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# X-ray Birefringence from a Model Anisotropic Crystal

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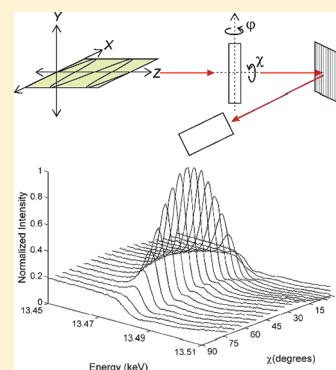
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 Supporting Information

**ABSTRACT:** Whereas the phenomenon of birefringence is well-established and widely applied in the case of linearly polarized visible light (for example, underpinning the use of the polarizing optical microscope), the study of birefringence using linearly polarized X-rays is an essentially unexplored field. To address this issue, we report a material that exhibits ideal birefringence behavior at X-ray energies near the Br K-edge. The designed material, the 1-bromoadamantane/thiourea inclusion compound, gives experimental behavior in excellent agreement with theoretical predictions for the dependence of transmitted X-ray intensity on both X-ray energy and crystal orientation. Our results vindicate the potential to exploit X-ray birefringence to establish a detailed understanding of molecular polarization, particularly as an experimental strategy to determine the orientational distributions of specific bonds in solids, for example, in the case of partially ordered materials or materials that undergo order–disorder phase transitions.

**SECTION:** Electron Transport, Optical and Electronic Devices, Hard Matter



The interaction of linearly polarized visible light with solids is well understood, including the phenomena of dichroism and birefringence,<sup>1</sup> for which absorption (in the case of dichroism) and refractive index (in the case of birefringence) depend on the orientation of an anisotropic material with respect to the plane of polarization of the incident radiation. While widely studied for visible light, these phenomena are far less established for linearly polarized X-rays, although we note that research on X-ray dichroism<sup>2–5</sup> has included recent studies of dichroic filter materials for applications in magnetic X-ray scattering<sup>3</sup> and X-ray astronomy.<sup>5</sup> In the present Letter, we report the first definitive demonstration of X-ray birefringence, reporting a material that exhibits essentially ideal birefringence behavior at X-ray energies near the Br K-edge. Our results vindicate the potential to exploit this phenomenon to establish a detailed understanding of molecular polarization and, in particular, to determine the orientational distributions of specific bonds in solids.

Although the phenomena of dichroism and birefringence give rise to different effects on the propagation of linearly polarized radiation through a material (dichroism causes rotation of the plane of polarization and birefringence causes the polarization to become elliptical), these phenomena are intimately related to each other and are related mathematically by a Kramers–Kronig transform.<sup>6</sup> Therefore, materials that exhibit linear dichroism generally also exhibit birefringence, and these phenomena depend on the same structural (and symmetry) properties of the material. Given our previous development of materials that exhibit significant X-ray dichroism,<sup>3–5</sup> we were motivated to

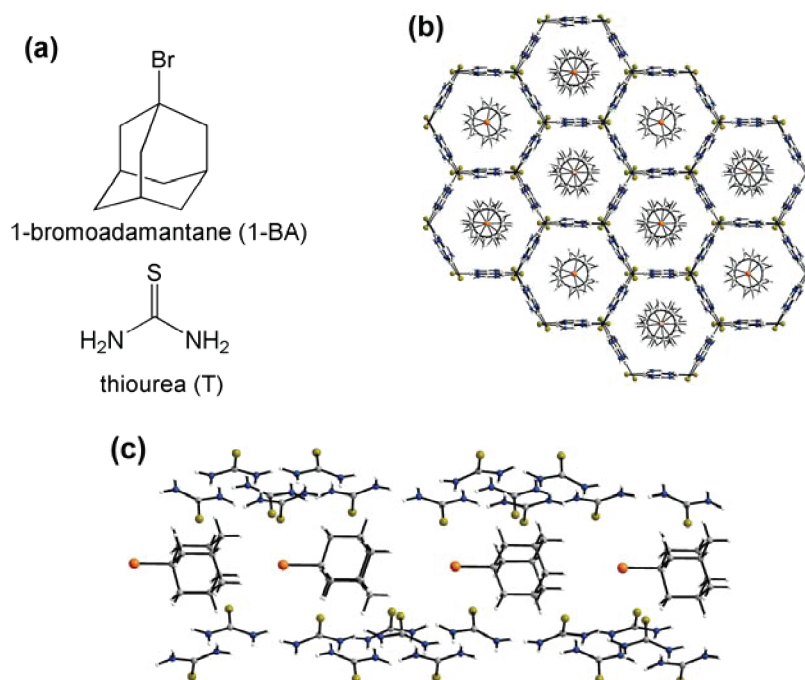
explore the possibility that such materials may also exhibit X-ray birefringence. Surprisingly, very few experimental studies of X-ray birefringence have been reported,<sup>7–9</sup> and significantly, all previous studies involved complex experimental setups, typically with the detection of extremely weak signals. In contrast, the model material studied here is shown to exhibit a huge birefringence signal, which permits a very simple experimental arrangement to be used, directly analogous to the setup in the conventional polarizing microscope for studies of optical birefringence. Our observations open up the realistic prospect of exploiting the phenomenon of X-ray birefringence to probe small changes in molecular polarization as well as to probe the dynamic properties and spatial distribution of molecular polarization in solids.<sup>10</sup>

The successful development<sup>3–5</sup> of X-ray dichroic filter materials suitable for operating at X-ray energies near the Br K-edge was based on urea and thiourea inclusion compounds,<sup>11–17</sup> which comprise guest molecules of suitable size and shape spatially confined within a host tunnel structure constructed from the urea or thiourea molecules. The key advantage of exploiting such solid inclusion compounds in the development of materials for applications based on X-ray dichroism (and here X-ray birefringence) devolves upon the fact that the host structure exerts a very strong orienting influence on the guest molecules, and thus with appropriate choice of both the host

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**Figure 1.** (a) Molecules present in the 1-BA/thiourea inclusion compound. (b) Crystal structure of the 1-BA/thiourea inclusion compound viewed along the tunnel axis ( $c$  axis) of the thiourea host structure, and (c) viewed perpendicular to the tunnel axis (horizontal), showing that the C—Br bonds of all 1-BA guests are parallel to the tunnel.

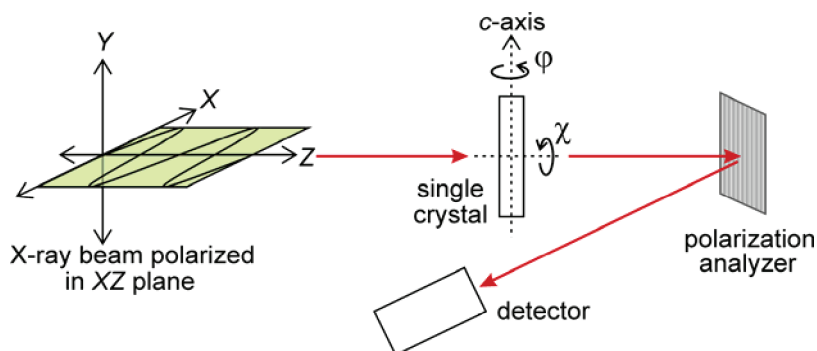
structure and the guest molecules, materials can be designed in which the orientations of specific bonds of the guest molecules (in the present case, C—Br bonds) can be exquisitely controlled.

Our initial studies of X-ray dichroism in the urea inclusion compound containing 1,10-dibromodecane guest molecules led to the theoretical prediction<sup>3</sup> that optimal X-ray dichroism at X-ray energies near the Br K-edge may be achieved for a material in which all C—Br bonds are aligned parallel to each other (a situation not realized for 1,10-dibromodecane/urea). On the basis of this prediction, we designed a new material, a solid inclusion compound comprising 1-bromoadamantane (denoted 1-BA; Figure 1a) guest molecules within the thiourea (Figure 1a) host tunnel structure, on the basis that the thiourea host structure would constrain the orientations of the 1-BA guest molecules such that all C—Br bonds in the material would be parallel to each other. This material was prepared, and determination of the crystal structure<sup>4</sup> (Figure 1b,c) vindicated the success of the design strategy. The material was shown to exhibit optimal performance as an X-ray dichroic filter near the Br K-edge, exhibiting the theoretically predicted maximum difference in the absorption of linearly polarized incident X-rays between two crystal orientations differing by 90° (specifically, the two orientations with the empty C—Br antibonding orbital parallel and perpendicular to the plane of incident polarization<sup>18</sup>). Because the 1-BA/thiourea inclusion compound represents a model material for X-ray dichroism, our initial studies of X-ray birefringence focused on the same material.

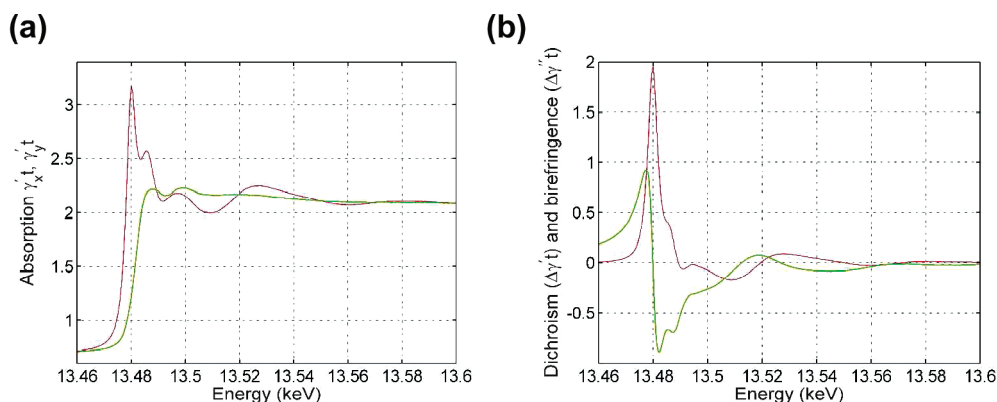
The crystal structure<sup>4</sup> of the 1-BA/thiourea inclusion compound (Figure 1b,c) has space group  $P321$ , and the thiourea host tunnels (which exhibit subtle structural differences from “conventional” thiourea inclusion compounds<sup>19–23</sup>) are parallel to the unique crystallographic axis ( $c$  axis). Within the periodic repeat (24.75 Å) along the tunnel, the 1-BA guest molecules occupy three independent sites, but importantly, the C—Br

bonds of all guest molecules are aligned parallel to the tunnel and hence parallel to the  $c$  axis. From the crystal symmetry, the material is uniaxial, with the optic axis parallel to the  $c$  axis, and is highly anisotropic with respect to the orientations of the C—Br bonds. A single crystal of 1-BA/thiourea (as used in the experiments discussed below) has a long-needle morphology, with the needle axis parallel to the tunnel axis of the host structure ( $c$  axis) and parallel to the direction of the C—Br bonds of the 1-BA guest molecules. In general, the cross-section ( $ab$  plane) of the long-needle morphology is hexagonal (with angles of 120° between adjacent faces in the hexagonal cross-section), although the six sides of the hexagon are not necessarily of equal length. The crystals of 1-BA/thiourea studied here were prepared as described in ref 4.

To study X-ray birefringence, the transmission of linearly polarized X-rays through the crystal was studied in the “crossed-polarizer” geometry shown in Figure 2 for X-ray energies near the Br K-edge. Measurements of X-ray dichroism employed the same experimental arrangement but with no polarization analyzer (and with the detector placed along the direction of propagation of the incident beam). The dimensions of the crystal were ca. 4 mm along the  $c$  axis and ca. 1 mm perpendicular to the  $c$  axis, and the dimensions (fwhm) of the focused X-ray beam were 0.2 (horizontal) and 0.05 mm (vertical). The crystal  $c$  axis was maintained perpendicular to the direction of propagation ( $z$  axis; Figure 2) of the incident X-ray beam, with an angle  $\chi$  between the crystal  $c$  axis and the direction of linear polarization of the incident beam (horizontal). Thus,  $\chi = 0^\circ$  when the crystal  $c$  axis is in the horizontal plane ( $xz$  plane). The orientation of the crystal with respect to rotation around the  $c$  axis is defined by angle  $\phi$  (Figure 2), with  $\phi = 0^\circ$  corresponding to the orientation with the incident X-ray beam ( $z$ -axis) parallel to the crystallographic  $a$ -axis (or a symmetry equivalent direction). Our experimental measurements of X-ray birefringence, using the



**Figure 2.** Schematic of the experimental setup for measurements of X-ray birefringence. The incident X-ray beam is propagated along the  $z$  axis and is polarized in the  $xz$  plane. The crystal orientation angles  $\chi$  and  $\phi$  are defined.



**Figure 3.** (a) X-ray absorption spectra measured with the  $c$  axis of a single crystal of 1-BA/thiourea parallel ( $x$ ; red line) and perpendicular ( $y$ ; green line) to the plane of polarization of the incident X-ray beam. (b) Measured X-ray dichroism spectrum (red line;  $\Delta\gamma'(E)t$ , the difference between the two curves in part (a) and the calculated X-ray birefringence spectrum (green line;  $\Delta\gamma''(E)t$ ).

setup in Figure 2, were carried out<sup>24</sup> on beamline I16 at the Diamond Light Source. We recall that synchrotron radiation provides a linearly polarized incident X-ray beam (>99% polarized on beamline I16).

For our measurements of transmitted X-ray intensity, it is convenient to adopt the terminology of linear absorption coefficients. Assuming a uniform material of thickness  $t$  and linear absorption coefficient  $\gamma$ , the ratio of transmitted X-ray intensity ( $I_1$ ) to incident X-ray intensity ( $I_0$ ) is given by  $I_1/I_0 = e^{-\gamma t}$ . The value of  $\gamma$  varies significantly as a function of X-ray energy near an absorption edge and also depends (for an anisotropic material) on the orientation of the crystal with respect to the direction of incident polarization. Although it is convenient to deal directly with intensities, this approach is inadequate when the phase of the photon plays an important role, and an analogous approach dealing with the electric field (or wave amplitude  $\epsilon$ ) of the photon must be adopted instead. Thus,  $I_1/I_0 = |\epsilon_1|^2/|\epsilon_0|^2 = e^{-\gamma' t}$ , where  $I \propto |\epsilon|^2$  and  $\gamma$  is a complex quantity. The real part of  $\gamma$  is the conventional absorption coefficient and describes the change in amplitude of the wave, whereas the imaginary part of  $\gamma$  gives the change in phase.

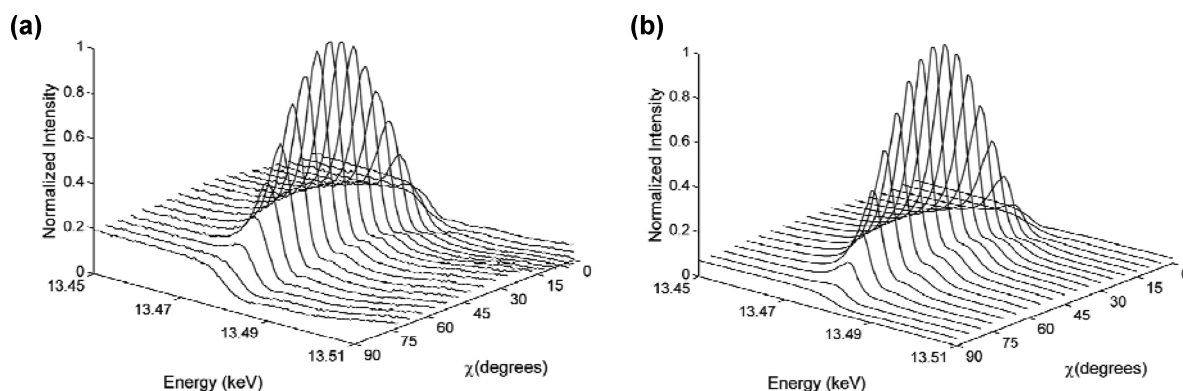
Dichroism and birefringence are the real (primed) and imaginary (double-primed) parts, respectively, of a continuous complex function  $\gamma(E)$ , where  $E$  is photon energy, and are related by the Kramers–Kronig transform.<sup>6</sup> In the present case, the linear dichroism ( $\Delta\gamma't$ ) is the difference between absorption spectra recorded (Figure 3a) with the crystal  $c$  axis parallel ( $\gamma_x't$ )

and perpendicular ( $\gamma_y't$ ) to the direction of polarization of the incident X-ray beam. Knowing the linear dichroism spectrum  $\Delta\gamma'(E)$ , obtained from experimental measurements of  $\gamma_x't$  and  $\gamma_y't$  (Figure 3a), the birefringence spectrum  $\Delta\gamma''(E)$  is calculated using the Kramers–Kronig transform<sup>6</sup> as

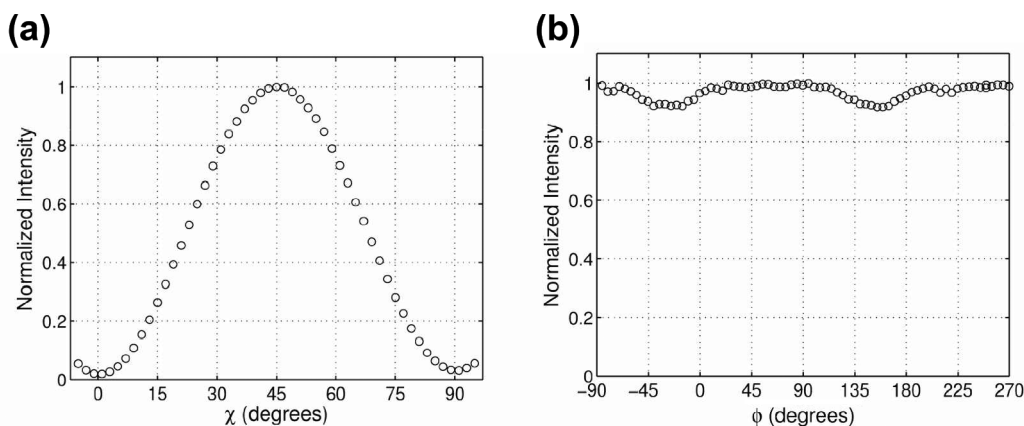
$$\Delta\gamma''(E) = \frac{2}{\pi} P \int_0^\infty \frac{E' \Delta\gamma'(E')}{(E'^2 - E^2)} dE' \quad (1)$$

where  $P$  is the “principal part” of the integral (which involves a singularity) and  $E$  and  $E'$  represent photon energy. For a symmetric dichroism spectrum, the birefringence is antisymmetric and vice versa.

In the present study, we compare experimental measurements and theoretical simulations of X-ray birefringence for a single crystal of 1-BA/thiourea using the setup in Figure 2. To calculate theoretically the properties of the polarized X-rays transmitted through the crystal, we first require to measure the total X-ray intensity transmitted through the crystal (i.e., with the polarization analyzer removed from the experimental assembly and with the detector placed along the direction of propagation of the incident beam) as a function of X-ray energy for two fixed crystal orientations, specifically with the optic axis ( $c$  axis) of the crystal fixed either parallel ( $\chi = 0^\circ$ ) or perpendicular ( $\chi = 90^\circ$ ) to the plane of polarization of the incident beam. We note in passing that these measurements (Figure 3a) demonstrate strong X-ray dichroism in the vicinity of the Br K-edge, as also previously



**Figure 4.** (a) Transmitted X-ray intensity recorded (for the setup in Figure 2) for a single crystal of 1-BA/thiourea as a function of angle  $\chi$  and X-ray energy and (b) the corresponding data simulated using the theoretical framework in the Supporting Information. The intensities are normalized to a maximum of unity in each case. The transmitted signal is very strongly enhanced close to the energy of the Br K-edge and passes through a maximum at  $\chi = 45^\circ$ .



**Figure 5.** (a) Transmitted X-ray intensity (normalized to a maximum of unity) as a function of  $\chi$  for the setup in Figure 2 with X-ray energy fixed at 13.4855 keV (near the maximum of the Br K-edge) and  $\phi$  fixed at  $0^\circ$ . (b) Same as part (a) but with transmitted X-ray intensity measured as a function of  $\phi$  with  $\chi$  fixed at  $45^\circ$ .

reported.<sup>4</sup> The dichroism spectrum  $\Delta\gamma'(E)t$  (Figure 3b) determined from these experimental data is then used to calculate the birefringence spectrum  $\Delta\gamma''(E)t$  (Figure 3b) using eq 1. We note from Figure 3b that the dichroism spectrum  $\Delta\gamma'(E)t$  is indeed (as discussed above) close to symmetric and the birefringence spectrum  $\Delta\gamma''(E)t$  is almost antisymmetric.

On the basis of the knowledge of these two spectra, we can calculate the properties of the X-rays transmitted through the crystal and the polarization analyzer using the theoretical framework developed in the Supporting Information (partially based on previous publications<sup>25–28</sup>) for comparison to the corresponding data measured in the detailed experimental studies discussed below. The theory outlined in the Supporting Information describes the changes in both amplitude and phase of a wave of specific polarization passing through a material and allows us to calculate the intensity of radiation transmitted through any material for which the absorption is dominated by electric dipole transitions, for any polarization of the incident beam, and for any orientation of the material. (Furthermore, the analysis allows for a nonideal polarization analyzer.) Therefore, the theoretical framework allows us to simulate the type of X-ray intensity data recorded using the experimental setup in Figure 2.

We now consider our experimental measurements of X-ray birefringence recorded using the setup in Figure 2, comprising data of transmitted intensity as a function of X-ray energy and crystal orientation angle  $\chi$  for a single crystal of 1-BA/thiourea (experimental data in Figure 4a; corresponding simulated results in Figure 4b). The transmitted X-ray intensity varies significantly as a function of both crystal orientation and X-ray energy because of the anisotropic X-ray optical properties of the crystal, directly analogous to the effects observed in optical microscopy with linearly polarized visible light. In the present case, the effects arise from X-ray dichroism and X-ray birefringence, which depend directly on local anisotropy at the atomic level. Therefore, the measured X-ray intensity depends on the molecular anisotropy within the material, and, in particular, the orientational properties of the C–Br bonds. The agreement between experimental and simulated results (Figure 4) is very satisfactory, indicating that the properties of the crystal and the physics underlying the technique are well understood. At a given X-ray energy, the maximum transmitted intensity arises when the optic axis of the crystal is at  $\chi = 45^\circ$  with respect to the plane of polarization of the incident radiation, in agreement with the familiar result for birefringence between crossed polarizers for visible light (e.g., in a polarizing optical microscope).



To examine this behavior more closely, we show in Figure 5a X-ray intensity as a function of  $\chi$ , with X-ray energy fixed at 13.4855 keV and with  $\varphi$  fixed at  $0^\circ$ . Clearly, the results demonstrate the classical sinusoidal variation of transmitted intensity as a function of  $\chi$ , as familiar in the analogous case of birefringence of visible light.

Figure 5b shows the transmitted intensity as a function of angle  $\varphi$  (i.e., for rotation of the crystal about the  $c$  axis), with  $\chi$  fixed at  $45^\circ$  (corresponding to maximum transmitted intensity in Figure 5a). Given the uniaxial nature of the crystal, the absorption coefficient should be independent of the direction of propagation of radiation within the  $ab$  plane of the crystal and hence independent of  $\varphi$ . In fact, a small variation of transmitted intensity is actually observed (Figure 5b) and is attributed to a slight variation in the effective crystal thickness as a function of  $\varphi$ . The specific variation of intensity observed in Figure 5b accords with this explanation for the typical cross-section of the crystal morphology perpendicular to the  $c$  axis for 1-BA/thiourea crystals, which comprises a distorted hexagon with one longer dimension within the  $ab$  plane. Therefore, two minima in transmitted intensity (maximum crystal thickness) separated by  $\Delta\varphi \approx 180^\circ$  are expected, as observed in Figure 5b.

In conclusion, our results demonstrate that the 1-BA/thiourea inclusion compound exhibits ideal X-ray birefringence, giving experimental behavior in excellent agreement with theoretical predictions for the dependence of transmitted X-ray intensity on both X-ray energy (near the Br K-edge) and crystal orientation. These results represent the first definitive demonstration of the phenomenon of X-ray birefringence and confirm that the underlying theory (as incorporated into the simulations) is adequately understood. Ultimately, the ideal X-ray birefringence behavior exhibited by this material emanates from the fact that the C–Br bonds of all 1-BA molecules are aligned parallel to each other. Clearly, the strong dependence between transmitted X-ray intensity and the orientational properties of specific bonds in a material (C–Br bonds in this case) was central to our design of the 1-BA/thiourea inclusion compound as a model system for exhibiting X-ray birefringence (and, in our previous work, X-ray dichroism).

In more general terms, the strong dependence between X-ray birefringence and the orientational properties of specific bonds in solids suggests that there is considerable potential to exploit measurements of X-ray birefringence as an experimental strategy for assessing and quantifying the orientational distributions of bonds in solids, for example, in the case of partially ordered materials or materials that undergo order–disorder phase transitions. Our ongoing research in this field is actively exploring this opportunity.

Other potential applications include materials for use as nondiffractive fixed-wavelength X-ray phase retarders, which may be applied, for example, to convert linearly polarized X-rays to circularly polarized X-rays. Devices based on this approach are potentially quite efficient and far less sensitive to beam angle than diffractive devices (i.e., a few degrees of divergence should have little effect, compared with divergence of the order of millidegrees in the case of diffractive devices).

Another important consequence of the work reported here relates to the fact that birefringence can lead to a dependence of resonantly diffracted X-ray intensities on circular polarization. Most diffraction experiments are interpreted within the kinematical scattering approximation, possibly with a simple correction for isotropic absorption. Here we have shown that anisotropy can

give rise to strong birefringence, which in turn can lead to circular dichroism in diffraction signals. This issue is especially significant in the context of experiments in which circular dichroism may otherwise be interpreted as a robust and unique “fingerprint” of a particular phenomenon of interest, such as chirality, noncollinear magnetic modulation, or an exotic (nondipolar) resonance process, all of which are of considerable topical interest. It follows from the present work that in the analysis of data in such cases it is essential that the effects of X-ray birefringence must be taken properly into account.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Theoretical background relevant to the present work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENT

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