

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

Page, Lee & Barclay, 1981). The anomalous-dispersion corrections, when needed, were obtained from a program called *FPRIME*, developed by Cromer & Liberman (1970*a,b*) at Los Alamos National Laboratory. The equivalent positions within the hexagonal unit cell were obtained from *International Tables for X-ray Crystallography* (1969) for space groups 152 and 154. Brown & Sadanaga do not specify in their paper whether the atomic coordinates are consistent with  $P3_121$  or  $P3_221$ .

A quick comparison between the structure factors calculated for this work and the values given in Table 2 of Brown & Sadanaga clearly indicates that the values are consistent for space group  $P3_121$  not  $P3_221$ .

The structure factors for the two enantiomorphs are simply related by

$$F_A(hkl) = F_B^*(hkl), \quad (1)$$

where  $A$  stands for  $P3_121$  and  $B$  for  $P3_221$ .

It has been shown previously (Shen & Colella, 1987) that for mosaic crystals of generic shape – most crystallographic determinations are performed under these conditions – the significant experimental information is on the wings of a multiple-beam peak of an azimuthal profile. The situation considered here is one in which the intensity of a weak reflection  $\mathbf{P}$  is measured for different values of the azimuthal angle  $\psi$  around the scattering vector  $\mathbf{P}$ , in the neighborhood of a  $\psi$  value corresponding to a strong simultaneous reflection  $\mathbf{H}$  being excited. In such a situation, an asymmetry effect is generally present on the wings of the multibeam peak, which has been referred to as virtual Bragg scattering VBS (Chapman, Yoder & Colella, 1981). The peak itself is generally not considered useful for phase information because, when the scattering is strong, the extent to which a crystal is perfect or imperfect plays a dominant role in the peak shape and intensity, difficult to keep under control.

A convenient way to extract phase information from the asymmetry effect is to use the perturbation theory developed by Shen (1986). Such a theory provides an expression for the azimuthal plot for which the triplet invariant  $\delta$  can be extracted:

$$\delta = \varphi_H + \varphi_{P-H} - \varphi_P. \quad (2)$$

It turns out that, for a plane-polarized incident X-ray beam, Shen's formula provides  $\cos \delta$ , so that positive and negative values of  $\delta$  can be used. In other words, the asymmetry effect is insensitive to the sign of  $\delta$ . It has been pointed out (Spence, Zuo, O'Keefe, Marthinsen & Hoier, 1994; Hümmer & Weckert, 1995) that Shen's perturbation theory is incorrect in this respect and that  $\sin \delta$  terms are not negligible. We have made accurate numerical comparisons between Shen's formula and the exact numerical solutions obtained by means of the *NBEAM* program (Colella, 1974), in which no approximations are used. We found, in every single case we

examined, a very good agreement, within 1 or 2%, between the reflectivities calculated with the two procedures, even in very close proximity of the exact  $n$ -beam excitation point. We believe, therefore, that Shen's approximations are entirely legitimate and that  $\sin \delta$  terms are negligible.

Considering (2), we see that the only difference between the same  $n$ -beam experiment performed with two different enantiomorphs is the sign of  $\delta$ . The wings of the azimuthal plots will be identical in the two cases, so that a distinction between the two enantiomorphs is impossible.

However, when the same perturbation theory is developed for circularly polarized X-rays, the  $\sin \delta$  terms play an important role and the sign of  $\delta$  can be determined unequivocally (Shen & Finkelstein, 1990). We can therefore conclude that, in the absence of anomalous dispersion, the helicity of a crystal like benzil can be determined by making use of circularly or elliptically polarized X-rays.

It should be added at this point that the presence of absorption may appreciably modify the phases of some weak reflections, to the point that (1) becomes completely invalid. For example, if we consider 505 in benzil as the primary reflection and 211 as the simultaneous reflection, the triplet invariants for the two enantiomorphs are quite different in magnitude. For  $P3_121$ ,  $\delta_1 = 141.92^\circ$ ; for  $P3_221$ ,  $\delta_2 = -150.33^\circ$ ; a noticeable difference that can be experimentally observed. This difference is due to the 505 reflection only, whose phases are widely different in magnitude for the two space groups because of absorption. This interesting result illustrates the general principle that phase effects are much more sensitive to structural details than intensities of Bragg reflections. In fact, the structure-factor magnitudes are identical for the two space groups for all reflections involved.

Turning now to Hümmer & Weckert's (1995) results, we have computer simulated the profiles presented in Fig. 7 of their paper. The results are presented in Fig. 1. The  $\psi$  angles at which the three-beam interaction occurs are different because of a different choice of the reference axis. The calculations have been done for a plane-parallel crystal slab of benzil, 2 mm thick, for X-rays with  $\lambda = 1.681 \text{ \AA}$ . Comparing Fig. 1 of this paper with Fig. 7 of Hümmer & Weckert's (1995) paper, it is clear that the effects observed experimentally are much greater than the theory predicts. The theoretical peaks are  $1.36 \times 10^{-4^\circ}$  wide, as opposed to the experimental values of  $\sim 180 \times 10^{-4^\circ}$ . If we consider the positive peaks, and take into account the different peak values and widths between theory and experiment, we conclude that the experimental integrated intensity is about 12 times greater than the value calculated from theory. Such a difference can be explained by crystal imperfections. Benzil is not a perfect crystal in the sense of dynamical theory and it is known that the multiple-peak intensities

can be greatly enhanced by imperfections (Colella & Merlini, 1966). What is important here is the qualitative agreement between theory and experiment. A positive peak can easily be distinguished from a negative peak.

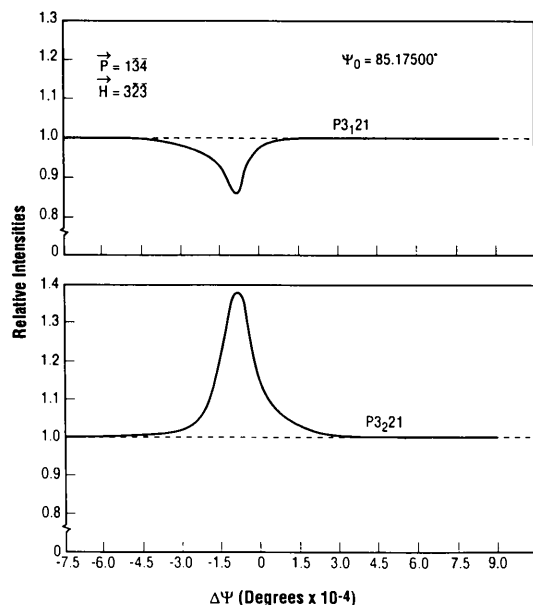


Fig. 1. Calculated azimuthal profiles for benzil. Main reflection  $\mathbf{P}$ :  $1\bar{3}4$ ; simultaneous reflection  $\mathbf{H}$ :  $32\bar{3}$ . The azimuthal angle  $\psi$  is zero when 100 is on the scattering plane, mostly antiparallel to the incident beam. Each point in these plots is an integrated intensity vs  $\theta$ , the angle of incidence on the lattice planes for the  $\mathbf{P}$  reflection. The values on the ordinate axis are relative to the two-beam value. The two profiles are calculated for the two different space groups:  $P3_121$  (top) and  $P3_221$  (bottom). On the abscissae axis variations in azimuthal angle are represented with respect to  $\psi_0$  ( $= 85.17500^\circ$ ), calculated without taking into account refraction effects. The maxima and minima of the two profiles are slightly off  $\psi_0$ .

Since the two theoretical profiles in Fig. 1 of this paper have been calculated for the two space groups  $P3_121$  (negative peak) and  $P3_221$  (positive peak), Hümmer & Weckert's results clearly show that the two enantiomorphs can indeed be identified by  $n$ -beam diffraction.

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## SHORT COMMUNICATIONS

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**Estimation of triplets with interatomic vectors. Erratum.** By M. J. KRONENBURG, *Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

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### Abstract

A typesetting error in equation (4) of Kronenburg [*Acta Cryst.* (1993), **A49**, 872–877] is corrected. The correct equation is

$$P(\psi_i \| F_\mu^{\text{obs}}, \mathbf{k}_\mu) \propto \exp(2\beta_1\beta_2\beta_3 |F_1 F_2 F_3|^{\text{obs}})$$

$$\times \{ \sigma_2 \cos \psi_i + \sum_{\nu \neq \kappa \neq \lambda} f_\nu f_\kappa f_\lambda \times \cos[\psi_i - \mathbf{k}_\mu \cdot (\mathbf{r}_\kappa - \mathbf{r}_\nu) - \mathbf{k}_\mu \cdot (\mathbf{r}_\lambda - \mathbf{r}_\nu)] \}. \quad (4)$$

All relevant information is given in the *Abstract*.