X-ray Birefringence, Forbidden Reflections, and Direct Observation of Structure-Factor Phases

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Abstract

Reflections forbidden by a screw-axis rule are observed in sodium bromate with synchrotron radiation at wavelengths where X-ray birefringence occurs. The change of intensity of 00*l* (*l* odd) with azimuthal angle gives the phase of the 0,0,2*l* structure factor.

In experiments with synchrotron radiation we observed reflections forbidden by a screw-axis rule but permitted by the effects of X-ray birefringence in crystals of sodium bromate (Templeton & Templeton, 1985, 1986). Both the real and imaginary parts of the scattering factor for bromine in this chemical state vary with polarization direction for wavelengths near the K absorption edge. The intensities of some 00*l* ($l = 1, 3, 5$) reflections were shown to change with azimuthal angle according to the theoretical prediction (Dmitrienko, 1984) for bromine atoms in x, x, x positions of space group $P2_13$:

$$|F|^2 = (8/9)|f_\sigma - f_\pi|^2 \cos^2 \theta (1 - \cos 4\pi l x \cos 2\psi), \quad (1)$$

where ψ is the azimuthal angle (defined as zero when the rays are in the yz plane) and f_σ and f_π are principal values of the complex scattering-factor tensor. This technique is a method of selective diffraction in which atoms of a single element, bromine in this case, contribute to the signal. It can be used to determine the locations of those atoms in the crystal structure.

Here we point out how this azimuthal dependence of intensity of one reflection gives in a direct way the phase of the structure factor of another reflection. We also report measurements, made in the same way, which show the azimuthal variation of additional 00*l* reflections ($l = 7$, 9 and 11) for sodium bromate (Fig. 1). The change of intensity with azimuth yields both the magnitude and sign of the factor $\cos 4\pi l x$. According to (1) this sign is positive (negative) when the minimum (maximum) occurs at $\psi = 0$.

The goal in a solution of the 'phase problem' is to learn the phase of each structure factor which is a coefficient of the Fourier representation of electron density, not the sometimes quite different phase which this structure factor has when anomalous-scattering effects are included. This Fourier-coefficient structure

factor for the reflection 0,0,2*l* for the bromine-only part of the structure is:

$$F_{Br}(0,0,2l) = 4f_0(Br) \cos 4\pi l x, \quad (2)$$

which has the same sign as the factor $\cos 4\pi l x$ because $f_0(Br)$ is a positive real number. That is, the azimuthal variation of intensity of the forbidden reflection gives the structure-factor phase of its second order. Thus we have determined the phases for 00*l* ($l = 2, 6, 10, 14, 18, 22$) to be +, −, +, −, −, +, in agreement with calculation from the known $x = 0.4064$ (Templeton & Templeton, 1985). Because the bromine contribution dominates the structure factors, these phases are the same as those for the whole structure. It is curious that two of these higher orders lie outside the Ewald sphere for the wavelength of the experiment (0.92014 Å).

A detail of crystal symmetry merits comment. One may designate the a axis in the direction we have chosen for b, without changing c. This rotation of
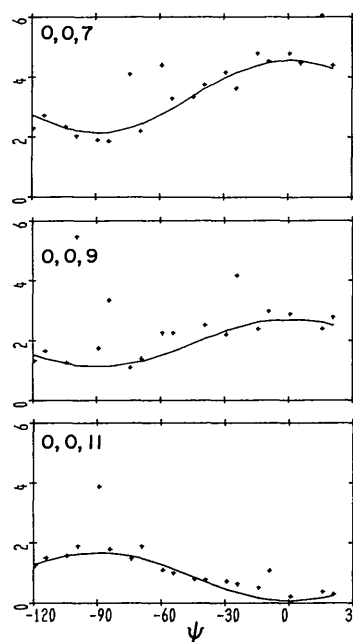

Fig. 1. Plots of observed (points) and calculated (lines) $|F|^2$ *vs* azimuthal angle ψ for 007, 009, and 0,0,11 reflections. Several points are high because of the Renninger effect.

coordinate system changes the zero of the ψ scale by 90° and reverses all the phases determined by this method for $0,0,(4n+2)$ structure factors. This is not an error. In space group $P2_13$ the c axis lacks fourfold symmetry. The analytical description of equivalent positions used to derive (1) is

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

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

The 90° rotation of cooordinates requires that the origin be moved (e.g. by $\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}$) and that a new value be chosen for x in order to describe the structure with this list of equivalent positions. This shift of origin changes these phases by 180°.

This example is a special case which is simplified by constraints on the scattering tensor from the three-fold symmetry of the special positions and by interference of scattering from two pairs of atoms. More complicated relationships occur for general positions or for some other space groups (Dmitrienko, 1983, 1984). It may not be easy to exploit these effects in

every case, but these kinds of data are rich in phase information. We hope that this report will stimulate more study of them.

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Polyhedra of Three Quasilattices Associated with the Icosahedral Group

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Abstract

A systematic approach is presented for the construction of families of polytopes associated with a given group G and subgroup H. This procedure is applied to the icosahedral group and its three dihedral subgroups yielding three families of polyhedra in $\mathbb{E}^3$. These families form the cells of three types of quasilattices associated with the icosahedral group, and hence are candidates for modelling quasicrystal structures. Some of the polyhedra are illustrated.

1. Introduction

In classical crystallography the icosahedral group $A(5)$ plays no role as it cannot occur as a subgroup

of a crystallographic space group in $\mathbb{E}^3$ except in relation to approximate local site symmetry (*cf.* Hahn & Klapper, 1983; § 10.4). The discovery of diffraction patterns with icosahedral point symmetry in 4:1 Al–Mn by Shechtman, Blech, Gratias & Cahn (1984) shows that this group cannot be excluded from crystallography. A type of non-periodic space filling in $\mathbb{E}^3$ obtained as a projection from $\mathbb{E}^{12}$ or $\mathbb{E}^6$ was associated with $A(5)$ by Kramer & Neri (1984). The cells of this space filling were shown by Kramer (1985) to form a family of polyhedra in $\mathbb{E}^3$ bounded by pairs of parallel rhombus faces. In the present paper we implement a systematic approach to the construction of families of polytopes associated with a given group G and subgroup H.

When a group G acts as a transformation group on a set X, this set can be partitioned into orbits $Gx', Gx'', \ldots, x', x'' \in X$. Each orbit is a homogeneous space under G and can be characterized up to conju-