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Polarized Dispersion, Glide-Rule-Forbidden Reflections and Phase Determination in Barium Bromate Monohydrate

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Abstract

Reflections forbidden by a glide-plane rule are observed in diffraction experiments with a crystal of barium bromate monohydrate using linearly polarized synchrotron radiation with wavelength near the bromine *K*-absorption edge. Their intensities change with azimuth in agreement with equations derived using a tensor model of the anomalous scattering of the bromate ion and are consistent in scale with earlier measurements of that tensor in sodium bromate. The intensity of each forbidden *h0l* reflection gives the magnitude and phase of the bromine part of the structure factor of the allowed *2h,0,2l* reflection. The *x* and *z* coordinates of the Br atom determined from such data for 11 reflections are within 0.02 Å of those from two crystal structure determinations.

1. Introduction

Polarization-dependent absorption of X-rays (dichroism or pleochroism) has been observed in many materials now that synchrotron radiation provides polarized beams at the wavelengths near absorption edges where this dichroism is most significant (see review by Brouder, 1990). With it comes birefringence of the complex index of refraction, polarization

anisotropy of the anomalous scattering terms and changes of intensities and polarization states of scattered rays (see, for example, Belyakov & Dmitrienko, 1989). One result is that some Bragg reflections that are forbidden by the ordinary space-group rules for screw axes and glide planes can be observed (Templeton & Templeton, 1980, 1985; Dmitrienko, 1983, 1984). These effects are new sources of information about the structures of crystals. The change of intensity of a Bragg reflection with azimuth can be used to determine phases of structure factors (Templeton & Templeton, 1991) in much the same way as the change with wavelength in the absence of birefringence (the MAD method). The azimuthal intensity variation of reflections forbidden by a screw-axis rule in sodium bromate, *00l* with *l* odd, gave the phases for *0,0,2l* reflections (Templeton & Templeton, 1987). The intensities of these forbidden reflections depend only on the structure of the anisotropic atoms and they can be used to determine that partial structure (Templeton & Templeton, 1986; Kirfel & Petcov, 1991). Here we report a study of reflections that are forbidden by a glide-plane rule and show how to get structure-factor phases from their intensities. The experiments were done at the Stanford Synchrotron Radiation Laboratory.

While this work was in progress, Kirfel, Petcov & Eichhorn (1991) published an analysis of how X-ray diffraction is affected by anisotropic anomalous dispersion and reported measurements of glide-forbidden reflections in Cu_2O , TiO_2 and MnF_2 that anticipate some of our results.

Barium bromate monohydrate (space group $I2/c$) was chosen for this study because the bromate ion is strongly birefringent at a convenient X-ray wavelength (Templeton & Templeton, 1985) and has its symmetry axis inclined to the glide plane and to the b axis in this crystal structure (Lutz, Alici & Buchmeier, 1985; Templeton & Templeton, 1989). A requirement for appearance of glide-forbidden reflections is that the scattering-factor tensor must not be symmetric with respect to reflection in the glide plane. This nonstandard setting of space group $C2/c$ has been used for this structure by authors since Kartha (1952) to bring β close to 90° .

2. Theory

If the scattering by each atom is described by a second-rank tensor \mathbf{f} , the factor for atom m and polarization ($\mathbf{e}_1, \mathbf{e}_2$) is

$$f_m = \mathbf{e}_1^T \mathbf{f}_m \mathbf{e}_2, \quad (1)$$

where T denotes the transpose. Atom n , related to m by a glide-plane operation ($x, -y, \frac{1}{2} + z$), has a scattering factor f_n that differs only in the signs of the xy and yz components of the tensor. For a reflection $h, 0, l$ (l odd) these atoms scatter with opposite phase and their scattering cancels in the absence of polarized dispersion. This cancellation is the origin of the glide-plane rule for absent reflections. When \mathbf{f}_m is anisotropic with nonzero xy or yz terms, as it is for bromine in the crystal studied here, the scattering does not cancel and the scattering amplitude A for polarization ($\mathbf{e}_1, \mathbf{e}_2$) is

$$A_{h0l} = \mathbf{e}_1^T \mathbf{F}_{h0l} \mathbf{e}_2, \quad (2)$$

where the tensor \mathbf{F} has the form (Dmitrienko, 1983)

$$\mathbf{F}_{h0l} = \begin{pmatrix} 0 & F_1 & 0 \\ F_1 & 0 & F_2 \\ 0 & F_2 & 0 \end{pmatrix} \quad (l \text{ odd}). \quad (3)$$

For space group $I2/c$, with j anisotropic atoms per asymmetric unit, the elements of the matrix (3) are

$$F_1 = 8 \sum_{i=1}^j T_i(f_{12})_i \cos(2\pi \mathbf{h} \cdot \mathbf{x}_i), \quad (4)$$

$$F_2 = 8 \sum_{i=1}^j T_i(f_{23})_i \cos(2\pi \mathbf{h} \cdot \mathbf{x}_i), \quad (5)$$

where T_i is a thermal factor. Each f_{12} and f_{23} is independent of \mathbf{h} except for a possible small variation of the anomalous scattering with Bragg angle. In the

general case they have different values for each of the j independent atoms.

To simplify the analysis we define two Cartesian coordinate systems: a crystal basis with axes in the directions of \mathbf{a} , \mathbf{b} and \mathbf{c}^* and a diffractometer basis with \mathbf{a}_1 toward the radiation source, \mathbf{a}_2 toward the detector when it is set for $2\theta = 90^\circ$ and \mathbf{a}_3 perpendicular to the plane of diffraction. In the latter basis the polarization vectors are

$$\mathbf{s} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad \mathbf{p}_1 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mathbf{p}_2 = \begin{pmatrix} \sin 2\theta \\ \cos 2\theta \\ 0 \end{pmatrix}. \quad (6)$$

To evaluate (2) for a particular crystal setting, these vectors must be transformed to the crystal basis used for \mathbf{F} . Like Schwarzenbach & Flack (1989) we define the zero of azimuthal angle ψ to be independent of the crystal orientation matrix, but for simplicity here we use $[0, 1, 0]$ as the reference vector \mathbf{u}^T for all $(h, 0, l)$; i.e. \mathbf{b} is parallel with \mathbf{s} when $\psi = 0$. If first the crystal is set on the diffractometer so that the two Cartesian systems coincide, it can be moved into diffraction position by the rotation \mathbf{R} :

$$\mathbf{R} = \mathbf{R}_z(-\theta)\mathbf{R}_y(\psi)\mathbf{R}_z(\pi/2)\mathbf{R}_x(\pi/2)\mathbf{R}_y(-\alpha). \quad (7)$$

The rotation matrices are defined according to Sands (1982) and α is the angle from \mathbf{a} to \mathbf{h} . During this rotation of the crystal the polarization vectors remain fixed in the diffractometer basis, but in the crystal basis are changed to

$$\mathbf{R}^T \mathbf{s} = \begin{pmatrix} -\sin \alpha \sin \psi \\ \cos \psi \\ -\cos \alpha \sin \psi \end{pmatrix}, \quad (8)$$

$$\mathbf{R}^T \mathbf{p}_1 = \begin{pmatrix} \cos \alpha \cos \theta - \sin \alpha \sin \theta \cos \psi \\ -\sin \theta \sin \psi \\ -\sin \alpha \cos \theta - \cos \alpha \sin \theta \cos \psi \end{pmatrix}, \quad (9)$$

$$\mathbf{R}^T \mathbf{p}_2 = \begin{pmatrix} \cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \psi \\ \sin \theta \sin \psi \\ \cos \alpha \sin \theta \cos \psi - \sin \alpha \cos \theta \end{pmatrix}. \quad (10)$$

Substitution of the four combinations of (8), (9) and (10) into (2) gives four amplitudes:

$$A_{ss} = -G_1 \sin 2\psi, \quad (11)$$

$$A_{pp} = -G_1 \sin^2 \theta \sin 2\psi, \quad (12)$$

$$A_{sp} = G_2 \cos \theta \cos \psi + G_1 \sin \theta \cos 2\psi, \quad (13)$$

$$A_{ps} = G_2 \cos \theta \cos \psi - G_1 \sin \theta \cos 2\psi. \quad (14)$$

The coefficients G_1 and G_2 are:

$$G_1 = F_1 \sin \alpha + F_2 \cos \alpha = F_3 \cos(\alpha - \gamma), \quad (15)$$

$$G_2 = F_1 \cos \alpha - F_2 \sin \alpha = -F_3 \sin(\alpha - \gamma), \quad (16)$$

where $F_1 = F_3 \sin \gamma$ and $F_2 = F_3 \cos \gamma$ and γ is an

angle that defines the orientation of the principal values of the F tensor in the xz plane.

How these amplitudes are added depends on the state of polarization and phase coherence of the incident beam (see, for example, Fanchon & Hendrickson, 1990). For the conditions of our experiment (vertical center of the synchrotron beam from a bending magnet) there is no phase connection between horizontal (s) and vertical (p) components of the beam, and therefore the amplitudes arising from A_{ss} and A_{ps} are added in quadrature. The same is true of the combination of terms from A_{sp} and A_{pp} . The total amplitudes for the two polarization components of the scattered ray are added in quadrature since s and p_2 are perpendicular. Thus the total intensity is

$$I = KI_s(M_{ss}|A_{ss}|^2 + M_{sp}|A_{sp}|^2) + KI_p(M_{pp}|A_{pp}|^2 + M_{ps}|A_{ps}|^2). \quad (17)$$

Here I_s and I_p are the intensities of the two linear polarization components in the incident beam and K is a scale factor that includes the Lorentz factor. This scale factor is the same as that for the ordinary strong reflections. The factors M are correction factors for absorption which in general are different for the different polarization combinations.

Observations of diffraction intensity at different azimuths give a set of equations (17) that are quadratic in F_1 and F_2 . Three observations at properly chosen values of ψ are sufficient to determine uniquely the magnitudes of these structure factors and the sign of their ratio.

3. Phases of structure factors

The phase problem of crystallography is the search for the phase φ_0 of each F_0 , a coefficient in the Fourier series that describes the electron density. The structure factor F corresponding to a diffraction intensity generally has a different magnitude and phase because of dispersion. In the MAD method with one kind of anomalous atom the problem is divided into two parts: the phase φ_A of the dispersion-free structure factor F_A for the anomalous atoms and the phase difference $\varphi_0 - \varphi_A$. Intensities for different wavelengths give equations that can be solved for $|F_0|$, $|F_A|$ and $\varphi_0 - \varphi_A$ (see, for example, Hendrickson, 1985). Effects of polarized dispersion are another way to obtain $\varphi_0 - \varphi_A$ (Templeton & Templeton, 1991). Typically, one calculates φ_A from the locations of the anomalous atoms, determined from a set of $|F_A|$ or in some other way.

Sometimes polarized dispersion lets one determine φ_A directly. In sodium bromate the azimuthal variation of intensity for screw-forbidden reflections gives φ_A for some allowed reflections (Templeton & Templeton, 1987). Here we examine how glide-forbidden reflections can do the same.

When the tensors of independent atoms have different magnitudes or orientations, F_1 and F_2 are linearly independent with different relative weighting of the atoms for different values of ψ . In principle the contribution of each independent atom, if there are not too many of them, can be derived from measurements at several azimuths and perhaps wavelengths. How to find them in a complicated general case is likely to be an interesting puzzle. The present experiment, with a single independent anisotropic atom, is much simpler. Each sum in (4) and (5) contains only one term and the ratio $F_2/F_1 = f_{23}/f_{12} = \tan \gamma$ is the same for all reflections. The angle γ measures the deviation from \mathbf{a} of one of the principal values of the macroscopic tensor and can be obtained from absorption spectra. Once the scale is determined, including the magnitude of the anisotropy, the intensity of each reflection measured at any azimuth gives the magnitude of $T_1 \cos(2\pi\mathbf{h} \cdot \mathbf{x}_1)$. The factor $U_A(\mathbf{h}) = \cos(2\pi\mathbf{h} \cdot \mathbf{x}_1)$ is the unitary structure factor for a structure consisting of half the anomalous atoms and its square can be measured if T_1 is known or estimated in some way. Values of U_A and φ_A for the allowed reflection $2\mathbf{h}$ can be derived with the trigonometric identity,

$$\cos 2x = 2 \cos^2 x - 1. \quad (18)$$

The inequality of Harker & Kasper (1948) for a center of inversion becomes this equality in the case of one independent atom, thereby gaining the power to imply negative phases for U_A .

4. Experimental

Integrated diffraction intensities were recorded using the Enraf-Nonius CAD-4 diffractometer on Beam Line I-5 at SSRL as described by Templeton & Templeton (1986). The kappa geometry of this instrument is favorable because it permits a wide range of azimuthal settings for many reflections. A crystal of $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ ($0.04 \times 0.06 \times 0.15$ mm, 9 faces) was glued to a glass fiber. The data reported here were measured during an uneventful 12 h overnight run during which the beam intensity declined 47%. The Si(111) double-crystal monochromator was set to 13 478.5 eV, 3.6 eV lower in energy than the peak of the bromate white line, with a precision no better than 0.5 eV. The energy spread is estimated as 3 eV (FWHM). The complex anisotropy is $\delta = f_\sigma - f_\pi = 2.7 - 1.4i$, with magnitude 3.0 at this energy, but is very sensitive to the setting (Templeton & Templeton, 1985). Each of 11 forbidden reflections (Table 1) was measured at 5° intervals of azimuth around a full circle except as prevented by mechanical limitations. About 11% of the measurements were obviously affected by multiple (Renninger) scattering. They were excluded from the least-squares calculations, but some are included in the plots shown below.

Table 1. *Unitary structure factors for bromine and their phases derived from forbidden reflections*

$R = \sum |\Delta F| / \sum |F_o|$ for N observations; $\alpha - \gamma$ (defined in the text) is an angle that determines the shape of the azimuthal profile.

\mathbf{h}	$\alpha - \gamma$ ($^\circ$)	R	N	$[U_A(\mathbf{h})]^2$		$U_A(2\mathbf{h})$	
				obs.	calc.	obs.	calc.
303	-109	0.20	67	0.80	0.80	0.60	0.59
503	-96	0.15	62	0.80	0.81	0.59	0.61
103	-135	0.10	67	0.67	0.78	0.33	0.57
101	-109	0.31	50	0.22	0.13	-0.56	-0.74
30 $\bar{3}$	-22	0.14	58	0.75	0.76	0.51	0.53
10 $\bar{5}$	-166	0.11	53	0.96	0.95	0.93	0.90
105	-142	0.12	64	0.89	0.94	0.78	0.89
305	-122	0.14	68	1.06	0.94	1.13	0.88
50 $\bar{3}$	-37	0.14	61	0.85	0.75	0.70	0.51
10 $\bar{3}$	6	0.15	48	0.75	0.77	0.51	0.55
101	-22	0.29	63	0.18	0.12	-0.63	-0.76

Periodic measurements of the 006 reflection were proportional to an ion-chamber monitor with a maximum deviation of 2%. Observed intensities were converted to F^2 values by normalizing according to this monitor, dividing by the Lorentz factor and correcting for absorption by analytical integration with neglect of the anisotropy. The macroscopic pleochroism is less than the anisotropy of the atomic tensor because two orientations of the tensor are averaged and because the absorption by Ba atoms is isotropic. These data were scaled to fit the calculated F^2 of 006. The degree of linear polarization, measured by the Borrmann effect in germanium, was 0.892. This value is lower than was typical at this station in the past (Templeton & Templeton, 1988).

In the crystal Cartesian basis

$$f_{12} = uv\delta \quad (19)$$

and

$$f_{23} = vw\delta \quad (20)$$

if the axis of the uniaxial tensor is the unit vector (u, v, w) (Templeton & Templeton, 1991). According to the atomic coordinates of the bromate ion (Lutz, Alici & Buchmeier, 1985; Templeton & Templeton, 1989), the direction of its threefold axis is $(u, v, w) = (0.669, 0.665, 0.328)$, $f_{12} = 0.446\delta$, $f_{23} = 0.219\delta$ and $\gamma = 64^\circ$. This orientation of the tensor was used with various values of δ in least-squares fitting of observed and calculated structure factors with the scale as the only parameter. The intensity of 006 depends on the phase of δ , but only to a small extent. The intensities of these forbidden reflections are proportional to $|\delta|^2$. Therefore only the magnitude of δ is determined in this experiment.

5. Results

When the scale was determined by the 006 reflection, the best agreement was $R = 0.16$ for 661 observations of the 11 forbidden reflections and $|\delta| = 2.6$. This anisotropy is the same as that measured in sodium bromate (Templeton & Templeton, 1985) at 0.4 eV below the nominal energy for this experiment and

within the precision of its setting. Plots of F^2 vs ψ in Figs. 1-4 are examples of how the azimuthal profiles agree with theory. According to (11)-(17) the profile is dominated by a $\sin^2 2\psi$ term when $\alpha - \gamma$ is near zero or 180° (Figs. 1 and 2) and by a $\cos^2 \psi$ term when it is near $\pm 90^\circ$ (Fig. 3). More complicated profiles are found for other angles (Fig. 4). Except for points affected by multiple reflection, the agreement is consistent with counting statistics. Similar curves for some other crystals are shown by Kirfel, Petcov & Eichhorn (1991).

An alternate analysis of the data is to determine $[U_A(\mathbf{h})]^2$ for each \mathbf{h} using assumed values for the scale, $|\delta|$, and T . Table 1 lists the results obtained

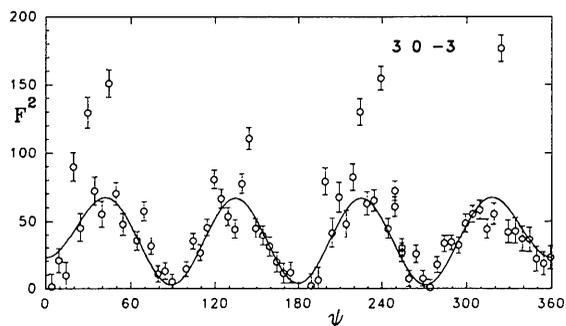


Fig. 1. Azimuthal profile of F^2 , observed (points with error bars) and calculated (curve) for 30 $\bar{3}$; $\alpha - \gamma = -22^\circ$.

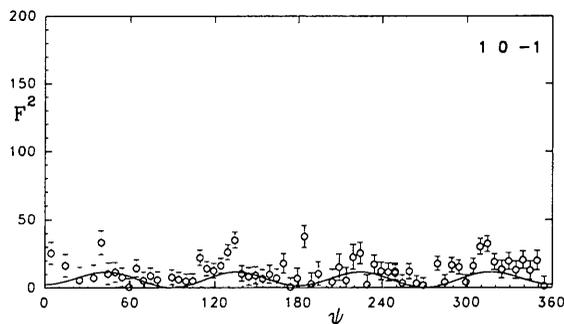


Fig. 2. Azimuthal profile for 10 $\bar{1}$; $\alpha - \gamma = -22^\circ$.

with the scale based on 006, $|\delta|=2.6$ and T from Templeton & Templeton (1989). Also listed are $U_A(2h)$ derived with (18) and the R factor for N observations in each set. From the definition of unitary structure factors, $U_A(2h)$ is the same for the half structure corresponding to $U_A(h)$ as for the whole structure. The reflections are listed in order of measurement and the lack of any systematic trend in the ratio of observed to calculated structure factors is evidence of high stability of wavelength during the experiment.

6. Discussion

This experiment shows that glide-forbidden reflections can be observed with intensities that are consistent with the tensor scattering model and kinematic diffraction theory in agreement with the work of Kirfel, Petcov & Eichhorn (1991). It adds to the evidence that the scattering tensor of the bromate ion is a molecular property that is not much affected by the environment. It demonstrates still another way in which polarization anisotropy of anomalous scattering can be used to give phases of structure factors.

The magnitudes derived for $U_A(2h)$ are in qualitative agreement with those calculated from the known structure and the signs are correct in every case. These data are sufficient to determine the bromine x and z coordinates with precision, but with the intrinsic

ambiguity of interchange of inversion and twofold rotation in the b -axis projection. A least-squares fit using the 11 observed $U_A(2h)$ values gave $x=0.249(1)$ and $z=0.557(1)$, within 0.02 \AA of $x=0.2510$ and $z=0.5574$ from the two full structure determinations. While this test is not entirely realistic for an unknown structure with uncertainty in the scale and error in the orientation of the tensor, we believe that these problems can be solved. We point out that in this type of one-atom case, regardless of the scale, a negative phase is implied for the structure factor of that atom for reflection $2h$ whenever the intensity of h , adjusted for Lorentz, absorption and temperature effects and for these peculiar polarization factors, is less than half that of any other forbidden reflection. Thus the weakness of 101 or $10\bar{1}$ relative to 303 or $30\bar{3}$ implies a negative phase for U_A of 202 or $20\bar{2}$ without any further analysis.

The puzzle is more intricate when there is more than one independent anisotropic tensor, but its solution is still possible. In principal, the contributions of two or three tensors can be resolved by the variation of contributions for different h . If individual-atom unitary structure factors can be extracted for any h , then those for $2h$ can be obtained as shown above. Otherwise the Harker-Kasper inequality still applies (in a rather unconventional way) and sometimes may be useful.

This experiment involved a tensor that is uniaxial, but (1)–(18) are equally valid for biaxial tensors and the procedure for phase determination would be much the same. In such a case (19) and (20) are not applicable and the connection of tensor components with absorption spectra is more complicated. The ratio F_1/F_2 and the shapes of the profiles may change with wavelength. This change is a possible source of information to compensate somewhat for the added complexity of the problem.

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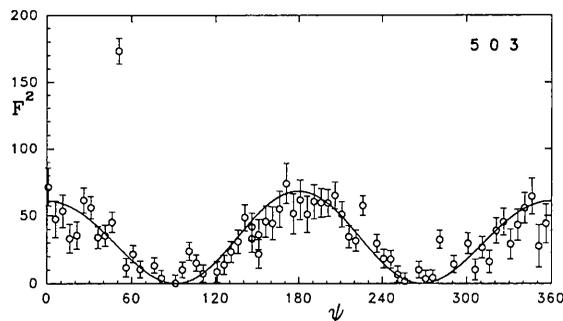


Fig. 3. Azimuthal profile for 503; $\alpha-\gamma=-96^\circ$.

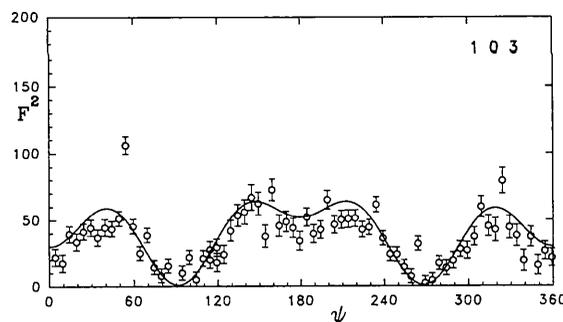


Fig. 4. Azimuthal profile for 103; $\alpha-\gamma=-135^\circ$.

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Improving Multiple Isomorphous Replacement Phasing by Heavy-Atom Refinement Using Solvent-Flattened Phases

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Abstract

Solvent flattening of macromolecular MIR electron density maps is frequently used to improve the quality of the phases and the interpretability of resultant electron density maps. A new method is presented by which the heavy-atom parameters of isomorphous derivatives are refined against these same solvent-flattened phases and is shown to enhance convergence of the parameters by decoupling heavy-atom-parameter adjustment from parent-phase calculation. This approach is described here in the first example of its application in the solution of the glutamyl-tRNA synthetase-tRNA^{Gln}-ATP co-crystal structure.

Introduction

While providing an unbiased view of a new macromolecular structure, the method of multiple isomorphous replacement often fails to yield interpretable electron density maps due to errors in the observed diffraction data and uncertainties in the estimation of heavy-atom parameters. The native and derivative amplitudes frequently contain errors arising

from residual absorption and decay well beyond their estimated standard deviations and the heavy-atom coordinates and occupancies extracted from difference Patterson maps occasionally lie outside the radius of convergence of refinement. Additionally, low-occupancy sites can resist identification. Together these errors culminate in misestimation of the parent phases against which the parameters themselves must be refined. Since the 'lack of triangle closure' that is minimized in the least-squares refinement of heavy-atom parameters requires the parent phases to be calculated, heavy-atom-parameter refinement is coupled to parent-phase refinement. Adjustment of one of the two sets of variables is a dependent function of the other and must be either simultaneously or alternately performed with the other *en route* to convergence (Blow & Matthews, 1973). The problem of 'feedback' is particularly severe in situations where there are a small number of heavy-atom derivatives with closely related heavy-atom sites. Any constraints that can be applied to either the phases or parameters help to decouple the refinement and speed convergence.

Phases produced by back-transforming a MIR electron density map in which the solvent-filled interstices of the crystal have been set to a constant electron density (solvent-flattened) are significantly less biased by the heavy-atom parameters. To the extent that the macromolecular crystal is composed of solvent and

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