X-ray Birefringence in highly Anisotropic Materials

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Abstract. Birefringence is the dependence of a material’s refractive index on the direction of linear polarization. It induces a phase shift between two perpendicular polarization directions and thus couples linear and circular polarization states. Birefringence in x-ray absorption is as common as linear dichroism but is rarely discussed in the literature. We outline a mathematical framework for describing experiments on birefringence and illustrate the importance of the phenomenon with three examples.

1. Introduction

Birefringence arises when an anisotropic material exhibits a refractive index that depends on the linear polarization direction of the light with respect to its molecular structure. The phenomenon induces a relative phase change between two orthogonally-polarized wave components [1] leading, for example, to the conversion of linear to circular polarization, i.e. a quarter-wave phase retarder. While the refractive index for x-rays tends to be very close to unity, and isotropic, a phase plate can be realized by the use of dynamical diffraction. Such devices are commonplace.

In the absence of diffraction, birefringence and linear dichroism can be observed close to x-ray absorption edges. Studies of x-ray linear dichroism from structural anisotropy and magnetism are well documented [2]. On the other hand, birefringence, which is related to dichroism through the Kramers-Kronig transform (Fig. 1) and therefore appears whenever linear dichroism exists, is rarely discussed. In this paper, we outline the importance of x-ray birefringence, though some experimental examples, and describe the mathematical framework for modeling the observed intensities.

Since x-ray scientists are familiar with the (real) linear absorption coefficient, it is convenient to extend this concept by introducing the complex linear absorption coefficient, \( \gamma = \gamma' + i\gamma'' \). Changes in the real and imaginary parts of the absorption coefficient lead to linear dichroism and birefringence, respectively. The average real part of the absorption coefficient gives an overall attenuation, and the average imaginary part leads to a global phase change which is of no interest for the present discussion.

For an isotropic material, the amplitude and intensity transmitted through a material of thickness \( t \) are simply

\[
\varepsilon_1 = e^{-\gamma t/2} \varepsilon_0 \quad \frac{I_1}{I_0} = \frac{|\varepsilon_1|^2}{|\varepsilon_0|^2} = e^{-\gamma' t}
\]
For an anisotropic material, the polarization generally changes as the wave propagates through
the material (it is not an eigenstate). By writing the complex absorption coefficient as four-
component matrix
\[ \Gamma = \begin{pmatrix} \gamma_{xx} & \gamma_{yx} \\ \gamma_{xy} & \gamma_{yy} \end{pmatrix} \]  
where \(x\) and \(y\) are two perpendicular linear polarization directions, we can preserve the simplicity
of Eqn. 1:
\[ A = \frac{\varepsilon_1}{\varepsilon_0} = e^{-\Gamma t/2} = e^{-(\gamma_{xx}+\gamma_{yy})t/4} \left( \begin{array}{cc} \cosh \phi - (\gamma_{xx} - \gamma_{yy})t/4 \sinh \phi & -\gamma_{xy}t/2 \sinh \phi/\phi \\ -\gamma_{yx}t/2 \sinh \phi/\phi & \cosh \phi + (\gamma_{xx} - \gamma_{yy})t/4 \sinh \phi \end{array} \right) \phi = \frac{t}{4} \sqrt{(\gamma_{xx} - \gamma_{yy})^2 + 4\gamma_{xy}\gamma_{yx}} \]  
where the rather complex final result is the consequence of taking the exponential of a matrix
[3]. The amplitude or transmittance matrix \(A\) provides a complete description of the amplitude
and polarization of the wave as it propagates through the material.

In order to describe experiments involving one or more polarization-sensitive component
and arbitrary incident beam polarization, it is useful to adopt the density matrix formalism,
described in detail in the literature [4]. In this approach, the measured intensity is given by the
trace of the initial polarization matrix, operated on either side by a set of transfer matrices that
represent scattering from, and transmission through, optical components and samples:
\[ \frac{I_1}{I_0} = \text{Tr} \left( A_n A_{n-1} \ldots A_1 \mu A_1^\dagger \ldots A_{n-1}^\dagger A_n^\dagger \right) \]  
where
\[ \mu = \frac{1}{2} \begin{pmatrix} 1 + P_3 & P_1 - iP_2 \\ P_1 + iP_2 & 1 - P_3 \end{pmatrix}, \]  
P\(_{3,2,1}\) are Stokes parameters for polarization along \(x\), circular polarization and \(45^\circ\) linear
polarization, respectively, and \(\dagger\) represents a Hermitian conjugate. Scattering matrices for
kinematical diffraction take on relatively simple forms, even for resonant and magnetic scattering.
The polarization dependence for charge (Thompson) scattering is given by \((\varepsilon_1^* \cdot \varepsilon_0)\), which
produces a scattering matrix of the form
\[ A_p = \begin{pmatrix} \cos \eta & -\sin \eta \\ \cos 2\theta \sin \eta & \cos 2\theta \cos \eta \end{pmatrix} \]  
where \(2\theta\) and \(\eta\) are the scattering angles and rotation about the beam direction, respectively.
Such a device provides a very effective polarization analyser which will be discussed further in
the experimental examples.

2. Example 1: A study of molecular polarization

Linear dichroism and birefringence can be very strong at absorption edges of many anisotropic
materials. Studies of guest-host structures containing brominated guest molecules have proved
particularly fruitful [5, 6, 7] as birefringence is particularly strong and the materials are of
interest for their static and dynamic properties. For this example, the goal is to elucidate the
temperature dependence of the polarization of bromocyclohexane molecules in a thiourea host
lattice. Diffraction studies had suggested that the bromine-carbon bonds are randomly oriented
at room temperature but become ordered below a structural phase transition at 233 K. The
detailed temperature dependence was unknown. The experimental layout involves two ‘optical’
components: the birefringent sample and a diffraction-based polarization analyser. The observed intensity is then given by

\[
\frac{I_1}{I_0} = \text{Tr} \left( A_p A_s \mu A_p^\dagger A_s^\dagger \right)
\]

(7)

where \( A_s \) is the sample transmittance matrix for the birefringent material with optical axis initially along \( x \) (\( \gamma_{xy} = \gamma_{yx} = 0 \)) then rotated through \( \chi \) about the beam direction (\( z \)-axis), which is given by

\[
A_s = R_z(\chi) e^{-\Gamma t/2} R_x^1(\chi) \quad R_z(\chi) = \begin{pmatrix}
\cos \chi & -\sin \chi \\
\sin \chi & \cos \chi
\end{pmatrix}.
\]

(8)

The intensity therefore depends on all three Stokes parameters, sample and polarization analyser angles, absorption, dichroism and birefringence. The latter two quantities are known to be proportional to the atomic quadrupole moment \( Q_{zz} \) [8], which we refer to (after normalization) as the molecular polarization. Eqn. 7 results in a complicated expression but taking the exponential in Eqn. 8 to first order we find:

\[
\frac{I_1}{I_0} \approx \text{Tr} \left( A_p A_s \mu A_p^\dagger \right) - \frac{t}{2} \left( \text{Tr} \left( A_p \Gamma_\chi \mu A_p^\dagger \right) + \text{Tr} \left( A_p A_s \mu \Gamma_\chi^\dagger A_p^\dagger \right) \right) + \frac{t^2}{4} \text{Tr} \left( A_p \Gamma_\chi \mu \Gamma_\chi^\dagger A_p^\dagger \right)
\]

(9)

where \( \Gamma_\chi \) is the rotation of \( \Gamma \) as per Eqn. 8. For a perfect analyser and linearly polarized incident beam (\( P_1 = P_2 = 0, P_3 = +1, \eta = 2\theta = 90^\circ \)) the first three terms in Eqn. 9 vanish and we find \( I_1 \propto t^2 \sin^2 2\chi \Delta \gamma^2 \), where \( \Delta \gamma = \gamma_{xx} - \gamma_{yy} \). We see that the signal is quadratic \( \Delta \gamma \) (which scales with the molecular polarization) and is maximum for \( \chi = \pi/4 \), as is familiar from optics.

The resulting data are illustrated in Fig. 2 and reveal an interesting temperature dependence, characterized by a sudden jump in polarization at the structural phase transition, followed by an almost linear increase as the temperature is reduced.

3. Example 2: A novel polarimeter

In the previous example it was found that the experimental set-up is extremely sensitive to the incident beam polarization. In fact, a least-squares refinement of the data gave very precise values for all three Stokes parameters, almost independent of the optical constants, suggesting useful application as a polarimeter. The goal of this example was to determine the Stokes
parameters of the x-ray beam emerging from the 0.4 mm thick diamond 111 quarter-wave phase plate on Beamline I16 at Diamond Light Source [9] - an important measurement not only to establish the new technique but also to characterize the phase retarder, which was expected to be too thin to provide perfect circular polarization at such high energies (~13.5 keV).

Figure 3. Experimental (top) and modeled (bottom) intensity emerging from a diamond phase retarder, set at an angle $\Delta\theta$ from the Laue diffraction condition, vs birefringent crystal angle, $\psi$.

Figure 4. Stokes parameters obtained from the fit in Fig. 3

The birefringent ‘sample’ was the well-characterized bromoadamantane/thiourea guest-host structure, deliberately engineered for it’s dichroic properties [5], using the same set-up as the previous example and therefore the same expression for observed intensity, given in Eqn. 7. The general expansion of Eqn. 7 is too complicated to usefully reproduce on the page. However, it is clear from both the experimental data and least-squares fit (Fig. 3) that there is an asymmetry between positive and negative phase-plate angle offsets, which is expected from the emerging circular polarization. The least-squares fit provided a complete and absolute characterization of the three Stokes parameters (Fig. 4), demonstrating the effectiveness of birefringence materials as a fixed-wavelength polarimeter, and suggesting further application as a circular polarizer.

4. Example 3: Resonant Diffraction

The third example outlines an unwelcome effect of x-ray birefringence. Resonant scattering experiments provide an extremely powerful and uniquely sensitive probe of important electronic ordering phenomena, including magnetism, orbital ordering, and the observation of exotic (e.g. magnetolectric) atomic multipoles. Such experiments are almost always interpreted within the ‘kinematical’ diffraction model, where scattering is assumed to be weak and the polarizing effect of the material on the way to and from the scattering layer within the sample is neglected. For studies of anisotropic (non-cubic) materials, such effects should not be neglected. Of particular concern is the effect of birefringence, that can cause an initially linearly polarized beam to become elliptical (Fig. 5) and vice versa, giving a dependence on circular polarization that is not expected from the resonant scattering cross-section and leading to potentially erroneous conclusions.
Calculation of the scattering signals is rather complex due to (a) the inherent complexity of the resonant scattering process and (b) the fact that each scattering layer of the sample, at a depth \( t \), experiences an incident beam with a different intensity and polarization. The observed intensity is given by the integral

\[
I \propto \text{Tr} \int_0^\infty dt \, e^{-\Gamma_{\text{out}} \frac{t}{\sin(\theta + \alpha)}} \mathbf{A}_{\text{scatt}} e^{-\Gamma_{\text{in}} \frac{t}{\sin(\theta') + \alpha}} \mu e^{-\Gamma_{\text{out}} \frac{t}{\sin(\theta'') + \alpha}} \mathbf{A}_{\text{scatt}}^i e^{-\Gamma_{\text{out}} \frac{t}{\sin(\theta''') + \alpha}} \tag{10}
\]

which requires a detailed knowledge of both the birefringent properties of the material and the resonant scattering. This problem has recently been solved by Joly et al. [10].

5. Conclusions

X-ray birefringence has been largely ignored in the literature. We have shown that it has several interesting and important applications in x-ray physics, and that is should be considered when interpreting resonant scattering data. The mathematical framework for describing complex experiments that include birefringence requires only a modest extension of established techniques, although quantitative evaluation relies on a large number of parameters and is best accomplished using advanced electronic structure codes.

**Figure 5.** The effect of absorption, dichroism and birefringence on an x-ray beam that scatters from a thin layer within a sample. A horizontally-polarized incident beam becomes a tilted ellipse before scattering.

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