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Resonant diffraction of circularly polarized x-rays by a chiral crystal (low quartz)

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Online at stacks.iop.org/JPhysCM/20/272201**Abstract**

A correlation in x-ray resonant scattering between crystal chirality and circular polarization (helicity) is explored in the context of an analysis of Bragg diffraction from low quartz (α -SiO₂). There is a one-to-one correlation between chirality and helicity when one resonant event is present in diffraction and thus, in this simple case, resonant Bragg diffraction of circularly polarized x-rays is a direct probe of crystal chirality. The presence of more than one resonant event is shown to add phase relations to the scattering amplitude and then coupling of helicity and chirality is no longer transparent.

1. Introduction

X-ray diffraction is an established experimental technique by which to determine electronic structure. Thomson scattering from charge distributions, and its magnetic counterpart, yield accurate information on the charge density and the configuration and distribution of the magnetization. Resonant enhancement of the scattering amplitude, achieved by tuning the primary energy to an atomic resonance, provides additional information on charge, orbital and spins degrees of freedom not available from other experimental techniques. In 1980 [1] and 1982 [2] Templeton and Templeton reported seminal studies of x-ray dichroism and polarized anomalous scattering. These, and related, diffraction methods have developed apace with burgeoning performance from x-ray synchrotron sources to a current status of almost standard experimental methods. A review of experiments on non-magnetic materials using resonant x-ray Bragg diffraction has been made by Dmitrienko *et al* [3].

Electronic properties of materials, and particularly molecular compounds, can depend on their structural handedness, or chirality. It has recently been demonstrated by Tanaka *et al* [4], in a study by resonant Bragg diffraction of the enantiomers of low quartz, that circular polarization in a

beam of x-rays directly couples to an enantiomorphic screw-axis. This finding demonstrates a new feature in resonant Bragg diffraction that may have wide ranging ramifications in our ability to characterize a chiral configuration of ions.

In the following sections we report a theoretical analysis of resonant Bragg diffraction from crystal structures $P3_121$ (#152, right-handed) and $P3_221$ (#154, left-handed) that are enantiomorphically (mirror) related. This particular enantiomorphic space-group pair, one of eleven such pairs, describes the enantiomers of low quartz [5].

An atomic model of electronic structure is described in section 2, together with the appropriate generic expressions for a unit-cell structure factor and the intensity of a diffracted x-ray beam endowed with both linear and circular polarization. The formalism used in section 2, and the subsequent sections, is reviewed by Lovesey *et al* [6] and Collins *et al* [7]. Structure factors for low quartz are given in section 3 and used in section 4 to derive relations between structure factors for the enantiomers that cover both parity-even (E1–E1) and parity-odd (E1–M1 and E1–E2) resonant events. Diffraction at the space-group forbidden reflections ($00l$) with $l \neq 3n$ and enhancement by an E1–E1 event is the subject of section 5. Applied to data gathered on low quartz [4] this scenario does not provide an adequate analysis. Thus we are led in section 6

to calculate intensity derived from a coherent mixture of parity-even and parity-odd events that has been shown to successfully describe the data available on low quartz [4]. In section 6 we use unit-cell structure factors for E1–M1 and E1–E2 events that are relegated to appendices. In section 7 we show that an extended version of diffraction by the E1–E1 event cannot account for observations on low quartz. To set off our findings for a crystal with an enantiomorphic screw-axis, we provide in section 8 unit-cell structure factors for space groups with the neutral screw-axis 2_1 . We conclude in section 9 with a brief discussion of our findings.

2. Diffracted intensity

Ground-state electronic structure at the site of a resonant ion is described by atomic multipoles that are expectation values of spherical tensor operators of rank K , where $K = 0$ (scalar), 1 (dipole), 2 (quadrupole), etc. We denote a sum of multipoles in a unit cell of the crystal by Ψ^K . The generic form of a unit-cell structure factor in the scattering amplitude for Bragg diffraction is,

$$F_{\mu\nu} = \sum_K \mathbf{X}_{\mu\nu}^K \cdot \mathbf{D}^K \cdot \Psi^K. \quad (2.1)$$

In this expression $\mathbf{X}_{\mu\nu}^K$ describes conditions of the primary and secondary x-rays and states of polarization are labelled by μ and ν . Later, we simulate diffraction enhanced by E1–E1, E1–M1 and E1–E2 events, and there is a different $\mathbf{X}_{\mu\nu}^K$ for each event. Orientation of the crystal, with respect to states of polarization and the plane of scattering, is accomplished by a rotation matrix \mathbf{D}^K . To describe the geometry of the diffraction instrument we use right-handed, orthonormal Cartesian coordinates (xyz) with σ -polarization parallel to the z -axis and the Bragg wavevector (hkl) anti-parallel to the x -axis.

Let us assume that a contribution to the resonant scattering amplitude can be written $G_{\mu\nu} = d(E)F_{\mu\nu}$, to a good approximation, where E is the energy of the x-ray beam and $d(E)$ describes the resonant behaviour of the particular event. The diffracted intensity, I_0 , is a sum of purely real products of $G_{\mu\nu}$, that in general are associated with different resonant events, plus Thomson intensity if the reflection is space-group allowed. I_0 is also a linear function of states of polarization in the primary beam. We describe polarization by Stokes parameters P_2 and P_3 and with full polarization $P_2^2 + P_3^2 = 1$. The parameter P_2 is the mean helicity in the beam and P_3 is the linear polarization with $P_3 = +1(-1)$ corresponding to complete linear σ -polarization normal (π -polarization parallel) to the plane of scattering. With this notation, the diffracted intensity is,

$$I_0 = \frac{1}{2}(1 + P_3) (|G_{\sigma'\sigma}|^2 + |G_{\pi'\sigma}|^2) + \frac{1}{2}(1 - P_3) (|G_{\pi'\pi}|^2 + |G_{\sigma'\pi}|^2) + P_2 \text{Im} (G_{\sigma'\pi}^* G_{\sigma'\sigma} + G_{\pi'\pi}^* G_{\pi'\sigma}). \quad (2.2)$$

As we shall see in our analysis of diffraction by low quartz, the coefficient of P_2 in this expression can be different from zero because the crystal contains an enantiomorphic screw-axis, and because there is an appropriate phase shift between

two or more resonant amplitudes. For Thomson scattering the coefficient of P_2 is zero because there are no contributions to diffraction in channels with rotated polarization.

3. Structure factors

Low quartz uses sites with multiplicity 3 and Wyckoff letter a for silicon ions in the enantiomorphic space-group pair $P3_121$ (#152, right-handed) and $P3_221$ (#154, left-handed). The site $-x, -x, 0$ occurs in unit cells of both enantiomers and because of its commonality it is used by us as the reference site. The remaining two sites in the cell are related by rotations $\pm 120^\circ$ about the c -axis to the reference site. A multipole for the reference site is written $\langle T_Q^K \rangle$ where the projection Q satisfies $-K \leq Q \leq K$. The structure factor for #152 and Miller indices (hkl) is found to be,

$$\Psi_Q^K = \langle T_Q^K \rangle \{ e^{2\pi i Q/3} e^{2\pi i (hx+l/3)} + e^{-2\pi i Q/3} e^{2\pi i (kx-l/3)} + e^{-2\pi i x(h+k)} \}. \quad (3.1)$$

Space-group allowed reflections satisfy the condition $\Psi_Q^K(hkl) \neq 0$, namely, $(00l) : l = 3n$. The structure factor for #154 can be derived from (3.1) simply by changing the sign of l . In consequence, diffraction at $(hk0)$ cannot distinguish between enantiomers.

Right-handed orthonormal quantization axes ($\xi\eta\zeta$) for the reference site have the ξ -axis coincident with the diad axis of rotation symmetry through $-x, -x, 0$ and the ζ -axis coincident with the crystal c -axis. Note that our ξ -axis lies in the plane spanned by reciprocal lattice vectors a^* (normal to cell vectors b_h and c_h) and b^* , and a^* and the ξ -axis enclose an angle of 30° . Physical properties of the crystal are unchanged by a rotation of 180° about the ξ -axis, of course.

In general, a multipole is a complex quantity $\langle T_Q^K \rangle = \langle T_Q^K \rangle' + i \langle T_Q^K \rangle''$ that satisfies $\langle T_Q^K \rangle^* = (-1)^Q \langle T_{-Q}^K \rangle$. The diad axis of symmetry at the reference site is satisfied if,

$$\langle T_Q^K \rangle = (-1)^K \langle T_{-Q}^K \rangle = (-1)^{K+Q} \langle T_Q^K \rangle^*. \quad (3.2)$$

Thus a multipole with $K + Q$ even (odd) is purely real (imaginary).

All results thus far in this section apply to both parity-even and parity-odd events, and their associated multipoles, since at no stage have we had occasion to use the operator that inverts signs of all spatial coordinates.

We will reserve $\langle T_Q^K \rangle$ to denote a parity-even multipole which occurs in an E1–E1 event, for example. For such an event, the rank K is even when the material of interest is non-magnetic. A time-even, parity-odd multipole is denoted $\langle U_Q^K \rangle$ and it is often called a polar multipole, e.g., an operator equivalent for a polar dipole, \mathbf{U}^1 , is the unit direction vector. Polar multipoles arise in E1–M1 ($K = 0, 1, 2$) and E1–E2 ($K = 1, 2, 3$) events. A polar multipole of even rank has the symmetry of a pseudotensor ($K = 0$ is a pseudoscalar like the Stokes parameter P_2 for helicity) and with K odd it has the symmetry of a true tensor.

4. Diffraction at (00*l*)

Setting $h = k = 0$ in (3.1) we find,

$$\Psi_Q^K(\#152) = \langle T_Q^K \rangle \left\{ 1 + 2 \cos \left[\frac{2\pi}{3}(Q + l) \right] \right\}. \quad (4.1)$$

Using the operation of a diad axis of rotation symmetry on a multipole, expressed in (3.2), it is a simple matter to show that, for the reflection (00*l*),

$$\Psi_Q^K(\#154) = (-1)^K \Psi_{-Q}^K(\#152). \quad (4.2)$$

The structure factor #152 can be different from zero if $l + Q = 3n$, while the corresponding condition is $l - Q = 3n$ for #154. In the following we consider the space-group forbidden reflection (001) and a maximum value of 4 for K . For these conditions allowed Q have a difference $\Delta Q = \pm 3$ where the upper (lower) sign applies to #152 (#154), and the sign in ΔQ is related to the hand of the enantiomorphic screw-axis. Allowed values for ΔQ express three-fold rotation symmetry caused by the enantiomorphic screw-axis. This is in contrast, say, to resonant diffraction from Fe ions in haematite or Cr ions in chromium sesquioxide. These ions lie on the trigonal axis of the corundum structure $R\bar{3}c$ with three-fold rotation site symmetry (point group C_3) [6].

4.1. Parity-even event

Unit-cell structure factors for channels of diffraction in which polarization is rotated ($\sigma \leftrightarrow \pi$) are related by a change in sign of the Bragg angle, θ . We find,

$$F_{\pi'\sigma}^t(\theta) = F_{\sigma'\pi}^t(-\theta), \quad (4.3)$$

where the prime is attached to polarization in the secondary beam, and the superscript t denotes a parity-even event described by multipoles $\langle T_Q^K \rangle$.

Expression (4.2) enables us to prove simple and very useful relations between structure factors for the enantiomers. Let a crystal be rotated by an angle ψ about the Bragg wavevector (00*l*). For diffraction without rotation of the polarization,

$$F_{\mu'\mu}^t(\#152, \psi) = F_{\mu'\mu}^t(\#154, -\psi),$$

while for the $\pi'\sigma$ channel,

$$F_{\pi'\sigma}^t(\#152, \psi) = -F_{\pi'\sigma}^t(\#154, -\psi), \quad (4.4)$$

and the structure factor for the $\sigma'\pi$ channel is derived from (4.3). These equalities taken together lead to the general statement,

$$F_{\mu\nu}^t(\#152, \psi) = \{F_{\mu\nu}^t(\#154, \psi)\}^*. \quad (4.5)$$

When (4.5) is used in expression (2.2) for the diffracted intensity it follows immediately that the coefficient of P_2 is of opposite sign for the enantiomers. In other words, in diffraction enhanced by a single resonant event, circular polarization (x-ray helicity) and crystal chirality are directly coupled. We reach the same conclusion with a parity-odd event although intermediate steps for parity-even and parity-odd are different.

4.2. Parity-odd event

In place of (4.3) and (4.4) we find,

$$F_{\pi'\sigma}^u(\theta) = -F_{\sigma'\pi}^u(-\theta), \quad (4.6)$$

and,

$$\begin{aligned} F_{\mu'\mu}^u(\#152, \psi) &= -F_{\mu'\mu}^u(\#154, -\psi), \\ F_{\pi'\sigma}^u(\#152, \psi) &= F_{\pi'\sigma}^u(\#154, -\psi). \end{aligned} \quad (4.7)$$

Taken together (4.6) and (4.7) lead to,

$$F_{\mu\nu}^u(\#152, \psi) = -\{F_{\mu\nu}^u(\#154, \psi)\}^*. \quad (4.8)$$

The last expression applied in (2.2) demonstrates, for a single parity-odd event, exactly the same correlation between helicity and an enantiomorphic screw-axis that we established for a single parity-even event.

It is perhaps worth remarking that, sign differences between (4.3)–(4.5) and (4.6)–(4.8) are a simple and direct consequence of differences between $\mathbf{X}_{\mu\nu}^K$ for the two types of event.

5. E1–E1 unit-cell structure factors (001)

Reference [6] contains an explicit expression for the rotation matrix \mathbf{D}^K required in (2.1). With the azimuthal angle $\psi = 0$ the crystal c -axis is anti-parallel to the x -axis, and the quantization ξ -axis is anti-parallel to the z -axis (σ -polarization).

The multipole $K = Q = 0$ is forbidden because (001) is a space-group forbidden reflection, and the parity-even dipole is zero in a non-magnetic structure. From (2.1) and (4.1) and a reflection (001) we find for the enantiomer #152,

$$F_{\sigma'\sigma}^t = \frac{3}{2} \langle T_{+2}^2 \rangle', \quad (5.1)$$

$$F_{\pi'\pi}^t = \frac{3}{2} \langle T_{+2}^2 \rangle' \sin^2 \theta, \quad (5.2)$$

$$F_{\pi'\sigma}^t = i \frac{3}{2} \left\{ \langle T_{+2}^2 \rangle' \sin \theta + \langle T_{+1}^2 \rangle'' \cos \theta e^{-3i\psi} \right\}. \quad (5.3)$$

From (4.3) one sees that $F_{\sigma'\pi}^t$ and $F_{\pi'\sigma}^t$ are not the same. In the expressions (5.1)–(5.3) we omit a common factor $\exp(2i\psi)$ since such a phase in a unit-cell structure factor cancels in the intensity. (The factor is only common to resonant events and it does not cancel in the intensity of a space-group allowed reflection derived from a coherent sum of Thomson scattering and resonant scattering.) The quadrupole is separated in to its real and imaginary parts; with respect to the quantization axes, $\langle T_{+1}^2 \rangle''$ and $\langle T_{+2}^2 \rangle'$ have angular symmetries $\zeta\eta$ and $\xi\xi - \eta\eta$, respectively. Note that three-fold rotation symmetry from the 3_1 -axis is manifest only in rotated channels of diffraction. Dependence of the diffracted intensity on circular polarization in the primary x-ray beam is permitted by a difference in the phase that can occur between structure factors diagonal and off-diagonal in the states of polarization. Unit-cell structure factors for #154 can be derived from (5.1)–(5.3) using (4.5).

The intensity (2.2) derived with (5.1)–(5.3) is a function of $\cos(3\psi)$ which does not match data gathered on low quartz [4]. Thus, in the next section we explore consequences of additional events in resonant diffraction.

6. Coherent mixture of parity-even and parity-odd events

Unit-cell structure factors for the parity-odd events E1–M1 and E1–E2 are provided in appendices. From these and results for the E1–E1 event in section 5, or directly from the general statements in section 4, one can quickly establish the generic form of structure factors that describe a coherent mixture of parity-even and parity-odd events. Such a mixture is required in a successful analysis of available diffraction data [4].

We extract in the scattering amplitude as a common factor the resonance denominator $d_e(E)$ associated with the E1–E1 event. Thus the mixing parameter between the parity-even and parity-odd events contains a ratio of their energy denominators $d_o(E)/d_e(E) = \exp(i\eta)|d_o(E)/d_e(E)|$. Only the phase $\exp(i\eta)$ is significant in setting properties of the diffracted intensity and the modulus of the ratio is absorbed in to polar multipoles. The mixing angle $\eta = 0$ if resonance events occur at the same energy, i.e., $\Delta_e = \Delta_o$, and $\eta = 90^\circ$ in the opposite extreme of well-separated resonances for which $|\Delta_e - \Delta_o| \gg \Gamma_o$ where Γ_o is the total width of the parity-odd resonance.

To simplify our expressions for the diffracted intensity as a function of Stokes parameters we use purely real quantities $T_a = (3/2)\langle T_{+2}^2 \rangle'$ and $T_\beta = (3/2)\langle T_{+1}^2 \rangle'' \cos \theta$. For polar multipoles, in either E1–M1 or E1–E2, we use purely real quantities U_f with $f = a, b, \alpha$ and β , and explicit expressions for U_f in terms of $\langle U_Q^K \rangle$ may be read off from results for F^u in the appendices. We will introduce a parameter $\nu = \pm 1$ that has the physical significance of crystal chirality with $\nu = +1(-1)$ for enantiomer #152 (#154). The four contributions to the space-group forbidden diffraction amplitude are,

$$G_{\sigma'\sigma} = T_a + \nu U_a e^{i\eta}, \quad (6.1)$$

$$G_{\pi'\pi} = T_a \sin^2 \theta + \nu U_b e^{i\eta}, \quad (6.2)$$

$$G_{\pi'\sigma} = i\{\alpha + \beta e^{-3iv\psi}\}, \quad (6.3)$$

$$G_{\sigma'\pi} = i\{-\alpha + \beta e^{-3iv\psi}\}, \quad (6.4)$$

with,

$$\alpha = \nu T_a \sin \theta + U_\alpha e^{i\eta}, \quad (6.5)$$

$$\beta = \nu T_\beta + U_\beta e^{i\eta}. \quad (6.6)$$

The corresponding intensity (2.2) is,

$$I_0 = I_0(\nu, P_2) + I_1(\nu, P_2) \cos(3\psi) + I_2(\nu, P_2) \sin(3\psi). \quad (6.7)$$

As anticipated, the intensity (6.7) is a three-fold periodic function of the azimuthal angle, ψ . Recall that, for $\psi = 0$ the ξ -axis is normal to the plane of scattering and anti-parallel to σ -polarization. Also, the ξ -axis does not coincide with a reciprocal lattice vector.

Explicit expressions for the three coefficients in (6.7) follow later in this section. First, however, we note the following physically significant properties of the coefficients. The coefficient $I_2(\nu, P_2)$ vanishes in the limit of a single resonance, with either $U_f = 0$ or $T_a = T_\beta = 0$. In this limiting case, the coefficients $I_0(\nu, P_2)$ and $I_1(\nu, P_2)$ satisfy the key identity $I_p(\nu, P_2) = I_p(-\nu, -P_2)$ with $p = 0, 1$, and

the identity expresses a one-to-one correspondence established in section 4 between crystal chirality and x-ray helicity. The coefficients $I_0(\nu, P_2)$ and $I_1(\nu, P_2)$ in the general case do not satisfy the identity, and chirality and helicity are not correlated. However, they do satisfy the identity in one other limit and that is when the parity-even and parity-odd resonances are well separated in energy and the mixing angle $\eta = 90^\circ$. Returning to properties of the third coefficient, one finds $I_2(\nu, P_2) = I_2(-\nu, -P_2)$ for all η . (The definition of $I_2(\nu, P_2)$ is changed compared to [4] by absorbing in it the factor ν from $\sin(3\nu\psi) \equiv \nu \sin(3\psi)$. This change of definition is merely cosmetic and it is done simply to give $I_2(\nu, P_2)$ properties akin to those of $I_0(\nu, P_2)$ and $I_1(\nu, P_2)$.) $I_2(\nu, P_2)$ vanishes for $\eta = 0$ but with this condition on the mixing angle the remaining two coefficients, I_0 and I_1 , need not satisfy the identity coupling helicity to chirality.

We conclude the section with expressions for the three coefficients in (6.7).

$$\begin{aligned} I_0(\nu, P_2) = & \frac{1}{2} \{ T_a^2 (1 + \sin^2 \theta)^2 + U_a^2 \\ & + U_b^2 + 2U_\alpha^2 + 2(T_\beta^2 + U_\beta^2) \\ & + 2\nu \cos \eta [T_a(U_a + U_b \sin^2 \theta) + 2(T_a U_\alpha \sin \theta + T_\beta U_\beta)] \\ & + P_3 [T_a^2 \cos^2 \theta (1 + \sin^2 \theta) + U_a^2 - U_b^2 \\ & + 2\nu \cos \eta T_a (U_a - U_b \sin^2 \theta)] \} \\ & + P_2 [\nu \{ T_a^2 \sin \theta (1 + \sin^2 \theta) + U_\alpha (U_a + U_b) \} \\ & + \cos \eta \{ T_a (U_a + U_b) \sin \theta + T_a U_\alpha (1 + \sin^2 \theta) \}], \quad (6.8) \end{aligned}$$

$$\begin{aligned} I_1(\nu, P_2) = & 2P_3 [T_a T_\beta \sin \theta + U_\alpha U_\beta \\ & + \nu \cos \eta \{ T_a U_\beta \sin \theta + T_\beta U_\alpha \}] \\ & + P_2 [\nu \{ U_\beta (U_b - U_a) - T_a T_\beta \cos^2 \theta \} \\ & + \cos \eta \{ T_\beta (U_b - U_a) - T_a U_\beta \cos^2 \theta \}], \quad (6.9) \end{aligned}$$

$$\begin{aligned} I_2(\nu, P_2) = & -\sin \eta \{ 2P_3 (T_\beta U_\alpha - T_a U_\beta \sin \theta) \\ & + \nu P_2 (T_a U_\beta \cos^2 \theta + T_\beta (U_b - U_a)) \}. \quad (6.10) \end{aligned}$$

7. Extended simulation of E1–E1 diffraction at (001)

Results presented in sections 5 and 6 are independent of the core state that participates in the virtual, intermediate state of the resonance process. The simplification is appropriate when the core state has no angular anisotropy, to a good approximation, and its dependence on the projection M_c in a spin–orbit split state J_c, M_c is safely eliminated. The actual situation is simulated by an effective exchange field H_s , derived from Slater integrals G^k [8, 9], that splits the core state in to $(2J_c + 1)$ sublevels with relative energy positions $= H_s(g - 1)M_c$ where g is the Landé factor. In consequence, unit-cell structure factors also depend on M_c . Here we consider how this correction of the E1–E1 scattering amplitude given in section 5 to its most general form alters conclusions about the dependence of the diffracted intensity on x-ray helicity and crystal chirality.

With $J_c = 1/2$ (K-shell absorption edge) in the work reported in [10, 11] it is a simple matter to show that for low quartz the correction has no effect on diffraction in channels with unrotated polarization. Hence, by using the notation in (6.1)–(6.6),

$$G_{\sigma'\sigma} = \frac{1}{2} d(E, M_c) T_a, \quad (7.1)$$

$$G_{\pi'\pi} = \frac{1}{2}d(E, M_c)T_a \sin^2 \theta, \quad (7.2)$$

where the energy denominator in $d(E, M_c)$ includes the exchange energy $H_s(g-1)M_c$ with $M_c = \pm 1/2$, and the prefactor $1/2$ accounts for the $(2J_c + 1) = 2$ multiplicity. One can also use,

$$G_{\pi'\sigma} = i d(E, M_c) \{ \alpha + \beta e^{-3iv\psi} \}, \quad (7.3)$$

$$G_{\sigma'\pi} = i d(E, M_c) \{ -\alpha + \beta e^{-3iv\psi} \}, \quad (7.4)$$

with,

$$\alpha = \frac{1}{2}vT_a \sin \theta. \quad (7.5)$$

However, the quantity β is now complex and it depends explicitly on M_c . We find,

$$\beta = v \left[\frac{1}{2}T_\beta + i \frac{1}{\sqrt{6}}M_c \langle \mathcal{P}_{+1} \rangle'' \sin \theta \right]. \quad (7.6)$$

The quadrupole $\langle \mathcal{P}_Q \rangle$ also arises in sum rules for linear dichroism [12]. Whereas the tensor $\langle T_Q^K \rangle$ is proportional to the unit Racah tensor $W^{(0K)K}$, the multipole $\langle \mathcal{P}_Q \rangle$ is proportional to $W^{(11)2}$. The additional term in (7.6) is consistent with the requirement that the amplitude satisfies crossing symmetry. Note that, a sum on the two values of M_c over the amplitudes (7.1)–(7.6) with $H_s = 0$ exactly reproduces results reported in section 5.

The amplitudes (7.1)–(7.6) are responsible for diffracted intensity like (6.7). As we also found in section 5, the coefficients $I_0(\nu, P_2)$ and $I_1(\nu, P_2)$ in the intensity for the extended simulation of E1–E1 diffraction under discussion satisfy the identity $I_p(\nu, P_2) = I_p(-\nu, -P_2)$ with $p = 0, 1$. Most importantly, in the extended simulation $I_2(\nu, P_2)$ can be different from zero, although it does not satisfy the key identity that correlates x-ray helicity with crystal chirality. We find,

$$I_2(\nu, P_2) = \frac{1}{8}\sqrt{\frac{3}{2}}\{ |d(E, 1/2)|^2 - |d(E, -1/2)|^2 \} \\ \times \langle T_{+2}^2 \rangle' \langle \mathcal{P}_{+1} \rangle'' \sin \theta [2\nu P_3 \sin \theta - P_2 \cos^2 \theta]. \quad (7.7)$$

As expected, this expression does vanish for a single resonance process achieved by the choice $H_s = 0$, for then the difference between the two energy factors vanishes. The expression (7.7) for $I_2(\nu, P_2)$ does not correlate ν with P_2 and in this respect it differs from (6.10) which is appropriate for diffraction from a coherent mixture of parity-even and parity-odd events.

8. Neutral screw-axis

Let us discuss properties of compounds whose structure is described by a space group that contains a neutral screw-axis to better appreciate features we have highlighted for an enantiomorphic screw-axis. We pay attention to the neutral screw-axis 2_1 and three structures that, in common with the space groups of low quartz, belong to crystal classes that allow optical activity and, also, are enantiomorphic; $P2_1$ (#4, monoclinic, crystal class C_2), $P2_12_12_1$ (#19, orthorhombic, crystal class D_2) and $P2_13$ (#198, cubic, crystal class T). Space groups #4 and #19 are the most common for single enantiomorphs of molecular compounds. The cubic space

group #198 applies to the much-studied compounds NaClO_3 and NaBrO_3 . These materials possess the same chirality yet opposite senses of optical rotation [13]. Templeton and Templeton [14] measured the azimuthal angle dependence of forbidden reflections, $(00l)$ with odd l , for NaBrO_3 at the bromine K-absorption edge. Previously, Templeton and Templeton [2] observed anisotropic anomalous scattering in a diffraction experiment with sodium uranyl acetate which has a crystal structure $P2_13$.

The structure factors for all space groups considered in this section possess the selection rule even $l + Q$ for reflections $(00l)$. Consequently, diffraction with odd l is space-group forbidden. In #4 we elect to have a unique axis c , and we may choose the position coordinate $z = 0$ without loss of generality. We find,

$$\Psi_Q^K(\#4) = \{1 + (-1)^{l+Q}\} \langle U_Q^K \rangle \quad : \text{sites } 2(a), \quad (8.1)$$

$$\Psi_Q^K(\#19) = \{1 + (-1)^{l+Q}\} \{ \langle U_Q^K \rangle e^{i\phi} \\ + (-1)^K \langle U_{-Q}^K \rangle e^{-i\phi} \} \quad : \text{sites } 4(a), \quad (8.2)$$

and,

$$\Psi_Q^K(\#198) = \{1 + (-1)^{l+Q}\} \{ \langle U_Q^K \rangle e^{i\phi} \\ + (-1)^K \langle U_{-Q}^K \rangle e^{-i\phi} \}. \quad (8.3)$$

In (8.2) and (8.3) the phase $\phi = 2\pi zl$. Expression (8.3) is valid for sites 4(a) in #198 used by Na and Br (Cl) in sodium bromate (chlorate) with $z = 0.078, 0.407$ for Na and Br, and $z = 0.069$ and 0.418 for Na and Cl [13]. The environments in #4 and #19 have no symmetry, whereas 4(a) in #198 has triad axes of symmetry about the four cube diagonals. We have written the structure factors (8.1)–(8.3) for parity-odd events but they hold equally for parity-even events with $\langle T_Q^K \rangle$ replacing $\langle U_Q^K \rangle$.

Let us note that the foregoing structure factors can be different from zero for Miller indices $h = k = l = 0$ when they describe bulk properties. From this we learn that natural circular dichroism $P_2\Psi_0^{u,K}$ with $K = 0, 2$ is allowed. The pseudoscalar $\Psi_0^{u,0}$ is the chirality of a crystal and it is found in the E1–M1 resonance event. Turning back to (3.1), all these findings also hold for the enantiomers of low quartz.

Diffraction is forbidden at $(00l)$ with odd l and space groups #4, #19, and #198 in channels with unrotated polarization. Absence of diffraction in the $\sigma'\sigma$ and $\pi'\pi$ channels for both parity-even and parity-odd events is a direct consequence of the condition that diffraction is only allowed for odd Q . Applied in (2.2), absence of diffraction in the $\sigma'\sigma$ and $\pi'\pi$ channels means that the diffracted intensity is independent of circular polarization, which contrasts with what we find in diffraction by a crystal with an enantiomorphic screw-axis.

Unit-cell structure factors for #198, and an E1–E1 event, are found to be,

$$F_{\pi'\sigma}^t(\#198) = F_{\sigma'\pi}^t(\#198) \\ = 4 \langle T_{+1}^2 \rangle' \cos \theta \{ \cos \phi \sin \psi - i \sin \phi \cos \psi \}, \quad (8.4)$$

and, for the E1–E2 event,

$$F_{\pi'\sigma}^u(\#198) = 4\sqrt{\frac{2}{15}} \sin(2\theta) \{ - \langle U_{+1}^2 \rangle' \Phi \\ + \frac{1}{2}\sqrt{\frac{3}{5}} \Phi^* (- \sqrt{\frac{3}{2}} \langle U_0^1 \rangle' + \langle U_0^3 \rangle') \}, \quad (8.5)$$

with,

$$\Phi = \sin \phi \sin \psi - i \cos \phi \cos \psi.$$

In these results the origin of the azimuthal angle dependence has the crystal a -axis normal to the plane of scattering and anti-parallel to σ -polarization. The results (8.4) agrees with Templeton and Templeton [14] when their parameter b in expression (9) is identified with our quadrupole $\langle T_{+1}^2 \rangle'$.

Lastly, we give the E1–E1 unit-cell structure factor for diffraction at $(00l)$ with odd l by space group #19. We find,

$$\begin{aligned} F_{\pi'\sigma}^t(\#19) &= F_{\sigma'\pi}^t(\#19) \\ &= 4 \cos \theta \{ \langle T_{+1}^2 \rangle'' \cos \phi \sin \psi - i \langle T_{+1}^2 \rangle' \sin \phi \cos \psi \}. \end{aligned} \quad (8.6)$$

The result (8.4) is obtained from (8.6) when the symmetry of the site 4(a) in #198 is imposed, leading to $\langle T_{+1}^2 \rangle' = \langle T_{+1}^2 \rangle''$. An expression for the intensity of forbidden reflections $(00l)$ in #19 derived by Kirfel and Petcov [15] agrees with the intensity $|F_{\pi'\sigma}^t(\#19)|^2$ when, as here, all contributions to the E1–E1 amplitude are taken at the same energy and there is one common energy factor $d(E)$.

9. Discussion

We have explored a correlation between x-ray helicity and crystal chirality in resonant Bragg diffraction. That a correlation may exist between these two pseudoscalar parameters is intuitively understandable. In the simplest model of resonant diffraction, a simple, one-to-one correlation between the two parameters does indeed exist. Thus resonant Bragg diffraction of circularly polarized x-rays can be a direct probe of crystal chirality. With the aid of an atomic model of electron degrees of freedom, we explore likely complicating features from coherent resonant events that introduce additional phase information in the scattering amplitude. In particular, we give a full account of diffraction by crystals that are an enantiomorphic space-group pair with scattering enhanced by a coherent sum of parity-even (E1–E1) and parity-odd (E1–E2 or E1–M1) resonant events. The derived intensity successfully explains all aspects of diffraction by low quartz (α -SiO₂) [4].

It is well known that, two crystal forms that differ by their handedness can be distinguished in x-ray diffraction by exploiting the violation of Friedel's law from anomalous scattering [16]. Less well established, at this time, for the determination of an absolute structure is the technique of three-beam diffraction [17]. This works independently of anomalous scattering with the attendant scope of determining absolute structure of compounds containing predominantly light ions. Crystal handedness may be observed in three-beam diffraction of circularly polarized x-rays [18–20]. With these techniques, anomalous scattering and three-beam diffraction, distinction between enantiomorphs is based on whether calculated quantities agree or not with observations, namely, for one of the two enantiomorphs matching calculated and observed intensities in suitable Bijvoet pairs or the sign of the three-beam phase. All these techniques are also less discerning than our use of resonant diffraction of circularly polarized

x-rays because, in principle, the techniques can distinguish crystal forms which use either self-enantiomeric space groups, of the type considered in section 8, and an enantiomorphic space-group pair, e.g., space groups #152 and #154.

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Appendix A. Unit-cell structure factors (E1–M1) for #152

$$F_{\sigma'\sigma}^u = F_{\pi'\pi}^u = 3 \langle U_{+2}^2 \rangle' \sin \theta \quad (A.1)$$

$$F_{\pi'\sigma}^u = i \frac{3}{2} \{ \langle U_{+2}^2 \rangle' (1 + \sin^2 \theta) - \langle U_{+1}^1 \rangle' \sin(2\theta) e^{-3i\psi} \}. \quad (A.2)$$

Appendix B. Unit-cell structure factors (E1–E2) for #152

$$F_{\sigma'\sigma}^u = \sqrt{\frac{3}{10}} \sin \theta \{ \sqrt{2} \langle U_{+2}^3 \rangle'' - \langle U_{+2}^2 \rangle' \} \quad (B.1)$$

$$F_{\pi'\pi}^u = \sqrt{\frac{3}{10}} \{ \sqrt{2} \langle U_{+2}^3 \rangle'' \sin^3 \theta + \langle U_{+2}^2 \rangle' \sin(3\theta) \} \quad (B.2)$$

$$\begin{aligned} F_{\pi'\sigma}^u &= i \left\{ \sqrt{\frac{3}{5}} \{ \langle U_{+2}^3 \rangle'' \sin^2 \theta + \frac{1}{4\sqrt{2}} \langle U_{+2}^2 \rangle' [1 + 5 \cos(2\theta)] \} \right. \\ &\quad + \frac{3}{10} \sqrt{\frac{3}{2}} \sin(2\theta) e^{-3i\psi} \left[\langle U_{+1}^1 \rangle' + \frac{4}{3} \langle U_{+1}^3 \rangle' \right. \\ &\quad \left. \left. + \frac{2}{3} \sqrt{5} \langle U_{+1}^2 \rangle'' \right] \right\}. \end{aligned} \quad (B.3)$$

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