels (b)–(e) in figure 3 display data gathered with a field–difference method and all measured dichroic signals must be time-odd, i.e., MCD, M\( _X \)D or NRLD.

In panel (b), light is unpolarized and the one signal, M\( _X \)D, is allowed. The field is parallel to \([0,1,0]\) and labelled (II), and \( \mathbf{q} \parallel [0,1,0] \). With \( \Psi_{1,-\mathbf{Q}}(g) = \Psi_{1,\mathbf{Q}}(g) \) one finds \( M_X D \) is allowed, which agrees with the reported observation.

The wavevector is parallel to \([0,1,0]\) in panel (c) and parallel to \([1,0,0]\) in panel (d). As the light is linearly polarized in both cases signals in question are NRLD. It is easy to confirm that for \( \mathbf{q} \parallel [0,1,0] \) NRLD is forbidden for (I) and allowed for (II), while for \( \mathbf{q} \parallel [1,1,0] \) NRLD is allowed for (II) and forbidden with (IV). These findings agree with observations. Note that data in figure 3d [1] and data in figure 2a [7], successfully analysed above, are gathered in identical conditions.

The last set of data in figure 3 [1] is gathered with circular polarization and MCD is possibly observed. The wavevector is parallel to \([0,1,0]\) and the field configurations are (I) and (II). Our predictions are that MCD is forbidden for (I) and allowed for (II). The observation is that the signal for both configurations of the field is zero, to a very good approximation. The finding for (II) can be understood by the small value of the ferromagnetic component of the magnetization, which is due to canting of the moments by a weak Dzyaloshinskii–Moriya interaction.

Data reported in figure 2 [1] is for \( \mathbf{q} \parallel \) c-axis. All data are alleged to be differences of signals measured with opposite hands of circular polarization. Signals are time-even since they do not change on reversing the polarity of the external field, cf data displayed in panels (b) and (d), and panels (c) and (e).

NCD and LD are the only dichroic signals composed of time-even multipoles. We expect these signals to be subject to constraints of symmetry in the point-group \( D_{2d} \) appropriate to the room temperature, non-magnetic structure. The rotation-inversion element \( S_{2c} = IC_{2c} \) of the point-group applied to a parity-even structure factor with projection \( Q \) multiplies it by a phase factor \( \exp(iQ\pi/2) \), while the corresponding phase is \( -\exp(iQ\pi/2) \) for a parity-odd structure factor. Thus LD \( (Q = \pm 2) \) and NCD \( (Q = 0) \) are forbidden by rotation-inversion symmetry, \( S_{2c} \), in the room-temperature structure.

By virtue of its proportionality to helicity, the NCD signal possesses cylindrical symmetry about the wavevector, \( \mathbf{q} \), which in figure 2 [1] is parallel to the crystal c-axis. Specifically, rotation of the crystal around the c-axis leaves NCD unchanged\(^4\), because rotation through an angle \( \psi \) around the c-axis introduces a factor \( \exp(i\psi Q) \) to \( \Psi_{K,\mathbf{Q}}(j) \) and \( Q = 0 \) in our expression for the NCD signal. Also, reorientation of an applied magnetic field from the a-axis to the b-axis, or vice versa, leaves NCD unchanged since this signal is the same for magnetic point-groups 222 and 222’. In consequence, NCD is not the source of signals displayed in figure 2 [1].

While LD is forbidden for \( D_{2d} \), because \( C_{2c} \) does not permit \( Q = \pm 2 \), these projections are permitted by the rotation element \( C_{2z} \), of point-group 222. In addition, \( C_{2x}(C_{2y}) \) changes \( \Psi_{K,\mathbf{Q}}(j) \) to \( (-1)^{k}\Psi_{K,-\mathbf{Q}}(j)(-1)^{k+\phi}\Psi_{K,-\mathbf{Q}}(j) \). Therefore, the LD signal, alongside NCD, can be different from zero in 222. Most importantly, rotation of the crystal by 90° about the beam changes the sign of the electron structure factors in the LD signal. (Rotation of the instrument by 90° about the beam, leaving the crystal unaltered, changes the sign of \( P_1 \) in the LD signal since the rotation places \( \pi \)-polarization parallel to the a-axis.)

These considerations make LD a prime candidate for signals displayed in figure 2 [1]. Conditions for the assignment to be correct include the following. (i) Crystal symmetry reduces on application of a magnetic field normal to the c-axis and the direction of the light beam, resulting in the loss of \( C_{2c} \) symmetry. (ii) Light that illuminates the crystal contains linear polarization which tracks the circular polarization when switched right \( \leftrightarrow \) left. (iii) Difference between data in panels in (b) and (c), and (d) and (e) is due to rotation of the crystal by 90° about the beam, or rotation of the instrument by 90° about the beam (see footnote 4). Two issues related to the magnitude of the LD signal merit comment. First, if the light is fully polarized and the helicity is 99% one has \( |P_1| = \sqrt{1 - (P_2)^2} = 0.14 \). Secondly, Templeton and Templeton scattering in diffraction, which can be readily observable because of its magnitude, is derived from the parity-even quadrupole that contributes to LD.

Finally, our expression for the LD signal provides a totally successful analysis of data in figure 2f [1]. With a field parallel to \([1,0,0]\), labelled (III), we earlier observed that \( \Psi_{K,-\mathbf{Q}}(t) = \exp(iQ\pi/2)\Psi_{K,\mathbf{Q}}(t) \). Use of this result in our expression for LD makes it zero.

8. Conclusions

It has been shown that, use of symmetry properties of dichroic signals from a crystal provides a good account of signals observed with copper metaborate in the presence of a magnetic field [1, 7]. Five different experiments are successfully analysed in total. With one experiment, we refute the claim by the authors [1] that their observation is evidence of magnetic control of crystal chirality.

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References


\(^4\) According to Arima data reported in [1] were obtained with rotation of the crystal around the beam, whereas the paper refers to rotation of the magnetic field. (See [10].)
[10] Collins S P 2009 private communication