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X-ray Birefringence and Forbidden Reflections in Sodium Bromate

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(*Received* 13 *February* 1986; *accepted* 17 *April* 1986)

Abstract

Reflections forbidden by a screw-axis rule are observed in sodium bromate with synchrotron radiation near the bromine K absorption edge, where X-ray birefringence occurs. The intensities vary with azimuthal angle according to theoretical predictions and indicate a larger magnitude for the birefringence than did earlier experiments. This technique is a method of selective diffraction in which atoms of a single element in a single chemical state contribute to the signal, and it can reveal their positions with precision.

1. Introduction

One effect of X-ray dichroism and birefringence is that the screw-axis and glide-plane rules for absent reflections are not rigorous (Templeton & Templeton, 1980; Dmitrienko, 1983, 1984). Atoms which are related by one of these symmetry elements may have different scattering factors if the orientations of their susceptibility tensors are different with respect to the polarization vectors of the photons. The rules depend on exact cancellation of scattering from these atoms.

We first observed reflections forbidden by a screw-axis rule in diffraction experiments with sodium bromate near the bromine K absorption edge (Templeton & Templeton, 1985, hereafter TT85), but lacked time then to study them in detail. Here we report some further experiments which confirm the novel dependence of these reflections on azimuthal angle and thus support the validity of the optical model which we have been using. This phenomenon offers a new method of selective diffraction in which atoms of only a single element contribute to the signal. The experiments show that the signals are strong enough to be observed without exceptional difficulty, and demonstrate that they can give accurate information about structure.

Because the method requires X-rays with a wavelength close to an absorption edge, and intense beams of such radiation are most readily available at a synchrotron source, we did this work at the Stanford Synchrotron Radiation Laboratory (SSRL). Although the effect arises from polarization-dependent properties, it turns out that polarized radiation is not needed. Nor are the requirements for narrow spread of wavelength and for high intensity particularly severe. Thus, similar experiments may be possible with more conventional sources.

2. Theory

In sodium bromate the bromine atoms are on threefold axes in the special positions of $P2_13$, with $x = 0{\cdot}40640\,(3)$ (TT85):

$$x, x, x; \tfrac{1}{2}+x, \tfrac{1}{2}-x, -x;$$
$$-x, \tfrac{1}{2}+x, \tfrac{1}{2}-x; \tfrac{1}{2}-x, -x, \tfrac{1}{2}+x.$$

We describe the scattering factor of each atom by a tensor with principal values f_π, f_π, and f_σ (complex numbers), oriented with f_σ parallel to the respective threefold axis. In the coordinate system of the cubic unit cell, these tensors are:

$$\mathbf{f}_1=\begin{pmatrix} a & b & b \\ b & a & b \\ b & b & a \end{pmatrix}, \quad \mathbf{f}_2=\begin{pmatrix} a & -b & -b \\ -b & a & b \\ -b & b & a \end{pmatrix},$$
$$\mathbf{f}_3=\begin{pmatrix} a & -b & b \\ -b & a & -b \\ b & -b & a \end{pmatrix}, \quad \mathbf{f}_4=\begin{pmatrix} a & b & -b \\ b & a & -b \\ -b & -b & a \end{pmatrix}, \tag{1}$$

$$a = f_0 + f' + if'' = (f_\sigma + 2f_\pi)/3, \tag{2}$$

$$b = (f_2' + if_2'')/3 = (f_\sigma - f_\pi)/3, \tag{3}$$

0108-7673/86/060478-04$01.50

where f', f_2', f'', and f_2'' are the mean values and the anisotropy terms of the real and imaginary anomalous scattering (TT85). For incident polarization $\mathbf{e}_1$ and scattered polarization $\mathbf{e}_2$, the ith atom has a scattering factor f_i (T indicates transpose):

$$f_i = \mathbf{e}_1^T \mathbf{f}_i \mathbf{e}_2. \tag{4}$$

The structure factor for a forbidden $00l$ reflection is

$$F_{00l} = (f_1 - f_4)\exp(i\alpha) + (f_2 - f_3)\exp(-i\alpha);$$
$$l \text{ odd}, \ \alpha = 2\pi lx. \tag{5}$$

Our electronic computations were carried out for one pair of polarization vectors at a time, with scattering factors corresponding to (4) substituted into the usual expressions for structure factors, along with conventional scattering factors for the other atoms. Appropriate polarization factors are included in pp' terms. This procedure is valid for all reflections, forbidden or not. However, it is instructive to follow Dmitrienko (1983, 1984), reversing the order and substituting the matrices (1) into (5) to derive tensor structure factors:

$$\mathbf{F}_{00l} = 2\begin{pmatrix} 0 & 0 & b \\ 0 & 0 & b \\ b & b & 0 \end{pmatrix}\exp(i\alpha) + 2\begin{pmatrix} 0 & 0 & -b \\ 0 & 0 & b \\ -b & b & 0 \end{pmatrix}\exp(-i\alpha)$$
$$= 4b\begin{pmatrix} 0 & 0 & i\sin\alpha \\ 0 & 0 & \cos\alpha \\ i\sin\alpha & \cos\alpha & 0 \end{pmatrix}, \quad l \text{ odd}. \tag{6}$$

One sees that $\mathbf{F}_{00l}$ depends on the atomic scattering factor only through the anisotropy term b and is zero when there is no anisotropy. For these reflections, the polarization vectors are

$$\mathbf{s} = \begin{pmatrix} \cos\psi \\ -\sin\psi \\ 0 \end{pmatrix}, \quad \mathbf{p} = \begin{pmatrix} -\sin\psi\sin\theta \\ -\cos\psi\sin\theta \\ \cos\theta \end{pmatrix}, \quad \mathbf{p}' = \begin{pmatrix} \sin\psi\sin\theta \\ \cos\psi\sin\theta \\ \cos\theta \end{pmatrix}. \tag{7}$$

The azimuthal angle ψ is defined as zero when the rays are in the yz plane, and θ is the Bragg angle. Substitution of vectors (7) into (4), with $\mathbf{F}$ from (6) in place of $\mathbf{f}_i$, gives

$$F_{ss} = F_{pp'} = 0, \tag{8}$$

$$F_{sp'} = F_{ps} = 4b\cos\theta(i\sin\alpha\cos\psi - \cos\alpha\sin\psi). \tag{9}$$

The intensity of the reflection is proportional to FF^*, which with the use of the trigonometric identities for double angles can be written:

$$|F_{sp'}|^2 = 8|b|^2\cos^2\theta(1 - \cos 2\alpha\cos 2\psi)$$
$$= \tfrac{8}{9}|f_\sigma - f_\pi|^2\cos^2\theta(1 - \cos 4\pi lx\cos 2\psi). \tag{10}$$

The result is the same for the ps term. Thus the intensity and its variation with azimuth are independent of the state of polarization of the incident radiation. Experimental integrated intensities require the usual Lorentz and scale factors, but no additional polarization factor; the polarization effects are all included in (10).

3. Experiment

Diffraction experiments with synchrotron radiation were done at SSRL on beam line I-5 with the Enraf-Nonius CAD-4 diffractometer (Phillips, Cerino & Hodgson, 1979), using Si(111) crystals in the double-crystal monochromator. To reduce contamination by harmonic wavelengths the crystals were set off-parallel enough to reduce the intensity about 25%. Wavelengths were set using the absorption spectrum of polycrystalline sodium bromate, with white-line peak at 13 482·1 (10) eV (TT85).

Integrated intensities for diffraction by a sodium bromate crystal were measured at many settings of the azimuthal angle and at various wavelengths near the bromine K edge for $00l$ reflections, $l = 1$ to 11. The measurements reported here were at 13 474 eV (0·92015 Å), a photon energy 8 eV below the peak of the white line, or about 7 eV below the inflection point of the edge. At higher photon energies, where greater birefringence was inferred (TT85), the results were less clear because of greater absorption and more background of fluorescent radiation. The crystal, about 0·3 × 0·3 × 0·15 mm, had (001) as its largest face and therefore had relatively little azimuthal variation of absorption for $00l$ reflections. Intensity was observed for every odd order, the ones forbidden by the screw-axis rule. Each intensity was corrected by a Lorentz factor, for absorption, and for variation in the synchrotron beam as described by TT85. Some of the intensities were enhanced by the Renninger (1937) effect (reflection in sequence by two sets of planes), sometimes by very large factors. The Renninger reflections could be recognized by their narrow widths in azimuth (less than 0·1°) when measured at close intervals. Often several were visible per degree of azimuth, but because of their sharpness they seem not to have affected most of the measurements very much.

One set of measurements was made at 0·1° intervals of ψ between −69 and −67°. The angle ψ, defined as in (7) and (10), is 39° more negative than that calculated by the diffractometer software for the actual

crystal setting. Of the 20 scans of each reflection, from one to four were rejected because they were possibly or obviously influenced by the Renninger effect. The scale was based on the 006 reflection. No polarization factor was applied to the forbidden reflections, but the intensity of 006 was increased by a factor 1·030 to allow for incomplete polarization of the beam. Average structure-factor magnitudes are listed in Table 1.

Another experiment, at wider intervals of ψ, gave values of $|F|^2$ which are plotted in Fig. 1 for three forbidden reflections.

4. Results

The curves in Fig. 1 display clearly the modulation of intensity with azimuth which is predicted by the factor in parentheses in (10). For $x = 0{\cdot}4064$, $\cos 4\pi lx$ is respectively 0·38, −0·93, and 0·92 for $l = 1$, 3, 5. Thus the modulation factor varies from less than 0·1 to more than 1·9 for 003 and 005, and with opposite phase. For 001 the modulation is less extreme, from about 0·6 to 1·4, and with the same phase as 005. Conversely, as suggested by Dmitrienko (1984), this modulation can be used to determine the value of x. The only possible solutions for +, −, + phases are near 0·1, 0·4, 0·6, and 0·9. These four values represent the two possible enantiomers with two choices of origin. These data do not distinguish the enantiomers. Consideration of the numerical values of the modulation factor limits x to a range about 0·403 to 0·410, if the 0·4 solution is chosen. This analysis does not require the absolute scale of the intensities. Therefore the numerical value of the birefringence is not involved, except that it must be large enough for the reflections to be measured.

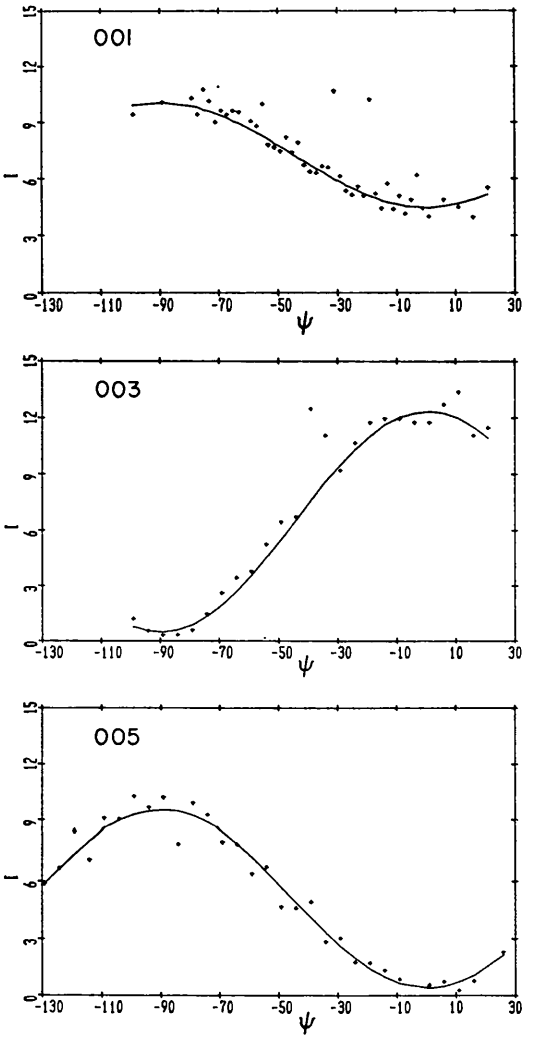

Fig. 1. Observed (points) and calculated (lines) squares of structure factors for 001, 003, and 005 plotted as a function of azimuthal angle, at photon energy 8 eV below the Br K white-line peak. A few high points, and another too far off scale to plot, indicate coincidence with Renninger reflections.

Table 1. *Structure-factor amplitudes for* 00l *reflections at* $\psi = -68°$

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
3	1·28 (3)	1·41
5	2·86 (3)	2·86
7	1·62 (3)	1·67
9	1·12 (4)	1·07
11	1·29 (3)	1·23
6	(43·61)*	43·61

* The scale factor was determined by this reflection.

From the earlier diffraction experiments (TT85) we estimated $f_\sigma - f_\pi$ to be $1{\cdot}5 - 0{\cdot}7i$, with magnitude 1·7 electrons/atom, for the wavelength of this work. A larger value, $|f_\sigma - f_\pi| = 2{\cdot}71$, is required to achieve agreement of the observed and calculated structure factors in Table 1. We attribute this difference to the finite wavelength spread of the radiation, which is comparable to the natural width of the levels which are the origin of the birefringence. Each experiment involves some kind of average of the effects over a range of wavelength. We lack information required for detailed analysis of this averaging. It seems reasonable to us that the present experiment should give the larger effect, since all signals from different wavelengths are additive. In the previous experiments, the form factors are derived in a less direct way from diffraction intensities, and there are more chances for cancellation of effects. The earlier data were also subject to attenuation by imperfect polarization of the radiation, but that source of error is inadequate to explain the difference.

A value of $x = 0{\cdot}408$ (1) was derived by least squares from the data for forbidden reflections in Table 1. This value of x is not significantly different from those determined by conventional methods [0·40640 (3), TT85; 0·4067 (2), Abrahams & Bernstein, 1977]. However, the origin of the birefringence involves wavefunctions which are not centered at the

nucleus of bromine, and it is not obvious that this method should give exact agreement with the nuclear coordinate. We hope to make a more precise determination by observation of high-index reflections both at $\psi = 0$ and 90°.

5. Discussion

The angular dependence displayed in Fig. 1 is a verification that the optical model based on kinematic diffraction and dipole scattering is valid for these experiments. It also demonstrates, except for a minority of the points, that the signals are not obscured by the Renninger reflections or by allowed reflections at other wavelengths. The detailed numerical results show that one can measure the magnitude of the polarization anisotropy of scattering in a new way. In the present case it indicates that the birefringence is even larger than was demonstrated in earlier experiments. This new method does not require polarized radiation and may have other advantages for some materials.

This new technique is a method of selective diffraction. The signal comes only from atoms of one element, and of that element only those atoms which are in a chemical state which has significant anisotropy of susceptibility. Thus it has potential for differentiation of oxidation states or bonding geometries. It is shown to be capable of rather precise determination of atomic coordinates. Perhaps its most obvious utility in contemporary science is to help locate a few heavy atoms in an otherwise very complicated crystal structure, a frequent objective in macromolecular crystallography. All of these things can be accomplished with other techniques if the data are accurate enough. The advantage of the new method is that the signal is observed directly, rather than derived from the sometimes small and inaccurate differences of large quantities.

This research was supported by the National Science Foundation under Grants CHE-8217443 and CHE-8515298. It was done in part at SSRL which is supported by the Department of Energy, Office of Basic Energy Sciences; and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources. It used some facilities of the Lawrence Berkeley Laboratory, supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract No. DE-AC03-76SF00098.

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Acta Cryst. (1986). A42, 481-483

On the Wavelength Dependence of the Reflectivity of One-Dimensionally Distorted Crystals

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(*Received* 17 *February* 1986; *accepted* 29 *April* 1986)

Abstract

Scaling properties of the integrated reflectivity of non-absorbing perfect or ideally imperfect crystals as a function of wavelength, in the symmetrical Laüe and Bragg cases, are shown also to be valid for distorted crystals where the gradient of the lattice phase factor is perpendicular to the crystal surfaces. This result is obtained by an analysis of the Taupin-Takagi equations. Some previous experiments (test of a proposal for extinction-free measurements of F_M/F_N in polarized neutron scattering by magnetic crystals, and neutron diffraction from curved and non-curved crystals) are discussed from this point of view.

1. Introduction

The integrated reflectivities of perfect crystals ρ_D (dynamical theory) and of ideally imperfect crystals ρ_K (kinematical theory) have common properties as functions of the wavelength λ, in symmetrical Bragg or Laue geometries. It will be shown that these properties are also verified for distorted crystals where the gradient of the lattice phase factor, which occurs in the Taupin-Takagi equations and is the scalar product of the local displacement field by the diffraction vector, is everywhere perpendicular to the crystal surfaces; this is actually a one-dimensional distortion, because the phase factor then depends only on the z coordinate of Fig. 1. The present analysis is related

0108-7673/86/060481-03$01.50