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Enantiomorphism and Three-Beam X-ray Diffraction: Determination of the Absolute Structure

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Abstract

It is shown that three-beam X-ray diffraction provides a means of resolving the enantiomorphism problem. It is based on the fact that three-beam interference leads to significantly different ψ -scan profiles for triplet phases close to $+90^\circ$ or -90° , which are selectors between enantiomorphs. Since this method works without the need of anomalous scattering, it is particularly suitable for resolving the absolute structure of light-atom compounds. The application of this method is discussed in detail. Its capability of distinguishing between enantiomorphs has been rejected in a recent paper by Colella [*Acta Cryst.* (1994), **A50**, 55–57]. Detailed comments on the invalid arguments of Colella's analysis are presented.

I. Introduction

For each non-centrosymmetric space group, there are two enantiomorphic forms that can be mapped onto each other by a center of symmetry, *i.e.* the two forms differ in their handedness, which cannot be distinguished in an ordinary X-ray diffraction pattern if Friedel's law is valid. This ambiguity has different meanings for different point groups. For enantiomorphic merohedral point groups, its resolution means the determination of the absolute configuration for chiral species or the determination of the absolute conformation for achiral species. For polar point groups, it means fixing the structure with respect to the polar direction. For non-centrosymmetric roto-inversional point groups, with roto-inversions 4 or

$\bar{6}$, it means assignment of absolute axes (Burzlaff & Hümmner, 1988). Jones (1986) summarized the resolution of these ambiguities by the expression 'determination of the absolute structure'. It ultimately reduces to a determination of structure-factor phases.

One possible method is to exploit the violation of Friedel's law due to anomalous scattering and compare the intensities of suitable Bijvoet pairs (Bijvoet, Peerdemon & van Bommel, 1951). However, difficulties arise for light-atom structures.

A second, newer, method is the direct experimental determination of triplet phase relationships by means of X-ray three-beam diffraction, which works independently of anomalous scattering. This method is, therefore, particularly suited to the determination of the absolute structure of light-atom compounds. It has been shown both theoretically and experimentally in several papers (Hümmner & Billy, 1986; Hümmner, Weckert & Bondza, 1989; Burzlaff *et al.*, 1989; Weckert & Hümmner, 1990; Chang, King, Huang & Gao, 1991; Weckert, Hümmner, Addae-Mensah & Achenbach, 1992; Hümmner, Schwegle & Weckert, 1992; Weckert, Hümmner, Dominguez, Horn & Achenbach, 1993; Platzbecker *et al.*, 1993; Weckert, Schwegle & Hümmner, 1993; Spence, Zuo, O'Keefe, Marthinsen & Hoier, 1994) that three-beam diffraction using ψ -scan experiments does provide a means of distinguishing between the two enantiomorphic forms of a compound.

However, in a very recent paper by Colella (1994), this point is openly rejected. Therefore, we will present in the following a short review and new experimental results on

this subject and will comment on the invalid arguments and conclusions presented in Colella's paper.

II. Determination of triplet-phase relationships by three-beam interference using the ψ -scan technique

An excellent review of the subject is given in a textbook published by the IUCr under the editorship of Giacobozzo (1992). However, the basic results are summarized here in order to aid the reader in following the discussion about the points of controversy brought up in Colella's paper.

1. To specify the nomenclature: the ψ scan is carried out by rotating the crystal around the scattering vector \mathbf{h} of the primary reflection that is aligned for reflection such that an additional scattering vector \mathbf{g} of the secondary reflection passes through the Ewald sphere (cf. Fig. 1). Such a three-beam case is denoted by $0/\mathbf{h}/\mathbf{g}$. All the ψ -scan profiles shown in this work refer to an 'in-out' scan: $\psi = 0$ marks the exact three-beam position (cf. Fig. 1); for $\psi < 0$, \mathbf{g} ends inside and, for $\psi > 0$, \mathbf{g} ends outside the Ewald sphere. The indices of \mathbf{h} and \mathbf{g} are inserted in each plot.

2. ψ -scan three-beam diffraction profiles can be separated into two contributions: a phase-dependent part due to the interference effect that gives the phase information and a phase-independent part due to the conservation of energy flow shared among the interacting beams (Chang & Tang, 1988; Weckert & Hümmner, 1990).

The solution of the fundamental equations of dynamical X-ray three-beam diffraction by means of a modified two-beam approximation (second-order Bethe approximation) shows that the three-beam intensity results from the interference of the primary diffracted wave and the *Umweg* wave. The total phase difference is given by $\phi_{(\text{tot})}(\psi) = \phi(\mathbf{h}, \mathbf{g}) + \Delta(\psi)$, where $\phi(\mathbf{h}, \mathbf{g})$ is a triplet phase given by $\phi(\mathbf{h}, \mathbf{g}) = -\varphi(\mathbf{h}) + \varphi(\mathbf{g}) + \varphi(\mathbf{h} - \mathbf{g})$ (Hümmner & Weckert, 1990) and $\Delta(\psi)$ is a ψ -dependent

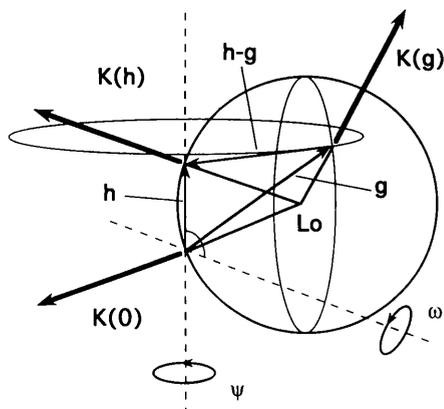


Fig. 1. Schematic representation of a three-beam case in reciprocal space generated by a ψ scan.

resonance phase that varies from 0 to 180° when the secondary scattering vector \mathbf{g} is moved from inside to outside the Ewald sphere (Hümmner & Billy, 1986). It is well known from the interference of coherent waves that the resulting intensity depends on the cosine of phase difference of the interfering waves. Therefore, in the case of $\phi(\mathbf{h}, \mathbf{g}) = -90^\circ$ ($+90^\circ$), the interference effect leads to a symmetric increase (decrease) of the two-beam intensity as $\phi_{(\text{tot})}$ varies from -90 to $+90^\circ$ ($+90$ to 270°); in that range, $\cos \phi_{(\text{tot})}$ is always positive (negative), giving a constructive (destructive) interference effect. In this way, triplet phases of -90 and $+90^\circ$ can be distinguished experimentally. In fact, if the sign of the triplet phase changes, the three-beam diffraction intensity changes. This important point is ignored by Shen (1986), who stated that the three-beam intensity depends only on $\cos \phi(\mathbf{h}, \mathbf{g})$. Obviously, he missed the point of the existence of an additional phase shift due to spatial resonance.

3. The phase-independent symmetrical *Aufhellung* and *Umweganregung* depends on the structure-factor ratio $Q = |F(\mathbf{g})||F(\mathbf{h} - \mathbf{g})|/|F(\mathbf{h})|^2$ (Weckert & Hümmner, 1990). If $Q > 6$, *Umweganregung* is observed in most cases, if $Q < 2$, *Aufhellung* is usually observed. Since *Aufhellung* and *Umweganregung* depend only on the structure-factor moduli, *Aufhellung* or *Umweganregung* effects will have equal magnitude for the two centrosymmetrically related three-beam cases $0/\mathbf{h}/\mathbf{g}$ and $0/-\mathbf{h}/-\mathbf{g}$ if Friedel's law is valid, i.e. $|F(\mathbf{n})| = |F(-\mathbf{n})|$ with $\mathbf{n} = \mathbf{h}$, \mathbf{g} , $\mathbf{h} - \mathbf{g}$. Comparison of the ψ -scan profiles of the two three-beam cases $0/\mathbf{h}/\mathbf{g}$ and $0/-\mathbf{h}/-\mathbf{g}$ allows the phase-independent part to be determined (Weckert & Hümmner, 1990). It should be noted that $\phi(\mathbf{h}, \mathbf{g}) = -\phi(-\mathbf{h}, -\mathbf{g})$ since $\varphi(-\mathbf{n}) = -\varphi(\mathbf{n})$ if anomalous scattering can be neglected.

4. If $Q \gg 6$, phase determination becomes more and more difficult because the phase-independent *Umweganregung* is predominant. Such cases should be avoided for determination of the triplet phase, in particular for $\phi(\mathbf{h}, \mathbf{g})$ close to $+90$ and -90° , since then all the contributions are symmetrical. Analogous arguments hold for $Q \ll 2$ and *Aufhellung*.

III. Determination of the absolute structure

The two enantiomorphic forms *A* and *B* of non-centrosymmetric structures are mapped onto each other by a center of symmetry. With the application of the operation of inversion - all the atomic coordinates (x_j, y_j, z_j) are changed to $(-x_j, -y_j, -z_j)$ - any structure-factor phase changes from $\varphi(\mathbf{n})$ to $\varphi(-\mathbf{n}) = -\varphi(\mathbf{n})$, omitting anomalous scattering, i.e. the structure-factor phase changes its sign. If the mapping includes a shift *s* of origin, an additional phase shift by $2\pi\mathbf{n} \cdot \mathbf{s}$ occurs for each reflection \mathbf{n} . Since a triplet phase is structure invariant, i.e. independent of the choice of the origin, the

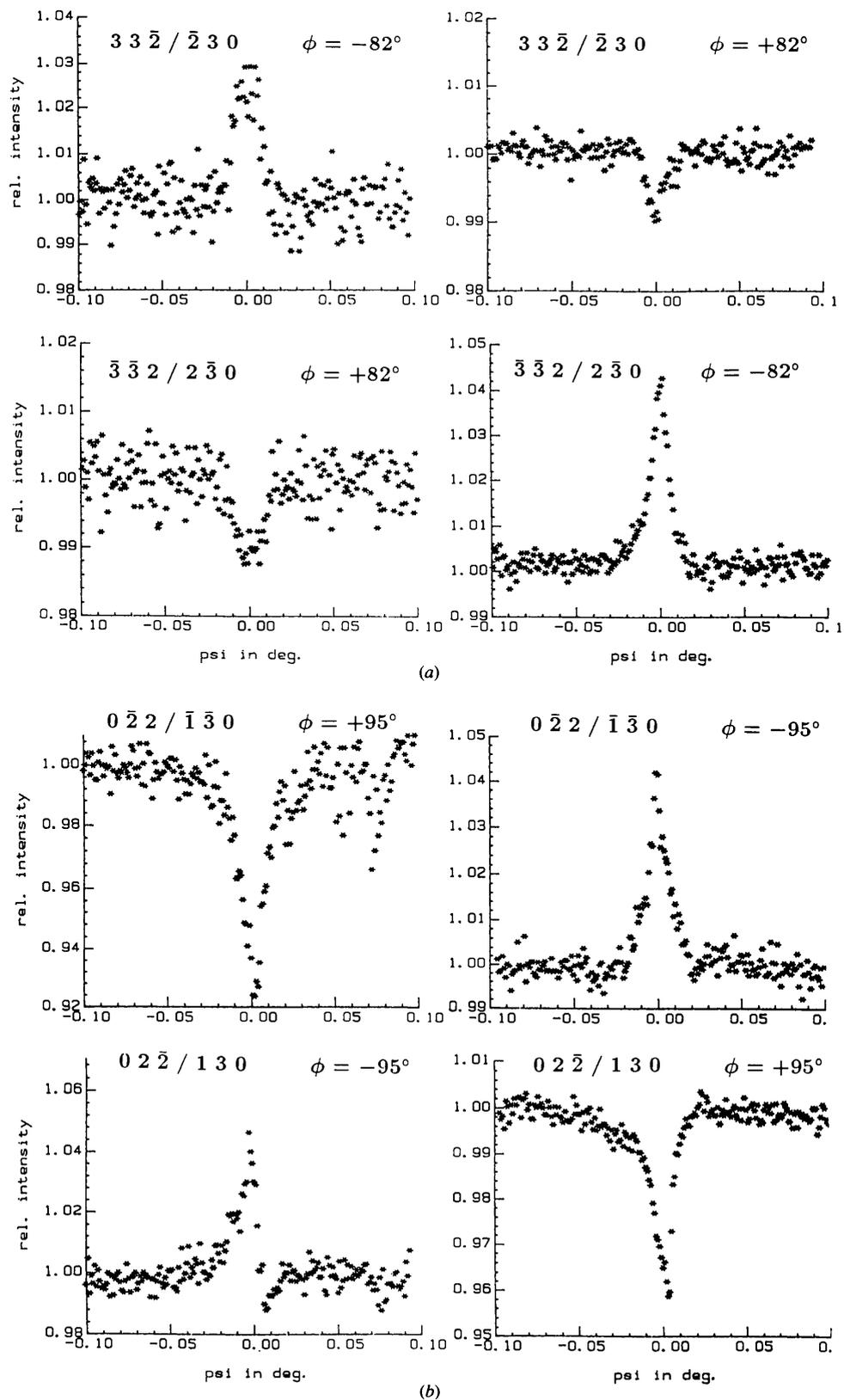


Fig. 2. ψ -scan profiles of centrosymmetrically related three-beam cases for structures with different chirality. (a) Rolipram: (-) left, (+) right; (b) dimetinden-maleic acid: (-) left, (+) right.

phase shifts of the three reflections \mathbf{h} , \mathbf{g} , $\mathbf{h}-\mathbf{g}$ cancel and

$$\phi_A(\mathbf{h}, \mathbf{g}) = -\phi_B(\mathbf{h}, \mathbf{g}) = \phi_B(-\mathbf{h}, -\mathbf{g}) = -\phi_A(-\mathbf{h}, -\mathbf{g}) \quad (1)$$

provided that the set of atomic coordinates refers to the same coordinate system in the two cases. Therefore, best selectors for distinguishing A and B are triplet phases with $\phi(\mathbf{h}, \mathbf{g}) = \pm 90^\circ$ or close to this value (Rogers, 1980).

It should be pointed out again that relations (1) hold only if no anomalous-dispersion effects are present. If the sign of a triplet phase with $|\phi(\mathbf{h}, \mathbf{g})| \simeq 90^\circ$ can be determined by three-beam diffraction, the absolute structure can therefore be fixed without using anomalous scattering. This is the distinct advantage of the three-beam method over anomalous-dispersion methods in determining the absolute structure of light-atom compounds.

IV. Experimental results

Experiments were performed with a special ψ -circle diffractometer using synchrotron radiation from a bending magnet of DORIS II at HASYLAB-DESY.

In the following, experimental verification of relations (1) is shown. The task was to determine the absolute

configuration with respect to the chirality of rolipram, $\text{C}_{16}\text{H}_{21}\text{NO}_3$ (space group $P2_1$, $a = 18.55$, $b = 7.38$, $c = 22.63$ Å, $\beta = 104.7^\circ$, $Z = 8$) and of dimetindenmaleic acid, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{-C}_4\text{H}_4\text{O}_4$ (space group $P2_1$, $a = 9.95$, $b = 19.42$, $c = 5.80$ Å, $\beta = 99.4^\circ$, $Z = 2$). Crystals with different chirality were used, denoted by (+) and (-), grown from enantiomorphic pure solutions separated by chromatographical methods (Blaschke, 1988). The structures were solved by direct methods. Since anomalous-scattering effects could not be easily exploited, the absolute configuration remains initially unknown. Three-beam cases with triplet phases $|\phi(\mathbf{h}, \mathbf{g})| \simeq 90^\circ$ were selected on the basis of one of the two possible configurations (A , B), say configuration A . ψ -scan profiles of both structures, (+) and (-), were measured for the selected three-beam cases. The results are shown in Fig. 2. In the left and right columns, the two centrosymmetrically related three-beam cases $0/\mathbf{h}/\mathbf{g}$ and $0/-\mathbf{h}/-\mathbf{g}$ are compared for the (+) and (-) structures. It can be seen from each column that $\phi_{A,B}(\mathbf{h}, \mathbf{g}) = -\phi_{A,B}(-\mathbf{h}, -\mathbf{g})$. In the upper and lower rows ψ -scan profiles for identical three-beam cases are compared. This very clearly confirms $\phi_A(\mathbf{h}, \mathbf{g}) = -\phi_B(\mathbf{h}, \mathbf{g})$ and

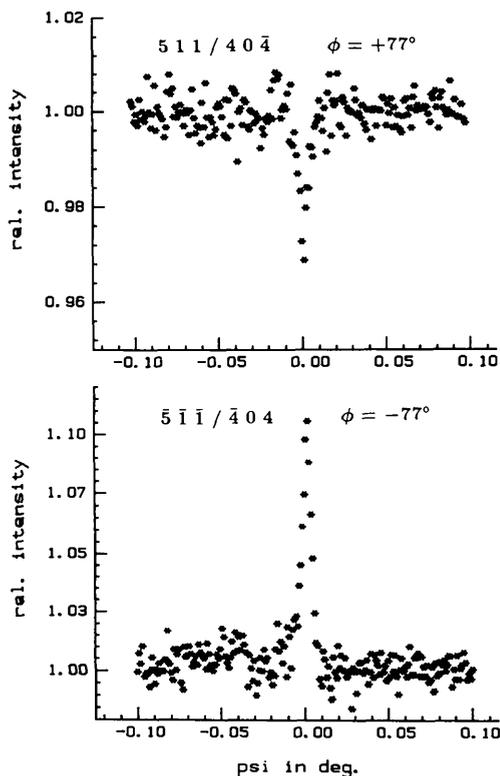


Fig. 3. ψ -scan profiles of $\text{C}_{22}\text{H}_{23}\text{NO}_7$ measured with synchrotron radiation at $\lambda = 1.6527$ Å.

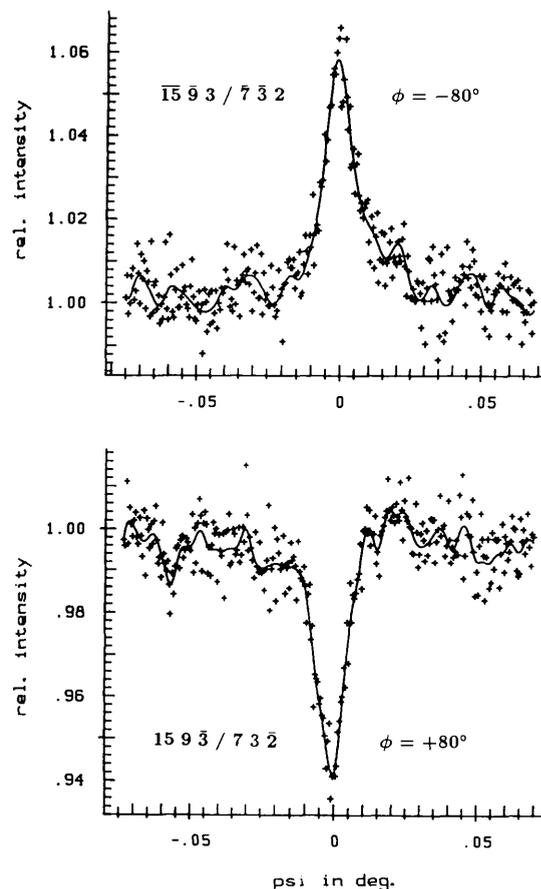


Fig. 4. ψ -scan profiles of tetragonal hen egg white lysozyme: $P4_32_12$, $a = 78.9$, $c = 38.1$ Å.

$\phi_A(-\mathbf{h}, -\mathbf{g}) = -\phi_B(-\mathbf{h}, -\mathbf{g})$, respectively, since it is known that the (+) and (-) structures have different configurations owing to different chirality. The next step is to exclude or to confirm one of the combinations $A(+)$, $B(-)$ and $A(-)$, $B(+)$. This can be done by comparison of the calculated sign and the sign of the triplet phase determined from the ψ -scan profiles. The sign of the calculated triplet phase on the basis of configuration A must be consistent with the measured signs of one of both enantiomorphs. Thus, one combination is fixed. The calculated phases Φ indicated in the diagrams correspond to the correct absolute configuration.

This discussion may appear somewhat lengthy, but we believe that it is necessary in order to avoid confusion brought about by Colella's (1994) paper. The same procedure is always used for determination of the absolute structure by three-beam diffraction: comparison of the calculated signs of the triplet phase based on one or other enantiomorphic form with the signs deduced from experiment. The same procedure is valid even if the two enantiomorphic forms have to be described with different space groups, which is the case for the 11 pairs of enantiomorphic space groups.

Figs. 3 and 4 show two more examples. The absolute structure of $C_{22}H_{23}NO_7$, space group $C2$, $a = 23.29$, $b = 6.47$, $c = 14.97$ Å, $\beta = 116.4^\circ$, could not be determined by means of anomalous-dispersion effects using copper radiation of an X-ray tube since the crystals were only available as very small needles. Fig. 4 shows that this method works also for macromolecular structures (Weckert, Schwegle & Hümmel, 1993). In that case, the experimental results confirm the well known configuration of lysozyme.

V. Comments on Colella's (1994) paper

In Colella's paper, several statements and arguments are either somewhat questionable or even wrong.

1. It is stated that '... our [Shen & Colella's] initial inability to distinguish between left- and right-handedness prevent us from determining the orientation of the crystal ...'. And in another paper by Shen & Colella (1986), one reads: 'Another limitation is that the orientation of the crystal must be completely known, in order to index properly all observed reflections. This may not be possible, for example, when enantiomorphism is present.' However, unique indexing of reflections is always possible. If a right-handed coordinate system is chosen for the description of the lattice, each node of the reciprocal lattice can be labeled by (hkl) indices. Both enantiomorphic forms can be embedded into the same lattice. Therefore, the attribution of (hkl) indices to reflections does *not* depend on which of the two possible enantiomorphic forms the proper structure belongs to, not even if the two enantiomorphs belong to different space groups as is the case, for example, for $P3_121$ or $P3_221$ of benzil. If this were a problem, then it would

also be impossible to distinguish between the enantiomorphs by means of anomalous dispersion. The procedure for both methods, three-beam diffraction and anomalous scattering, is completely analogous: the distinction is based on whether the calculated sign of the triplet phase or the calculated intensities of Bijvoet pairs for one of the two enantiomorphs coincide with or contradict the experimental results.

If different symmetrically equivalent basis systems are used, then symmetrically equivalent labels are put on symmetrically equivalent reflections. In this context, it becomes clear that relation (1), $F_A(h, k, l) = F_B(-h - k, k, -l)$ of Colella's paper is wrong. A and B stand for the two enantiomorphic forms. (hkl) and $(-h - k, k, -l)$ are symmetrically equivalent by a twofold axis along the b axis $2[010]$ using hexagonal axes. This is a symmetry operation that belongs to both space groups under discussion, $P3_221$ and $P3_121$, that does not map enantiomorphs onto each other. Therefore, $F_A(hkl) = F_A(-h - k, k, -l) \exp 2\pi i \mathbf{h} \cdot \mathbf{t}$, where $\mathbf{h} = (hkl)$ and $\mathbf{t} = (t_1 t_2 t_3)$ is a possible translation connected

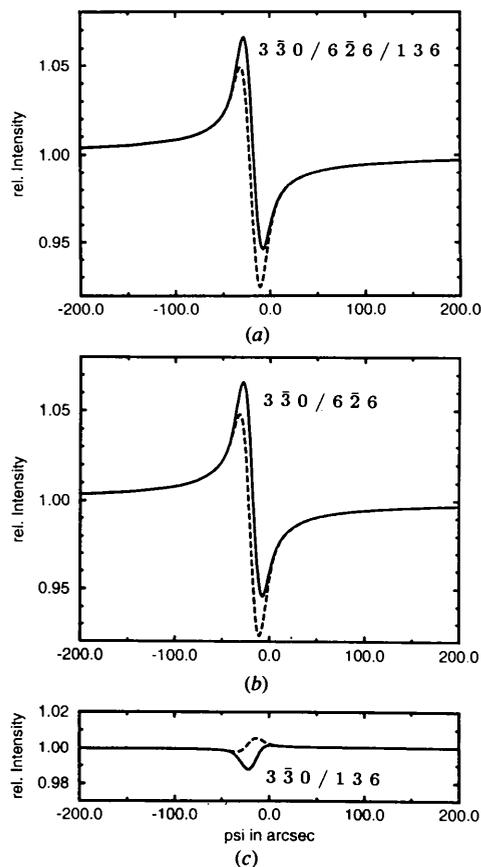


Fig. 5. Calculated integrated ψ -scan profiles of benzil with coordinates consistent with $P3_121$. (a) Four-beam case: $0/h/g/g'$ solid line; $0/-h/-g/-g'$ dashed line; (b) three-beam case: $0/h/g$ solid line; $0/-h/-g$ dashed line; (c) three-beam case: $0/h/g'$ solid line; $0/-h/-g'$ dashed line. The indices h , g and g' are indicated.

with the symmetry operation $2[010]$. If the origin is chosen on $2[010]$, then $F_A(hkl) = F_A(-h-k, k, -l)$. The same relation holds for $F_B(hkl)$. Thus, all the conclusions based on relation (1) in Colella's paper do not hold.

2. As already discussed above, Shen (1986) ignored the fact that the three-beam ψ -scan profiles depend on the sign of the triplet phase. Colella reviews: 'In fact, changing the sign of the triplet invariant did not change the multibeam diffracted intensity since the triplet invariant appears only as an argument of the cosine function in the formula for intensity.' This statement is wrong. The dependence of the diffracted intensity on the sign of the triplet invariant is the essential point for the distinction of enantiomorphs by three-beam diffraction, which was discussed for the first time at the XIII Congress of the IUCr in Hamburg by Hümmer & Billy (1984). It was finally confirmed by recalculating the numerical solutions of the dynamical three-beam diffraction theory (Weckert & Hümmer, 1990) and proven experimentally by several examples (see references in §I).

3. It is very unprofitable to argue with four-beam cases. In a four-beam case, in general, four triplet phases and three quartet phases are involved. Systematic theoretical and experimental investigations on four-beam cases (Hümmer, Bondza & Weckert, 1991) have shown that the ψ -scan profiles are governed by the two first-order triplet terms containing the structure factor of the primary reflection. For the example given by Colella in the four-beam case $0/h/g/g'$: $000/330/626/136$, the two first-order three-beam cases $0/h/g$: $000/330/626$ and $0/h/g'$: $000/330/136$ are involved.

Table 1. Calculated structure-factor moduli and phases of the reflections involved in the discussed four-beam case of benzil using coordinates consistent with $P3_121$

	hkl	$ F(hkl) $	$\varphi(hkl) (^\circ)$	$\phi(\mathbf{h}, \mathbf{g}) (^\circ) = -\varphi(\mathbf{h}) + \varphi(\mathbf{g}) + \varphi(\mathbf{h}-\mathbf{g})$
\mathbf{h}	$3\bar{3}0$	2.36	2.2	
\mathbf{g}	$6\bar{2}6$	3.31	-116.0	
$\mathbf{h}-\mathbf{g}$	$3\bar{1}6$	9.88	90.6	-27.5
$-\mathbf{g}$	$62\bar{6}$	3.29	118.0	
$-(\mathbf{h}-\mathbf{g})$	316	9.92	-89.2	26.6
\mathbf{g}'	136	1.24	50.2	
$\mathbf{h}-\mathbf{g}'$	$2\bar{6}6$	2.05	73.0	121.0
$-\mathbf{g}'$	$1\bar{3}6$	1.27	-47.1	
$-(\mathbf{h}-\mathbf{g}')$	266	2.02	-72.1	-121.4

The structure-factor moduli and phases are listed in Table 1. The data were calculated using atomic coordinates consistent with space group $P3_121$, recently re-refined with anisotropic displacement parameters (Weckert, 1993) and dispersion corrections of Cromer & Liberman (1981) at wavelength $\lambda = 2.29 \text{ \AA}$.

In Fig. 5, the theoretical ψ -scan profiles for the four-beam case and the two leading three-beam cases are shown separately. In each case, the relative change of the integrated intensity convoluted with a Gaussian of FWHM of $18''$ is plotted, normalized with respect to the two-beam intensity $000/330$ far from the multiple-beam position. It can be seen that the four-beam profile is governed by the three-beam profile of $000/330/626$ (Fig. 5b). The contribution of the second three-beam case $000/330/136$ [Fig. 5(c), plotted on the same scale] is

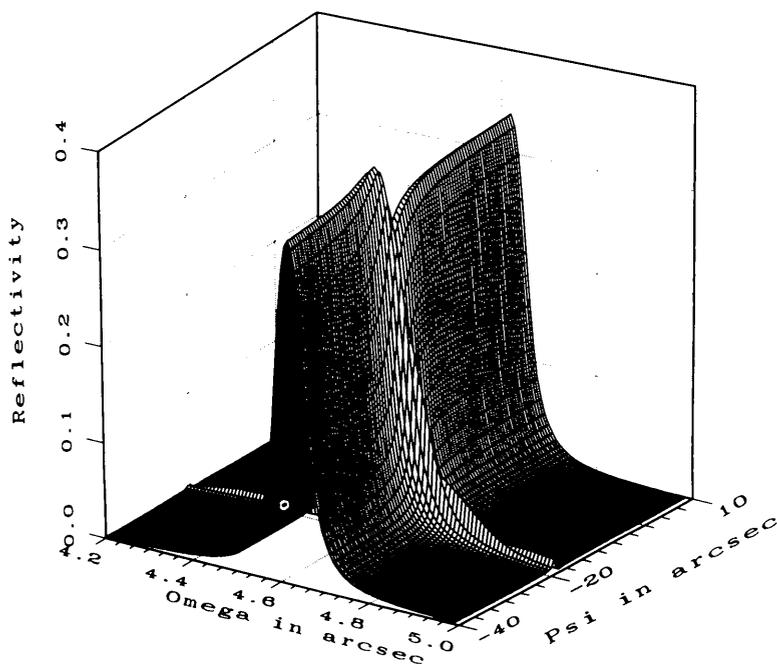


Fig. 6. Calculated $I(\omega, \psi)$ profile of the four-beam case $000/330/626/136$ of benzil using plane-wave dynamical theory at $\lambda = 2.29 \text{ \AA}$ for symmetrical Bragg geometry and an infinitely thick crystal plate. It is assumed that the incoming beam is polarized parallel to the scattering plane of $0/h$. $\omega = 0$, $\psi = 0$ gives the four-beam position calculated with the wavelength λ in vacuum.

almost one order of magnitude smaller. This will become clear on looking at the structure-factor moduli listed in Table 1. The triplet phase of the dominant three-beam case 000/330/626 is -27.5° . This means that it is not optimally suited for determination of the absolute structure. Nevertheless, theoretically there is a difference of approximately 2% between maximum and minimum, which indicates the different resulting intensities for the two centrosymmetrically related three-beam cases. So we cannot understand Colella's results giving a difference of 0.1%. However, it is not clear how the reflectivity is defined in Colella's paper.

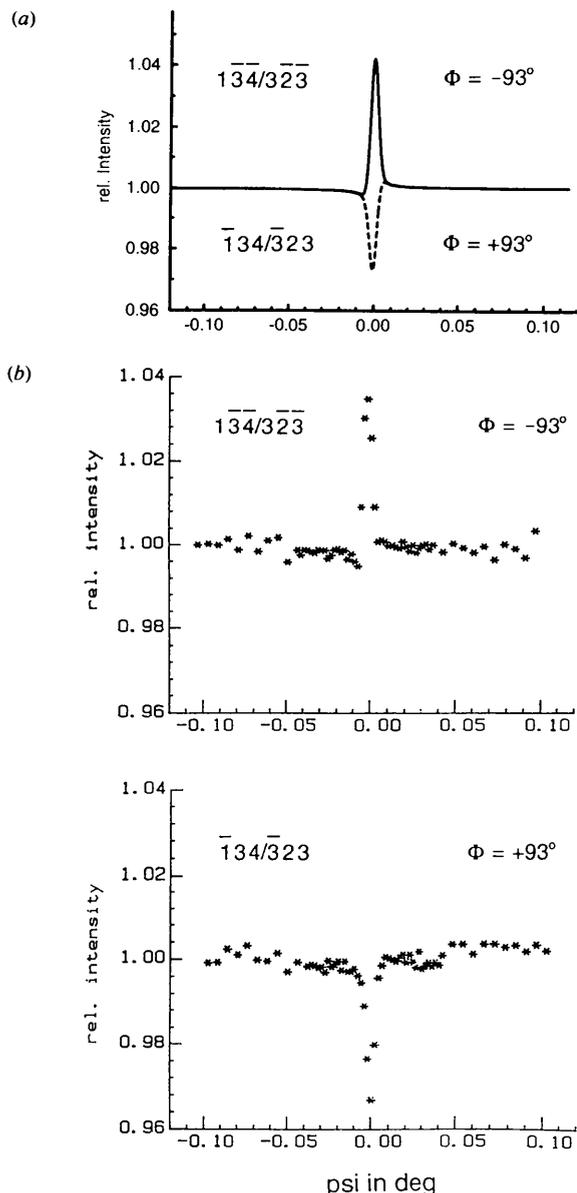


Fig 7. Comparison of (a) calculated and (b) measured ψ -scan profiles of benzil using synchrotron radiation at $\lambda = 1.681 \text{ \AA}$. The coordinates taken are consistent with $P3_221$.

4. It is also precarious to argue with peak intensities of $I(\omega, \psi)$ instead of integrated intensities (we use here ω instead of θ). In an ordinary experiment where the incident-beam divergence exceeds 0.1 mrad, an integrated intensity is always observed (Hümmel & Billy, 1986), *i.e.* integrated over the two-beam profile $I(\omega, \psi = \text{constant})$ and $I(\psi)$ convoluted with the divergence and spectral width of the incident beam and other broadening effects like mosaicity. It is usually very difficult to interpret an $I(\psi, \omega)$ plot for phase determination. An example is shown in Fig. 6 of the four-beam case of Fig. 5 for symmetric Bragg geometry. It shows the intensity distribution on the sheets of the dispersion surface. The peak intensities of $I(\omega, \psi)$ give no significant phase information.

The value of about 6×10^{-7} for the reflectivity given in Colella's paper looks very strange. The reflectivity is uniquely defined (*cf.* von Laue, 1960).

5. There is obviously a severe inconsistency in the argument of Colella. On the one hand, he argues that the ψ -scan profiles are very different for the *A* and *B* species for the same (*hkl*) indices. This is correct since $\phi_A(\mathbf{h}, \mathbf{g}) = -\phi_B(\mathbf{h}, \mathbf{g})$. On the other hand, he states that no difference is to be expected because all the structure factors are essentially unchanged after reversal of the signs of the (*hkl*) indices. This is wrong since $\phi_A(\mathbf{h}, \mathbf{g}) = -\phi_A(-\mathbf{h}, -\mathbf{g})$, which leads to significantly different ψ -scan profiles for $|\phi(\mathbf{h}, \mathbf{g})|$ close to 90° , in spite of the fact that in both cases the moduli of the structure factors remain essentially unchanged.

6. In order to demonstrate the validity of our theoretical and experimental results, calculated and measured three-beam ψ -scan profiles for benzil are shown in Fig. 7. The experiments have been published by Hümmel, Weckert & Bondza (1989). The following parameters were used in the calculation: symmetrical Laue case, thickness of the crystal plate $d = 0.07 \text{ mm}$, wavelength $\lambda = 1.681 \text{ \AA}$, convoluted by a Gaussian with FWHM of $18''$. The agreement is quite good considering that crystals with grown faces were used for the measurements, so that a superposition of profiles with different diffraction geometry were measured.

VI. Concluding remarks

The analysis of former theoretical and experimental results given in this paper shows that three-beam X-ray diffraction is a new method for resolving the enantiomorphism problem without the need of anomalous scattering. This is a distinct advantage in determining the absolute structure of light-atom compounds. The disadvantage of this method is that good-quality crystals are needed in order to obtain a measurable interference contrast. There is no general rule with respect to the mosaicity spread whether a crystal can be used for this type of experiment or not. This must be tested from time

to time though past experience has shown that there are some rules of thumb.

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Enantiomorphism and Multiple-Beam X-ray Diffraction. Revised

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Abstract

The conclusions of a previous paper [Colella (1994). *Acta Cryst.* **A50**, 55–57] are revised in view of an error found in a formula for structure factors. With the correct formula, it is found that, indeed, in the virtual Bragg scattering (VBS) approximation, multibeam diffraction can be used to identify the handedness of the enantiomorphic space groups $P3_121$ and $P3_221$, provided circularly polarized X-rays are used. Outside the VBS approximation, three-beam diffraction can still be used to distinguish the two enantiomorphs through a qualitative comparison of the experimental azimuthal plots with theory.

The idea of using multibeam diffraction for distinguishing the handedness of two enantiomorphs has been discussed in detail in a previous paper (Colella, 1994). The particular case of the two enantiomorphs $P3_121$ and $P3_221$ was considered in detail. It was concluded in that paper that multiple-beam diffraction could not be used to

distinguish between the two enantiomorphs in the absence of anomalous dispersion. Such a conclusion was reached on the basis of a formula [equation (1) in the paper], relating structure factors for the two enantiomorphs, which has been found to be in error (Burzlaff, Lange & Zimmermann, 1995).

Such a formula was indeed obtained on the basis of an incorrect procedure for calculating structure factors for the two enantiomorphs. The conclusions of the previous paper must therefore be retracted.

With the correct procedure, it is found that equation (1) is still valid for the reflections mentioned in the paper. It turns out that, by coincidence, the reflections used there were all of the kind $l = 3n$. When $l \neq 3n$, equation (1) still holds for magnitudes. The phases of F_A and F_B are different.

The whole problem has been re-examined in detail, and different conclusions have now been obtained.

Structure factors have been calculated again for benzil, using the atomic positions given by Brown & Sadanaga (1965). Isotropic thermal factors were used (Gabe, Le