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Enantiomorphism and Multiple-Beam X-ray Diffraction

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Abstract

It is shown that multiple-beam X-ray diffraction does not provide a means of distinguishing between the two enantiomorphic forms of the same crystal. A detailed proof is presented for the case of benzil. It is also shown that, without anomalous dispersion, multiple-beam diffraction is equally incapable of determining the polarity of acentric crystals. Applications are presented to results published in recent literature.

It is well known that multiple Bragg scattering, a situation in which two or more Bragg reflections are excited simultaneously, can be used to determine the phases of structure factors. It is also well known that enantiomorphic forms of the same structure cannot be distinguished in ordinary X-ray experiments since the diffraction patterns are identical. Only when anomalous scattering occurs (*i.e.* the X-ray energy is not too far from the absorption edge of one atomic species present in the crystal) are certain Bragg reflections, otherwise identical in the two enantiomorphic forms, slightly strengthened or weakened, depending on the space group, thereby making it possible to distinguish between the two enantiomorphic forms.

Such has been the case, for example, for α-quartz, which is found with either the $P3_12$ or $P3_22$ space group. It has been shown (De Vries, 1958) that anomalous scattering can indeed be used to determine the absolute configuration, or handedness, of α-quartz.

Since the determination of handedness ultimately reduces to a phase determination, it would seem that multiple Bragg scattering could be fruitfully applied to the solution of the enantiomorphism problem. Such a proposition was seriously considered recently (Shen, 1984) and looked very attractive because it seemed that it could be used with organic crystals containing light atoms, such as C, O and H atoms, for which anomalous scattering is not feasible. However, it was soon realized that even multiple Bragg scattering could not solve the enantiomorphism problem in the absence of anomalous scattering and this conclusion was reported in a review paper (Shen & Colella, 1986) in which the case of benzil (isomorphous with quartz) was considered. The explanation given in the paper was essentially based on the fact that our initial inability to distinguish between left- and right-handedness prevents us from determining the orientation of the crystal and, therefore, drawing conclusions from any conceivable multibeam experiment.

Since then, a number of papers have appeared in the literature in which this conclusion is either openly rejected or ignored and cases have been reported in which multiple-beam diffraction has been used to solve the enantiomorphism problem. Such is the case, for example, for the experiment on benzil described by Hümmer, Weckert & Bondza (1989), in which it is claimed that the handedness of the sample used in the experiment was unambiguously determined by comparing *Umweganregung* peaks with different intensities.

Another case in point is the paper by Chang, King, Huang & Gao (1991), in which some multibeam experiments on large macromolecular crystals are described. It is mentioned in the *Abstract* of this paper that 'the crystal polarity (enantiomorph) is determined unambiguously from the peak intensity measurement'. The measurement the authors refer to in the *Abstract* was performed on single crystals of horse oxyhemoglobin, whose space group is $C2$ (no. 5). The authors here use the word 'enantiomorphism' as synonymous with 'polarity'. Their claim then is that by using three-beam diffraction it is possible to distinguish the polarity of a non-centrosymmetric crystal. This can be achieved, of course, using standard two-beam diffraction, when absorption is important. This is not usually the case for organic macromolecular crystals, composed mostly of C, O and H atoms, whose absorption cross sections for X-rays are very small and to whom Friedel's law applies.

Adding a third Bragg reflection to the scattering process does not change the physics of the experiment. Reversing the signs of the Miller indices of the main Bragg reflection entails reversing the signs of all the other Bragg reflections involved, namely the simultaneous and coupling reflections. If changes are observed in the measured intensities, they are due to the small difference between F_H and F_{-H} as a result of the small imaginary component of the atomic scattering factors (generally negligible). To prove that phase effects are not useful in determining the polarity of an acentric crystal, we performed some three-beam calculations using the *NBEAM* program (Colella, 1974). We considered the case of benzil:* main reflection $3\bar{3}0$; simultaneous reflections $6\bar{2}6$, 136. It is a four-beam case, which occurs at an azimuthal angle of $\psi = 54.77°$, the zero on the ψ scale being defined by the c axis lying in the scattering plane, mostly antiparallel to the incident beam. As usual, several θ scans were computed for different values of ψ, θ being the angle of incidence on the ($3\bar{3}0$) lattice planes. The maximum reflectivity value, for a symmetric Bragg case of diffraction with an infinite thickness, was 6.042×10^{-7}. The calculations were obtained using an X-ray wavelength of $\lambda = 2.29$ Å and realistic values for the imaginary components of the scattering factors were used.

The same calculations were repeated for the opposite set of Miller indices, namely for $\bar{3}30$ as the main reflection and $\bar{6}2\bar{6}$ and $\bar{1}\bar{3}\bar{6}$ as simultaneous reflections at $\psi = -54.77°$. The peak intensity was found to be 6.035×10^{-7}, differing from the previous value only by 0.1%, well below experimental error. This result was expected because all the structure factors were essentially unchanged after reversal of the signs of the Miller indices. All the phases changed in sign but the relative phase relationships were not affected. 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 (Shen, 1986). It is clear then that phase effects cannot be used to determine the polarities of acentric crystals.

We now turn our attention to the paper which directly addresses the problem of enantiomorphism in benzil (Hümmer, Weckert & Bondza, 1989). The problem is different here. There are two varieties of benzil crystals, namely (A) and (B), corresponding to space group no.'s 152 and 154, respectively.

In order to perform a multibeam experiment, the first priority is to orient the crystal. Several methods can be used, such as Laue photographs, precession photographs, diffractometer measurements *etc.* All methods are based on the same principle, namely finding Bragg reflections and putting labels (*i.e.* Miller indices) on each one. Suppose a reflection is found, which we call 030, and a multibeam experiment in which 426 and $4\bar{3}6$ are used as simultaneous reflections (again, a four-beam case) is performed. We also know that benzil can be obtained in two different varieties, (A) and (B), and that the diffraction patterns produced by the two species are *identical.* Therefore, we assume that the crystal we are using is (A). We can simulate a multibeam experiment by computer, with $\psi = -54.77°$, using the same X-ray wavelength and reference axis as in the previous case. Let I_1 be the peak intensity of 030, excited simultaneously with 426 and $4\bar{3}6$. We then repeat the same computation assuming that the crystal is of the (B) species. To do this we have to recalculate all the structure factors, for the same Miller indices, using atomic positions consistent with space group no. 154. As expected, very different results are obtained, the peak intensity being I_2, and it is believed that, by comparison with experimental data, (A) and (B) will be distinguishable.

The problem is that we really did not know, when we began our experiment, that we were dealing with an (A) crystal. It could have been a (B) crystal, in which case what we called 030 was really $\bar{3}30$. In fact, the general rule for these space groups (no.'s 152 and 154) is:

$$F_A(h, k, l) = F_B(-h-k, k, -l) \tag{1}$$

in a rigorous sense, even considering the imaginary components of the scattering factors. The simultaneous reflections will then also have different Miller indices: $\bar{6}2\bar{6}$ and $\bar{1}\bar{3}\bar{6}$. The azimuthal angle for the multibeam excitations will still be $-54.77°$ and the results of our new computation will be identical to those obtained in the first case. The peak intensity I_3 will be identical to I_1, for the very simple reason

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* One single space group, $P3_221$, was arbitrarily chosen for these calculations, $a = 8.409$, $c = 13.672$ Å.

that all the structure factors, recalculated for the (B) species and different Miller indices, are *identical*, in magnitudes and phases, to those calculated when it was thought the crystal was of type (A). Repeating the computations for an (A) crystal with the same Miller indices ($\bar{3}30$ for the main reflection, $\bar{6}2\bar{6}$ and $\bar{1}\bar{3}\bar{6}$ for the simultaneous reflections) will give different results, as in the previous case, with a peak intensity equal to I_4. However, the peak intensities found now are identical to those found earlier ($I_1 = I_3$, $I_2 = I_4$), since all the structure factors are rigorously identical when switching from one space group to another and changing the Miller indices accordingly.

It should be stressed that anomalous dispersion does not help here, as in the previous case. Our calculations were performed with large unrealistic values for the imaginary components of the scattering factors and the equality expressed in (1) was always found to be rigorously true, to within computer accuracy.

The situation is quite different in high-energy electron diffraction ($E = 30$–50 keV or higher). In this case, inelastic scattering (plasmon scattering, single-electron excitations, thermal diffuse scattering and radiation losses) is responsible for a substantial imaginary part of the Fourier components of the crystal potential, typically 10% of the real part, even with light atoms. In such a situation the absolute determination of polarity and enantiomorphism is always possible. Multiple diffraction, in this case, is not an essential ingredient, but rather an unavoidable feature, necessitated by the geometry of the diffraction process (see, for example, the paper by Taftø & Spence, 1982). The situation is reviewed in a recent book by Spence & Zuo (1992).

In conclusion, multiple-beam diffraction cannot resolve the enantiomorphism problem and does not help in solving the polarity problem of acentric crystals in comparison with standard two-beam experiments, in which anomalous-dispersion effects are exploited to differentiate between Friedel pairs.

In view of the analysis given in this paper, the results presented by Chang, King, Huang & Gao (1991) and by Hümmer, Weckert & Bondza (1989) are somewhat questionable.

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Thermal Diffuse Scattering in Time-of-Flight Neutron Diffractometry

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Abstract

The coherent one-phonon scattering cross section measured in time-of-flight (TOF) neutron diffractometry is derived for any ratio between the sample-to-detector flight path and the total flight path. For the particular case of scattering by acoustic phonons in monocrystals, the differential cross section is described in terms of the scattering surface in four-dimensional space ($\mathbf{Q}_e,\omega$), where $\hbar\mathbf{Q}_e$ is the momentum transfer for elastic scattering and $\hbar\omega$ is the energy transfer. This cross section is required in calculating the thermal diffuse scattering (TDS) correction for TOF neutron diffractometry.