Double cone of eigendirections in optically active ethylenediammonium selenate crystals

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Received 22 March 2017

Accepted 26 May 2017

Edited by S. Sasaki, Tokyo Institute of Technology, Yokohama, Japan

Keywords: isotropic point; magnetoelectric tensor; gyration; optical activity; ellipsometry; X-ray diffraction.

CCDC reference: 1552556

Supporting information: this article has supporting information at journals.iucr.org/j

Circular birefringence (CB) is generally responsible for only a small perturbation to the state of light polarization in crystals that also exhibit linear birefringence (LB). As such, the magnetoelectric tensor of gyration, which gives rise to CB and optical activity, is less well determined than the electric permittivity tensor in optical models of the Mueller matrix. To visualize the effect of the magnetoelectric tensor on polarimetric measurements, reported here are experimental mappings of the Mueller matrix and of the CB in a new chiral crystal with accidental null LB at an accessible optical frequency. Single crystals of ethylenediammonium selenate (EDSeO₄) were synthesized and characterized by X-ray diffraction and Mueller matrix measurements in transmission and reflection. The crystals are isomorphous with the corresponding sulfate salt. They are tetragonal, space group $P4_1(3)2_12$. The constitutive relations of EDSeO₄ were recovered using a partial wave summation of incoherent reflections. The extraordinary and ordinary refractive indices cross at 364 nm (3.41 eV), a scenario commonly called the ‘isotropic point’ or ‘iso-index point’. At this wavelength, the magnetoelectric tensor fully describes the polarization transformation, giving rise to a double cone of eigendirections.

1. Introduction

Two centuries of struggle in the measurement of the anisotropy of the circular birefringence (CB) of crystals has been well documented (Kaminsky, 2000). A landmark result in this tortuous history was Hobden’s measurement of the optical activity along the low-symmetry dyad axes of AgGaS₂ at the particular wavelength of 485 nm, where it was observed that the dispersion curves of the ordinary and extraordinary electric permittivities cross (Hobden, 1967). Consequently, the linear anisotropy vanishes at this wavelength. By obviating the linear birefringence (LB) in this way, the optical anisotropy of the crystal is exclusively a consequence of the much smaller CB, and thereby intensity changes in transmitted light can be used to characterize the optical activity directly. An example of the same kind of analysis based on accidental equivalences was subsequently made for potassium trihydrogen di(*cis*-4-cyclohexene-1,2-dicarboxylate) dihydrate (Kim *et al.*, 1993).

Despite Hobden’s ingenious solution to the problem of measuring the optical rotatory power of an anisotropic crystal, his method required a special crystal with dispersion curves crossing at an accessible optical frequency. Techniques for measuring optical activity along general low-symmetry directions were subsequently described (Kobayashi & Uesu, 1983) and employed to measure the optical activity in AgGaS₂ even at a wavelength (632.8 nm) at which the LB was manifest (Etxebarria *et al.*, 2000). Full dispersion curves for AgGaS₂ were obtained by spectroscopic polarimeters with

sophisticated light polarization modulation schemes in transmission (Arteaga, Freudenthal & Kahr, 2012) and reflection (Arteaga, 2015).

Recently, we used the aforementioned methodology of sufficient flexibility to yield the dispersion of the anisotropies of optical activity of a previously uninvestigated chiral crystal, ethylenediammonium sulfate (EDSO₄) (Nichols, Martin *et al.*, 2016). The dispersion curves of the ordinary and extraordinary rays of this crystal do not cross in the visible part of the electromagnetic spectrum. Here, we report the synthesis, structure and optical properties of the isomorphous ethylenediammonium selenate (EDSeO₄), a new chiral crystal whose permittivity dispersion curves *do* cross, leading to an LB sign inversion. Few gyrotropic crystals with crossing ordinary and extraordinary dispersion curves have so far been identified [see, for example, CdGa₂S₄ (Hobden, 1968, 1969), LiKSO₄ (Gaba *et al.*, 1996) and Rochelle's salt (Romanyuk *et al.*, 2002)] and therefore we aim here to make a more detailed study of the optical properties of EDSeO₄.

In crystal optics, directions of zero linear anisotropy are commonly called 'optic axes', but these directions may still have circular anisotropy. At a frequency where the electric permittivities are accidentally coincident, all directions are optic axes. Because the magnetoelectric response is frequently bisignate, there are also directions at the isotropic point along which circular anisotropy likewise vanishes. In optically active point groups having an *n*-fold rotation axis with *n* ≥ 3, the loci of the system of axes of optical isotropy and optical inactivity form a double cone, described throughout as a double cone of eigendirections. When the wavevector is parallel to the cone, the polarization of the incoming light is not transformed. A full analysis of the double cones of eigendirections in EDSeO₄ is made here. Theoretical crystal optical analyses of these phenomena were described previously (Semchenko *et al.*, 2000; Vasyukiv *et al.*, 2006; Alshits & Lyubimov, 2008; Merkulov, 2014, 2015).

2. Experimental: synthesis and crystal growth of EDSeO₄

EDSeO₄ [(H₃NCH₂CH₂NH₃)²⁺SeO₄^{2−}] was obtained by modifying the established procedure for the synthesis of ethylenediammonium sulfate (EDSO₄) (Cheung *et al.*, 2008). Selenic acid solution (40 wt% in H₂O, 99.95%, Sigma–Aldrich) was added dropwise with continuous stirring to a solution of freshly distilled ethylenediamine (≥99.5%, Sigma–Aldrich) and ethanol (95%, Pharmco–Aaper). The reaction was exothermic and required continuous cooling in an ice bath. The resulting precipitate was washed with ethanol and diethyl ether and dried in air. Large crystals of EDSeO₄ (approximately 1 cm × 1 cm × 2 mm) were grown from aqueous solution at room temperature with a bidirectional stirring plate. Most crystals of EDSeO₄ grown *via* this method exhibited (001) twinning, with a single twin boundary that probably formed upon nucleation. Plates lying on the dish bottom grew unevenly in the vertical direction as ion delivery to the downward growing direction was hindered by the

crystallization dish. The twinned crystals thus have a single (001) twin boundary separating a major and minor enantiomorphous component, and must be cleaved into enantiomorphous sections prior to optical and/or structural characterization.

3. Results and discussion

3.1. X-ray crystallography

We previously correlated the absolute structure of EDSO₄ with the sign of optical rotation (Nichols, Martin *et al.*, 2016), an assignment that we later found to be incorrect. After re-examining our data, it was determined that the error probably originated from the rather large aspect ratio of the crystal section used for X-ray diffraction; the crystal was much thinner along *c* than along *a* or *b*. Because absolute structure determination relies on small differential extinctions of mirror symmetric reflections, its reliability depends on the accuracy of the multi-scan absorption correction performed by *SADABS* (Sheldrick, 1996), which in turn depends on the crystal morphology. Grinding crystals to a spherical shape obviates an absorption correction altogether, so we attempted to obtain crystals with isotropic path lengths. A single crystal of EDSeO₄ was cleaved into several 200 μm-thick sections. A section was determined to be free of a twin plane by observing that adjacent sections were of the same hand and that the measured CB (strictly the path-dependent circular retardance, but we will use 'CB' throughout to adhere to common usage) was consistent with the path length. The section was cut with a razor blade to create a 200 μm³ cube. Samples of EDSO₄ were similarly fabricated. We attempted to obtain spherical crystals

Figure 1
Packing diagrams and crystal habit of *P*₄₃₂₁₂ EDSeO₄. (a) The unit cell viewed along [010], (b) the unit cell viewed along [001], the fourfold screw axis, and (c) the crystal habit, generated with the software *WinXmorph* (Kaminsky, 2005).

Table 1
Full X-ray diffraction analysis of ethylenediammonium selenate.

Space group	$P4_32_12$
Empirical formula	$C_2H_{10}N_2O_4Se$
Temperature	300 K
Wavelength	0.71073 Å
Unit-cell dimensions	$a = 6.1352(4)$ Å, $c = 18.1726(12)$ Å
Volume	684.03 (10) Å ³
Absorption coefficient	5.443 mm ⁻¹
θ range for data collection	3.5–30.94°
Limiting indices	h –8 to 8, k –8 to 8, l –25 to 24
Reflections collected, unique	11625, 1050
Refinement method	Full-matrix least-squares on F^2
Data, restraints, parameters	1050, 0, 42
Goodness of fit on F^2	1.202
Final R indices [$I > 2\sigma(I)$]	961 data: $R_1 = 0.0208$, $wR_2 = 0.0549$ All data: $R_1 = 0.0243$, $wR_2 = 0.0557$
Largest difference peak and hole	0.0299 and –0.919 e Å ⁻³
Refined Flack parameter	0.024 (7)
Hooft y parameter	0.022 (6)

by tumbling cubes in a vial lined with sandpaper. After *ca* 24 h, the corners were only slightly rounded and most specimens were cracked, so we settled on the cube-shaped specimens.

Diffraction patterns were measured with a Bruker SMART APEXII single-crystal diffractometer. The structure was solved using the program *SHELXT* (Sheldrick, 2015), in which space groups $P4_{1(3)}2_12$ were the obvious choice based on systematic absences. *XPREF* (Sheldrick, 2001) confirmed the choice of space group. The structure was refined in *SHELXL* (Sheldrick, 2015) without using restraints on heavy atoms, giving a final R factor of 0.024. All hydrogen positions were calculated using appropriate riding models. Our final structure is plotted without hydrogen atoms in Fig. 1, with anisotropic displacement ellipsoids that are suitable for room-temperature data, along with a representation of the crystal habit. The absolute structure of $P4_32_12$ was assigned by Bijvoet pair analysis in *PLATON* (Hooft *et al.*, 2008). The Hooft y parameter, calculated from 300 select Bijvoet pairs, was 0.022 (6), which agrees with the traditional Flack parameter of 0.024 (7). Full details are provided in Table 1.

3.2. Transmission

All polarimetric measurements were acquired with a home-built polarimeter that uses four photoelastic modulators to measure the full normalized Mueller matrix in transmission or reflection (Arteaga, Freudenthal *et al.*, 2012; Nichols *et al.*, 2015). Optical characterization is informed by the X-ray structure analysis, which confirms that EDSeO₄ is a new gyrotropic uniaxial crystal isomorphous with EDSO₄. As such, the optical tensors of EDSeO₄ have a form consistent with point group 422 (D_4),

$$\begin{aligned}\boldsymbol{\epsilon} &= \text{diag}(\epsilon_{11}, \epsilon_{11}, \epsilon_{33}), \\ \boldsymbol{\alpha} &= \text{diag}(\alpha_{11}, \alpha_{11}, \alpha_{33}), \\ \boldsymbol{\mu} &= \mathbf{I},\end{aligned}\quad (1)$$

relative to the crystallographic optic axis, where $\boldsymbol{\epsilon}$, $\boldsymbol{\alpha}$ and $\boldsymbol{\mu}$ are the relative permittivity, magnetoelectric and permeability

tensors, respectively, and $\mathbf{I}$ is the identity matrix. The tensor $\boldsymbol{\alpha}$ has sometimes been called the ‘gyration tensor’, but we will reserve this term as a synonym for the commonly reported optical rotation tensor ($\boldsymbol{\rho}$).

Single crystals of EDSeO₄ were cleaved normal to [001] into 100–600 μm -thick plates, and the sign of CB along [001] was determined by viewing the sample through crossed polarizers and rotating the first polarizer to the extinction position. Two enantiomorphous sections were selected for normal incidence measurements along the crystallographic optic axis. Ignoring the very small effect of interfaces at normal incidence, Mueller matrix measurements along the optic axis of a uniaxial crystal depend only on α_{11} and the sample thickness d ,

$$\mathbf{M}(\lambda) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(4\pi d\alpha_{11}/\lambda) & \sin(4\pi d\alpha_{11}/\lambda) & 0 \\ 0 & -\sin(4\pi d\alpha_{11}/\lambda) & \cos(4\pi d\alpha_{11}/\lambda) & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \quad (2)$$

Here, the central block of the Mueller matrix fully describes the polarization transformation of the Stokes vector, and measurement of any individual central-block element, or of CB, can be used to calculate α_{11} at a particular wavelength. Moreover, the orthogonal eigenpolarization states along the optic axis are right and left circularly polarized states, whereas these are generally elliptically polarized for linear birefringent gyrotropic uniaxial media.

Mueller matrix spectra were measured in transmission at normal incidence for a 226 μm EDSeO₄ slab of the $P4_32_12$ enantiomorph, and for a 517 μm EDSeO₄ slab of the $P4_12_12$ enantiomorph, from 300 nm (4.13 eV) to 750 nm (1.65 eV) in 10 nm increments. Fig. 2 displays the central block of the Mueller matrix. For crystals that are sufficiently thin to rotate the plane polarization of light less than 90°, the sign of the M_{23} element coincides with that of both the α_{11} component of the magnetoelectric tensor and CB, which can be calculated from

Figure 2
The central block of the transmission Mueller matrix at normal incidence from 1.65 to 4.13 eV. Measured spectra are shown for a 226 μm sample of $P4_32_12$ EDSeO₄ (red) and a 517 μm sample of $P4_12_12$ EDSeO₄ (blue). The α_{11} dispersion relation was fitted using a partial-wave optical model and the corresponding calculated spectra are overlaid in black.

the Mueller matrix by analytic inversion (Arteaga *et al.*, 2014). Although tabulated values of α_{11} can be calculated directly from transmission spectra, we fit these spectra to an oscillator model of the form

$$\alpha_{ii} = \frac{A_{\alpha_{ii}} \lambda^3}{(\lambda^2 - E_{\alpha_{ii}}^2)^2}, \quad (3)$$

where λ is the wavelength in nanometres. This step in the fitting procedure provides a robust measurement of the α_{11} component of the magnetoelectric tensor, but is based on a fixed crystal thickness estimate from a digital micrometer (Aerospace Instruments, Model IP54, 1 μm resolution) and must be refined in reflection.

3.3. Reflection

Mueller matrix measurements in reflection were acquired from 300 nm (4.13 eV) to 750 nm (1.65 eV) in 2 nm steps for the same 226 μm slab of the $P4_12_12$ enantiomorph cleaved normal to the optic axis. Optical models were constructed using a recently developed general partial wave method that accounts for multiple incoherent reflections or transmissions from any homogeneously stratified medium (Berreman, 1972; Postava *et al.*, 2002, 2004; Nichols *et al.*, 2015) and are discussed in Appendix A. The α_{33} component of the magnetoelectric tensor and the full permittivity tensor were fitted to oscillator models using two similar algorithms: a bounded trust-region-reflective nonlinear least-squares fitting algorithm in MATLAB (The MathWorks Inc., Natick, MA, USA) and a bounded Levenberg–Marquardt least-squares algorithm in LabVIEW (National Instruments Corporation, Austin, TX,

Table 2
Dispersion relations for $P4_12_12$ EDSeO₄.

Tensor component	Parameter	Fitted value
ε_{11}	$A_{\varepsilon_{11}}$	1.10387
	$B_{\varepsilon_{11}}$	0.500036
	$C_{\varepsilon_{11}}$	7.12503 μm
	D_{11}	1.27344
	$E_{\varepsilon_{11}}$	0.112695 μm
ε_{33}	$A_{\varepsilon_{33}}$	1.12003
	$B_{\varepsilon_{33}}$	1.60328
	$C_{\varepsilon_{33}}$	11.4018 μm
	D_{33}	1.26142
	$E_{\varepsilon_{33}}$	0.110290 μm
α_{11}	$A_{\alpha_{11}}$	−0.0173619
	$E_{\alpha_{11}}$	114.747 nm
α_{33}	$A_{\alpha_{33}}$	0.0245107
	$E_{\alpha_{33}}$	134.927 nm

USA). The reduced χ^2 figure of merit was calculated from the standard deviation of four repeated measurements with an error cut-off value of 0.0005. Oscillator equations for the magnetoelectric tensor elements follow the form given in equation (3), while the oscillator equations for the electric permittivity tensor elements follow the form

$$\varepsilon_{ii} = D_{ii} + \frac{A_{\varepsilon_{ii}} \lambda^2}{(\lambda^2 - E_{\varepsilon_{ii}}^2)} + \frac{B_{\varepsilon_{ii}} \lambda^2}{(\lambda^2 - C_{\varepsilon_{ii}}^2)}, \quad (4)$$

and fitted values can be found in Table 2.

Fig. 3 shows reflection spectra for three angles of incidence, overlaid in black with calculated spectra using the fitted

Figure 3
Measured Mueller matrix spectra of a 226 μm sample of $P4_12_12$ EDSeO₄ in reflection at 40° (red), 48° (green) and 56° (blue) angles of incidence. Calculated spectra are overlaid in black.

constitutive relations. Excellent agreement is found between the measured spectra and the fitted optical model ($\chi^2_{\text{red}} = 5.24$; $R^2 = 0.99994$). Additional fitting parameters included the following: an azimuthal orientation offset between the instrument x axis and the projection of the optic axis onto the surface normal (-37.85°), a fixed angle of incidence offset (-0.217°), and the refined thickness of the crystal ($225.97 \mu\text{m}$). Although the crystals have cleavage normal to $[001]$, a miscut from the crystallographic optic axis was allowed to refine to confirm a stable value near zero degrees (0.211°). The isotropic point manifests in reflection measurements of the Mueller matrix as near-zero values for the off-diagonal elements of the last row and column, resulting in crossing points in the spectra for these elements regardless of the thickness and relative orientation of the sample.

The fitted dispersion relations for the permittivity and magnetoelectric tensors are plotted in Fig. 4, along with the LB perpendicular to the optic axis. The electric permittivity tensor components cross at 3.408 eV (364 nm) at a value of 2.493 , and $\text{LB}_\perp$ is given by

$$\text{LB}_\perp = (\varepsilon_{33})^{1/2} - (\varepsilon_{11})^{1/2}. \quad (5)$$

The absolute values of the magnetoelectric tensor components are included in Fig. 4 and the sign of α_{11} is $- (+)$ for the $P4_{1(3)}2_12$ enantiomorph. The sign of the α_{33} magnetoelectric tensor component is always opposite to that of the α_{11} component for a given enantiomorph of EDSeO_4 . Note, however, that optical rotation *can* be of the same sense for all directions through a material; a bisignate magnetoelectric tensor does not necessarily correspond to a bisignate optical rotation tensor. Additionally, the optical rotation tensor is always monosignate for isotropic crystals of the point groups $23 (T)$ and $432 (O)$, for which

$$\alpha = \text{diag}(\alpha_{11}, \alpha_{11}, \alpha_{11}). \quad (6)$$

3.4. Polar mapping

For a uniaxial material with accidental null LB at a particular wavelength, the optical response is invariant to rotation for every direction, giving rise to a sphere of optic axes with respect to linear anisotropy. As such, the existence of an isotropic wavelength in an optically active crystal, such as EDSeO_4 , provides an excellent opportunity to visualize the effects of the magnetoelectric tensor on Mueller matrix measurements. As discussed in the previous section, the form of the magnetoelectric tensor is determined by the crystal point group, while the sign and magnitude of optical rotation for different directions are related to the spatial dispersion of the electric field with respect to the crystal structure (Landau *et al.*, 1984). The general representation surface of a 422 magnetoelectric tensor with positive optical rotation in all directions is an ellipsoid of revolution. However, as the independent elements of the magnetoelectric tensor may have opposite signs, as is the case with EDSeO_4 , optical rotation can also become bisignate.

To visualize the optical activity tensor, polar maps of the transmission Mueller matrix were obtained at 364 nm for 32 angles of incidence (ranging from 0 to 30°) and 59 azimuthal orientations (ranging from 0 to 360°) using an automated measurement program and a motorized goniometer. As EDSeO_4 has cleavage normal to $[001]$, polar maps were obtained along this direction and exhibit axial symmetry. The polar maps of the Mueller matrix elements were converted analytically to the corresponding polar map of CB (Arteaga & Canillas, 2010). Fig. 5(a) shows experimental (left) and calculated (right) polar mappings of CB for the $517 \mu\text{m}$ crystal of the $P4_32_12$ enantiomorph, with the angle of incidence radius marked in black and the azimuthal orientation marked in blue. This measurement at the isotropic point allows us to refine the fitted constitutive relations from reflection ellipsometry, with much more sensitivity to the magnetoelectric tensor. The refined values from the polar mapping at 364 nm are $\alpha_{11} = 5.875 \times 10^{-5}$ and $\alpha_{33} = -8.705 \times 10^{-5}$, which differ by 0.09 and 3.96% , respectively, from the values obtained from the fitted dispersion relations.

Figure 4
Fitted dispersion spectra for the electric permittivity tensor ε (top), LB perpendicular to the crystallographic optic axis (center) and the magnetoelectric tensor α (bottom).

A better visualization of the magnetoelectric tensor comes from a crystal cut normal to [010]. Fig. 5(b) contains a calculated polar map of CB for an *x*-cut crystal at an angle of incidence (azimuthal orientation) ranging from 0 to 80° (360°). The color map features a global zero (black) that traces the double cone of eigendirections, highlighted with the white dashed line. A third polar map of CB was calculated for a crystal cut at 63.9° from [001], shown in Fig. 5(c) with the same angle of incidence and azimuthal orientation range depicted in Fig. 5(b). The particular crystal cut in Fig. 5(c) coincides with the double cone of eigendirections at 364 nm. Accordingly, the central position of this polar map, which corresponds to a normal incidence measurement, represents an eigendirection through the crystal. Again, the white dashed line traces one portion of the double cone of eigendirections.

The representation surface of the magnetoelectric tensor at 364 nm is included in Fig. 5(d) (left). As a visual tool, the

magnetoelectric tensor is a less intuitive depiction of optical activity, as it acts on the field components of the electromagnetic wave, and thus light experiences the average of tensor components in the plane normal to the wavevector. The more commonly reported description of optical activity is given by the optical rotation tensor,

$$\rho = \frac{\pi d}{\lambda} \begin{pmatrix} \alpha_{22} + \alpha_{33} & -\alpha_{12} & -\alpha_{13} \\ -\alpha_{21} & \alpha_{11} + \alpha_{33} & -\alpha_{23} \\ -\alpha_{31} & -\alpha_{32} & \alpha_{11} + \alpha_{22} \end{pmatrix}, \quad (7)$$

which operates on the wavevector and describes the accumulation of optical rotation of plane-polarized light in radians over a distance *d* traveled through the medium, where $CB = 2n^T \rho n$ and *n* is the direction of the incident light. The representation surface of the optical rotation tensor is included in Fig. 5(d) (right), along with labeled directions that correspond to the polar maps of CB depicted in Figs. 5(a), 5(b) and 5(c). EDSeO₄ crystals show moderate optical activity at accessible optical frequencies, measured at $\pm 58.1^\circ \text{ mm}^{-1}$ along [001] and $\mp 14.0^\circ \text{ mm}^{-1}$ in the (001) plane at 364 nm.

The opportunity to study optical activity near an isotropic wavelength has been the subject of prior theoretical work. The constitutive relations for various classes of chiral materials with anisotropy compensation, including superlattices and helical media, were previously derived by Semchenko *et al.* (2000). A theoretical description of the phenomenon measured in this work (Alshits & Lyubimov, 2008) and simulated conoscopic patterns for various crystal parameters near an isotropic point (Vasylykiv *et al.*, 2006) are found in the literature. Recent work considers the more complex optical response from optically active crystals with significant linear dichroism in the spectral region near an isotropic point in the real portion of the electric permittivity tensor (Alshits & Lyubimov, 2004; Merkulov, 2014, 2015; Sturm & Grundmann, 2016). This scenario results in the splitting of double cones of eigendirections into cones of singular optical axes.

Figure 5

Polar maps of CB in radians of a 517 μm crystal of the $P4_32_12$ enantiomorph. (a) Experimental map along [001] (left) and calculated map along [001] (right) with a maximum angle of incidence equal to 30°. (b) Calculated map of a crystal cut normal to [010] with a maximum angle of incidence equal to 80°. (c) Calculated map of a crystal cut at 63.9° from [001] with a maximum angle of incidence equal to 80°. The white dashed lines represent polar positions associated with eigendirections. (d) Normalized representation surfaces of the magnetoelectric tensor, α (left), and of the optical rotation tensor, ρ ($^\circ \text{ mm}^{-1}$; right), plotted with the software WinTensor (<http://cad4.cpac.washington.edu/WinTensorhome/WinTensor.htm>). The double cone of eigendirections is overlaid in black, and the dashed lines indicate the viewing directions depicted in the polar maps in panels (a), (b) and (c).

4. Conclusion

Crystals of EDSeO₄ are easily fabricated, can be included in the list of known substances with accidental anisotropy compensation that generate interesting *k*-space shapes of eigendirections, and should find use in the polarimetric community in studies of optical activity.

Future experimental studies using sophisticated polarization modulation schemes should corroborate theoretical findings for uniaxial and biaxial gyrotropic crystals and expand the scope and improve the accuracy of optical activity measurements for commonly used crystals, especially those with LB sign inversion at accessible optical frequencies.

APPENDIX A Optical models

The optical models employed in this work treat the complete light–matter interaction in reflection or transmission and are

sufficiently general to describe arbitrarily oriented bi-anisotropic crystals in homogeneously stratified media. The constitutive relations of the media (permittivity, permeability and magnetoelectric tensors), along with the layer thickness and crystallographic orientation, are used to define the layer matrix, which describes the polarization transformation through any specific layer with homogeneous optical properties. The optical model used here for EDSeO₄ includes an incoherent summation of multiply reflected beams, where the appropriateness of implementation depends on the magnitude of the birefringence in a certain direction, the crystal thickness and the coherence volume of the light source (Postava *et al.*, 2002, 2004; Nichols, Arteaga *et al.*, 2016). As EDSeO₄ has very modest LB across the accessible spectral region, co-propagating eigenwaves that have made the same number of passes through the crystal remain coherent, while multiply reflected or transmitted beams that have made a different number of passes become incoherent, given the modest coherence volume of the spectroscopic light source. A detailed explanation (Nichols *et al.*, 2015) and implementation (Nichols, Martin *et al.*, 2016; Martin *et al.*, 2016) of the partial wave method can be found in the recent literature.

As an alternative, propagation can be modeled analytically in certain cases. For crystals with symmetric constitutive relations, the z component of the wavevectors for the four induced eigenmodes (two forward propagating and two backward) that result from an incident wave in free space are given (Onishi *et al.*, 2011) by the four nontrivial solutions to the following system of equations:

$$\det[\boldsymbol{\varepsilon} + (\mathbf{K} - i\boldsymbol{\alpha}) \cdot \boldsymbol{\mu}^{-1} \cdot (\mathbf{K} - i\boldsymbol{\alpha})] = 0, \quad (8)$$

$$\mathbf{K} = \begin{pmatrix} 0 & -k_z & k_y \\ k_z & 0 & -k_x \\ -k_y & k_x & 0 \end{pmatrix}, \quad (9)$$

where $\boldsymbol{\varepsilon}$, $\boldsymbol{\mu}$ and $\boldsymbol{\alpha}$ are the electric permittivity, magnetic permeability and magnetoelectric tensors, respectively, and $\mathbf{K}$ is the three-dimensional cross-product operator. For a c -cut crystal of point group 422 at an isotropic wavelength, the constitutive relations are further simplified in the laboratory reference frame:

$$\begin{aligned} \boldsymbol{\varepsilon} &= \text{diag}(\varepsilon_{11}, \varepsilon_{11}, \varepsilon_{33}) = \text{diag}(\varepsilon, \varepsilon, \varepsilon), \\ \boldsymbol{\alpha} &= \text{diag}(\alpha_{11}, \alpha_{11}, \alpha_{33}) = \text{diag}(\alpha_x, \alpha_x, \alpha_z), \\ \boldsymbol{\mu} &= \mathbf{I}. \end{aligned} \quad (10)$$

An incident wavevector in the xz plane requires that $k_y = 0$ and $k_x = \sin(\theta_i)$ for all eigenwaves, where θ_i is the angle of incidence. Analytic expressions for the eigenvalues are complicated for generally anisotropic and gyrotropic media, but are simplified at the isotropic point. The four analytic solutions to equation (8) are tractable:

$$k_z^{1,3} = \pm \left\{ \frac{(\varepsilon^{1/2} + \alpha_x)[\cos(2\theta_i) + 2(\varepsilon^{1/2} + \alpha_x)(\varepsilon^{1/2} + \alpha_z) - 1]}{2(\varepsilon^{1/2} + \alpha_z)} \right\}^{1/2} \quad (11a),$$

$$k_z^{2,4} = \pm \left\{ \frac{(\varepsilon^{1/2} - \alpha_x)[\cos(2\theta_i) + 2(\varepsilon^{1/2} - \alpha_x)(\varepsilon^{1/2} - \alpha_z) - 1]}{2(\varepsilon^{1/2} - \alpha_z)} \right\}^{1/2}, \quad (11b)$$

and can be used to solve the electromagnetic field vectors for the eigenpolarization states that correspond to each eigenwave.

Acknowledgements

The authors are grateful for the assistance of Dr Chunhua Hu at the Department of Chemistry of New York University with the X-ray analysis, and acknowledge the Molecular Design Institute of NYU for purchasing the single-crystal diffractometer.

Funding information

This work was supported by the National Institutes of Health (5R21GM107774-02), the National Science Foundation (DMR-1105000), an NSF Predoctoral Fellowship to SMN (DGE-12342536) and a Margaret Strauss Kramer Fellowship from the NYU Department of Chemistry to ATM. This work was supported partially by the MRSEC Program of the National Science Foundation (DMR-1420073).

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