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

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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 (\(\alpha\)-SiO\(_2\)). 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 space 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 \(P\text{\textsubscript{3}}\text{\textsubscript{1}}\text{\textsubscript{2}}\text{\textsubscript{1}}\) (#152, right-handed) and \(P\text{\textsubscript{3}}\text{\textsubscript{2}}\text{\textsubscript{1}}\) (#154, left-handed) that are enantiomorphically (mirror) related. This particular enantiomorphous 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 (00\(l\)) 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 21. We conclude in section 9 with a brief
discussion of our findings.

2. Diffraacted 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 \( \Psi^K \). The generic form of a
unit-cell structure factor in the scattering amplitude for Bragg
diffraction is,

\[
F_{\mu\nu} = \sum_K X^K_{\mu\nu} \cdot D^K \cdot \Psi^K. \tag{2.1}
\]

In this expression \( X^K_{\mu\nu} \) describes conditions of the primary and
secondary x-rays and states of polarization are labelled by \( \mu \)
and \( \nu \). Later, we simulate diffraction enhanced by E1–E1,
E1–M1 and E1–E2 events, and there is a different \( X^K_{\mu\nu} \) for
each event. Orientation of the crystal, with respect to states of
polarization and the plane of scattering, is accomplished by
a rotation matrix \( D^K \). To describe the geometry of the
diffraction instrument we use right-handed, orthornomal
Cartesian coordinates (xyz) with \( \sigma \)-polarization parallel to the
z-axis and the Bragg wavevector (hk0) 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 diffraacted 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 \( P_0 \) and \( P_1 \) 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 \( P_1 = +1 \)
(corresponding to complete linear \( \sigma \)-polarization normal (\( \pi \)-polarization parallel) to the plane of scattering. With this
notation, the diffraacted intensity is,

\[
I_0 = \frac{1}{2}(1 + P_1) \left\{ |G_{\sigma\sigma}|^2 + |G_{\pi\pi}|^2 \right\} + \frac{1}{2}(1 - P_1) \left\{ |G_{\sigma\pi}|^2 + |G_{\pi\sigma}|^2 \right\} + P_0 \text{Im}(G_{\sigma\pi}^{*} G_{\sigma\sigma} + G_{\pi\sigma}^{*} G_{\pi\pi}). \tag{2.2}
\]

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 P3121
(#152, right-handed) and P3121 (#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 \( \langle T^K_Q \rangle \) where the projection \( Q \)
satisfies \(-K \leq Q \leq K \). The structure factor for #152 and Miller
indices \( hkl \) is found to be,

\[
\Psi^K_Q = \langle T^K_Q \rangle \left\{ e^{2\pi i Q/k} e^{2\pi i (kx+l/3)} + e^{-2\pi i Q/k} e^{2\pi i (kx-l/3)} \right\} + e^{-2\pi i (h+k)b}. \tag{3.1}
\]

Space-group allowed reflections satisfy the condition \( \Psi^K_Q(hkl) \neq 0 \), 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
enantioomers.

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

In general, a multipole is a complex quantity \( \langle T^K_Q \rangle = \langle T^K_Q \rangle^* + i \langle T^K_Q \rangle \) that satisfies \( \langle T^K_Q \rangle^* = (-1)^K \langle T^K_Q \rangle \). The diad
axis of symmetry at the reference site is satisfied if,

\[
\langle T^K_Q \rangle = (-1)^K \langle T^K_{-Q} \rangle = (-1)^K Q \langle T^K_Q \rangle^*. \tag{3.2}
\]

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 \( \langle T^K_Q \rangle \) 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
\( \langle U^K_Q \rangle \) and it is often called a polar multipole, e.g., an operator
equivalent for a polar dipole, \( U^1 \), 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 (00l)

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

\[
\Psi_Q^K(\#152) = \langle T_Q^K \rangle \left\{ 1 + 2 \cos \left( \frac{2\pi}{3} (Q + l) \right) \right\}.
\]  
(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 (00l),

\[
\Psi_Q^K(\#154) = (-1)^K \Psi_Q^K(\#152).
\]  
(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 \( \Delta Q \) is related to the hand of the enantiomorphous screw-axis. Allowed values for \( \Delta Q \) express three-fold rotation symmetry caused by the enantiomorphous 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 \( \alpha-K_3C \) 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, \( \theta \). We find,

\[
F^\dagger_{\sigma \pi}(\theta) = F^\dagger_{\pi \sigma}(-\theta),
\]  
(4.3)

where the prime is attached to polarization in the secondary beam, and the superscript \( \dagger \) denotes a parity-even event described by multipoles \( T_Q^K \).

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 \( \psi \) about the Bragg wavevector (00l). For diffraction without rotation of the polarization,

\[
F^\dagger_{\mu \nu}(\#152, \psi) = F^\dagger_{\mu \nu}(\#154, -\psi),
\]  
(4.4)

while for the \( \pi \sigma \) channel,

\[
F^\dagger_{\pi \sigma}(\#152, \psi) = -F^\dagger_{\pi \sigma}(\#154, -\psi),
\]  
(4.5)

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

\[
F^\dagger_{\mu \nu}(\#152, \psi) = (F^\dagger_{\mu \nu}(\#154, \psi))^*,
\]  
(4.6)

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,

\[
F^\dagger_{\pi \sigma}(\theta) = -F^\dagger_{\sigma \pi}(\theta),
\]  
(4.6)

and,

\[
F^\dagger_{\mu \nu}(\#152, \psi) = -F^\dagger_{\mu \nu}(\#154, -\psi),
\]  
(4.7)

\[
F^\dagger_{\pi \sigma}(\#152, \psi) = F^\dagger_{\pi \sigma}(\#154, -\psi).
\]  
(4.8)

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

\[
F^\dagger_{\mu \nu}(\#152, \psi) = -(F^\dagger_{\mu \nu}(\#154, \psi))^*.
\]  
(4.9)

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 \( X^K_{\mu \nu} \) for the two types of event.

5. \( \text{E1} - \text{E1} \) unit-cell structure factors (001)

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

\[
F^\dagger_{\sigma \sigma} = \frac{1}{2} (T_2^2)^x y',
\]  
(5.1)

\[
F^\dagger_{\pi \pi} = \frac{1}{2} (T_2^2)^y x' z',
\]  
(5.2)

\[
F^\dagger_{\pi \sigma} = i \frac{1}{2} \left( (T_2^2)^y x' z' \cos \theta + (T_2^2)^x y' \sin \theta \right) e^{-\text{i}3\pi \phi}.
\]  
(5.3)

From (4.3) one sees that \( F^\dagger_{\sigma \sigma} \) and \( F^\dagger_{\pi \pi} \) are not the same. In the expressions (5.1)-(5.3) we omit a common factor \( \exp(2i \phi) \) 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 its real and imaginary parts; with respect to the quantization axes, \( (T_2^2)^x \) and \( (T_2^2)^y \) have angular symmetries \( \xi \eta \) and \( \xi \xi - \eta \eta \), respectively. Note that three-fold rotation symmetry from the \( 3z \)-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 \( d_{\alpha}(E) \) 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 \( d_{\alpha}(E)/d_{\alpha}(E) = \exp(i\theta)\). Only the phase \( \exp(i\theta) \) is significant in setting properties of the diffracted intensity and the modulus of the ratio is absorbed in to polar multipole. The mixing angle \( \theta = 0 \) if resonance events occur at the same energy, i.e., \( \Delta E = \Delta_{\alpha} \) and \( \eta = 90^\circ \) in the opposite extreme of well-separated resonances for which \( |\Delta E - \Delta_{\alpha}| \gg \Gamma_{\alpha} \) where \( \Gamma_{\alpha} \) 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 \( T_{\alpha} = (3/2)(T_{\alpha})^2 \) and \( T_{\beta} = (3/2)(T_{\beta})^2 \) \( \cos \theta \). For polar multipole, in either E1–M1 or E1–E2, we use purely real quantities \( U_{\alpha} \) with \( f = a, \beta, \alpha, \beta, \alpha, \beta \) and explicit expressions for \( U_{\alpha} \) in terms of \( U_{\alpha}^0 \) may be read off from results for \( F^m_i \) in the appendices. We introduce a parameter \( \eta = \pm 1 \) that has the physical significance of crystal chirality with \( \eta = +1(-1) \) for enantiomer #152 (#154). The four contributions to the space-group forbidden diffraction amplitude are,

\[
G_{\sigma'\nu} = T_{\alpha} + \nu U_{\alpha} e^{i\eta},
\]

\[
G_{\pi'\pi} = T_{\alpha} \sin^2 \theta + \nu U_{\alpha} e^{i\eta},
\]

\[
G_{\pi'\pi} = i(\alpha + \beta e^{-3i\eta}),
\]

\[
G_{\sigma'\sigma} = i(-\alpha - \beta e^{-3i\eta}),
\]

with,

\[
\alpha = T_{\alpha} \sin \theta + U_{\alpha} e^{i\eta},
\]

\[
\beta = v T_{\alpha} + U_{\beta} e^{i\eta}.
\]

The corresponding intensity (2.2) is,

\[
I_0 = I_0(v, P_2) + I_1(v, P_3) \cos(3\psi) + I_2(v, P_5) \sin(3\psi).
\]  

As anticipated, the intensity (6.7) is a three-fold periodic function of the azimuthal angle, \( \psi \). Recall that, for \( \psi = 0 \) the \( \xi \)-axis is normal to the plane of scattering and anti-parallel to \( \sigma \)-polarization. Also, the \( \xi \)-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 \( I_2(v, P_5) \) vanishes in the limit of a single resonance, with either \( U_{\alpha} = 0 \) or \( T_{\alpha} = T_{\beta} = 0 \). In this limiting case, the coefficients \( I_0(v, P_2) \) and \( I_1(v, P_3) \) satisfy the key identity \( I_p(v, P_3) = I_p(-v, -P_3) \) 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 \( I_0(v, P_2) \) and \( I_1(v, P_3) \) 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 \( I_2(v, P_5) = I_2(-v, -P_5) \) for all \( \eta \). (The definition of \( I_2(v, P_5) \) is changed compared to [4] by absorbing in it the factor \( v \) from \( \sin(3\psi) \equiv v \sin(3\psi) \). This change of definition is merely cosmetic and it is done simply to give \( I_2(v, P_5) \) properties akin to those of \( I_0(v, P_2) \) and \( I_1(v, P_3) \). \( I_2(v, P_5) \) 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).

\[
I_0(v, P_2) = \frac{1}{2} T_{\alpha}^2 (1 + \sin^2 \theta)^2 + U_{\alpha}^2 + U_{\beta}^2 + 2 U_{\alpha}^2 + 2 T_{\alpha}^2 + T_{\beta}^2
\]

\[
+ 2 \nu \sin \eta (T_{\alpha} U_{\alpha} - U_{\alpha} \sin^2 \theta + 2(T_{\alpha} U_{\beta} \sin \theta + T_{\beta} U_{\alpha}))
\]

\[
+ \nu T_{\alpha} [T_{\alpha} \cos \theta (1 + \sin^2 \theta) - (1 - \sin^2 \theta) U_{\beta}] + 2 \nu \cos \eta T_{\alpha} (U_{\alpha} - U_{\alpha} \sin^2 \theta)],
\]

(6.8)

\[
I_1(v, P_3) = 2 \nu T_{\alpha} \sin \theta + U_{\alpha} U_{\beta} + \nu \cos \eta T_{\alpha} \sin \theta + T_{\beta} U_{\alpha})
\]

\[
+ \nu T_{\alpha} U_{\beta} \cos \theta + T_{\beta} U_{\alpha} (1 + \sin^2 \theta)],
\]

(6.9)

\[
I_2(v, P_5) = - \nu \sin \eta [2 \nu T_{\alpha} U_{\beta} - T_{\alpha} U_{\beta} \cos \theta]
\]

\[
+ \nu P_5 (T_{\alpha} U_{\beta} \cos \theta - T_{\beta} U_{\alpha} - U_{\alpha} \sin^2 \theta).
\]

(6.10)

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 \( H_e \), derived from Slater integrals \( G^0 \), which splits the core state in to \( (2J_c + 1) \) sublevels with relative energy positions \( H_e(g - 1)M_c \), 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),

\[
G_{\sigma'\sigma} = \frac{1}{2} d(E, M_c) T_{\alpha}.
\]
$G_{r,r} = \frac{i}{2} d(E, M_c) T_{se} \sin^2 \theta$, \hspace{1cm} (7.2)

where the energy denominator in $d(E, M_c)$ includes the exchange energy $H_4(g - 1) M_c$ with $M_c = \pm 1/2$, and the prefactor $1/2$ accounts for the $(2 g + 1) = 2$ multiplicity. One can also use,

$G_{r' r} = i d(E, M_c) \{ \alpha + \beta e^{-3iw} \}$, \hspace{1cm} (7.3)

$G_{r' r'} = i d(E, M_c) \{ -\alpha + \beta e^{-3iw} \}$, \hspace{1cm} (7.4)

with,

$\alpha = \frac{1}{2} v T_{se} \sin \theta$. \hspace{1cm} (7.5)

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

$\beta = v \left( \frac{1}{2} T_{se} + \frac{1}{\sqrt{6}} M_c \langle P_{+1} \rangle'' \sin \theta \right)$. \hspace{1cm} (7.6)

The quadrupole ($Q_0$) also arises in sum rules for linear dichroism [12]. Whereas the tensor ($Q^K_0$) is proportional to the unit Racah tensor $W^{0(K)}_0$, the multipole ($Q_0$) is proportional to $W^{(12)}$. 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 $H_4 = 0$ 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 $I_0(v, P_3)$ and $I_1(v, P_3)$ in the intensity for the extended system of E1-E1 diffraction under discussion satisfy the identity $I_0(v, P_3) = I_0(-v, -P_3)$ with $\rho = 0, 1$. Most importantly, in the extended system $I_0(v, P_3)$ can be different from zero, although it does not satisfy the key identity that correlates x-ray helicity with crystal chirality. We find,

$I_0(v, P_3) = \frac{1}{2} \sqrt{6} \left[ d(E, 1/2 \Omega)^3 - d(E, -1/2 \Omega)^3 \right] \times \langle P_{+1} \rangle'' \sin \theta 2v P_3 \sin \theta - P_3 \cos^2 \theta \rangle$. \hspace{1cm} (7.7)

As expected, this expression does vanish for a single resonance process achieved by the choice $H_4 = 0$, for then the difference between the two energy factors vanishes. The expression (7.7) for $I_0(v, P_3)$ does not correlate $v$ with $P_3$ 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 enantiomorph screw-axis. We pay attention to the neutral screw-axis $S_1$ and three structures that, in common with the space groups of low quartz, belong to crystal classes that allow optical activity and, also, are enantiomorphetic. $P2_1 \#4$, 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,

$\Psi_0^K(\#4) = [1 + (-1)^l Q \langle U^K_{0} \rangle]$ : sites 2(a), \hspace{1cm} (8.1)

$\Psi_0^K(\#19) = [1 + (-1)^l Q \langle U^K_{0} \rangle e^{i\phi} \rangle$ : sites 4(a), \hspace{1cm} (8.2)

and,

$\Psi_0^K(\#198) = [1 + (-1)^l Q \langle U^K_{0} \rangle e^{i\phi} \rangle \times (-1)^l \langle U^K_{0} \rangle e^{-i\phi} \rangle$. \hspace{1cm} (8.3)

In (8.2) and (8.3) the phase $\phi = 2\pi c l$. Expression (8.3) is valid for sites 4(a) in #198 used by Na and Br 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 $\langle T^K_0 \rangle$ replacing $\langle U^K_0 \rangle$.

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 $P_3 \Psi_0^K$ with $K = 0, 2$ is allowed. The pseudoscalar $\Psi_0^K$ 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 enantiotomers 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 $\sigma^+$ 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 $\sigma^+$ 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-E2 event, are found to be,

$F_{\alpha\alpha}^{\#198}(\#198) = 4 \langle T^2_{3} \rangle \cos \theta \left[ \cos \phi \sin \psi - i \sin \phi \cos \psi \right]$, \hspace{1cm} (8.4)

and, for the E1-E2 event,

$F_{\alpha\alpha}^{\#198}(\#198) = 4 \left( \frac{2}{13} \sin(2\theta) \langle -U^2_{0} \rangle / \Phi 
+ \frac{1}{2} \sqrt{\frac{5}{3}} \Phi \left( -\frac{1}{2} \langle U^2_{0} \rangle / \langle U^2_{0} \rangle \right) \right)$. \hspace{1cm} (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 \(\sigma\)-polarization. The results (8.4) agrees with Templeton and Templeton [14] when their parameter \(b\) in expression (9) is identified with our quadrupole \(Q_{2}^{\pm}\).

Lastly, we give the E1–E1 unit-cell structure factor for diffraction at \((00l)\) with odd \(l\) by space group \#19. We find,
\[
F_{\pi \sigma}^l (\#19) = F_{\pi \pi}^l (\#19)
= 4 \cos \theta (T_{2}^{\pm})^{i} \sin \phi \sin \psi - i(T_{2}^{\pm})^{i} \sin \phi \cos \psi. \tag{8.6}
\]

The result (8.4) is obtained from (8.6) when the symmetry of the site 4(a) in \#198 is imposed, leading to \((T_{2}^{\pm})^{i} = (T_{2}^{\pm})^{o}\).

An expression for the intensity of forbidden reflections (00l) in \#19 derived by Kirfel and Petrov [15] agrees with the intensity \([F_{\pi \sigma}^l (\#19)]^2\) when, as here, all contributions to the E1–E1 amplitude are taken at the same time 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 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 (\(\alpha\)-SiO\(_{2}\)) [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 enantiomers is based on whether calculated quantities agree or not with observations, namely, for one of the two enantiomers 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-enantiomer 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

\[
F_{\pi \sigma}^\alpha = F_{\pi \pi}^\alpha = 3(U_{1}^{\pm} + U_{2}^{\pm}) \sin \theta
\]

\[
F_{\pi \pi}^\alpha = i \frac{3}{8} [U_{1}^{\pm}(1 + \sin \phi \theta) - U_{2}^{\pm}] \sin (\theta \phi) e^{-3i \psi}. \tag{A.2}
\]

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

\[
F_{\pi \sigma}^\alpha = \sqrt{\frac{3}{15}} \sin \theta [\sqrt{2} (U_{1}^{\pm})^{i} - (U_{2}^{\pm})^{i}]
\]

\[
F_{\pi \pi}^\alpha = \sqrt{\frac{3}{15}} [\sqrt{2} U_{2}^{\pm} \sin \phi \theta + (U_{1}^{\pm})^{i} \sin(3 \theta)]
\]

\[
F_{\pi \pi}^\alpha = i \left\{ \sqrt{\frac{3}{5}} [(U_{1}^{\pm})^{i} \sin ^{2} \theta + \frac{1}{4} \sqrt{6} (U_{2}^{\pm})^{i} [1 + \cos (2 \theta)]] + \sqrt{3} \frac{1}{8} \sin (2 \theta \phi) e^{-3i \psi} [(U_{1}^{\pm})^{i} + \frac{2}{3} (U_{2}^{\pm})^{i}]
\]

\[
+ \frac{1}{3} \sqrt{2} (U_{2}^{\pm})^{i} \right\}. \tag{B.3}
\]

References