SHORT COMMUNICATIONS

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On the minimum number of beams needed to distinguish enantiomorphs in X-ray and electron diffraction.

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Abstract

The minimum strategy for distinguishing enantiomorphs by dynamical diffraction is determined. It is found that, in the absence of anomalous dispersion, it is possible to determine the absolute hand of an enantiomorphic crystal by three-beam dynamical X-ray or electron diffraction in a general orientation only if a fourth noncoplanar reciprocal-lattice point can be identified. Three-beam dynamical diffraction alone is unable to distinguish enantiomorphic forms. Identification is possible using four or more dynamical beams, in general, unless all relevant structure factors lie on a plane in reciprocal space passing through the origin. Supporting computations are given.

It has recently been suggested that, because of the ambiguity in the sign of indices, N-beam X-ray multiple scattering conditions do not allow enantiomorphs to be distinguished in the absence of anomalous dispersion (Shen & Colella, 1986). By contrast, Hummer, Weckert & Bondza (1989) and Chien, Tang & Chang (1989) have recently claimed to determine the hand of crystals using experimental three-beam X-ray measurements. The purpose of this note is to show that three dynamical beams alone are not sufficient to distinguish enantiomorphs in the absence of dispersion (or 'absorption' for electron diffraction), whereas four or more beams may be used for this purpose. We are concerned only with the predictions of exact many-beam theory without dispersion; structure factors therefore satisfy $F_g = F^*_{-g}$.

For a crystal A with charge density $\rho(r)$, we define crystal B with $\rho'(r) = \rho(-r)$ as the enantiomorph of A. Crystal B is then defined to be in the 'same' orientation as crystal A; its structure factors are the conjugates of those of A and lie on the same lattice (see Fig. 1). As a consequence of Friedel's law, kinematic X-ray and electron diffraction patterns are therefore insensitive to the hand of crystals. The center of symmetry in these patterns results in an ambiguity in sign for all indices, reflecting the loss of information on hand. This information is recovered under certain multiple scattering conditions, since multiple scattering renders the diffracted intensities sensitive to the phase of the structure factors. As shown in Figs. 1(*a*) and (*c*), crystal B may be brought into a mirror relationship with (but not into coincidence with) crystal A by twofold rotation.

Since most enantiomorphic crystal pairs belong to the *same* space group (*e.g.* $P2_13$ for FeSi), general methods for distinguishing space groups by electron diffraction (Eades, 1988) are not useful for distinguishing enantiomorphs, except for those cases where pairs have different space groups (*i.e.* for one of the 11 enantiomorphic space groups that contain screw axes of one hand only). For the other space groups, additional symmetry elements (centers of symmetry, mirrors) make $\rho'(r) = \rho(r)$ so that distinct enantiomorphs do not exist. It has been known for many years that X-ray diffraction patterns affected by anomalous dispersion may be used to determine hand (DeVries, 1958). Then, the absorptive part of the optical potential results in intensity differences between conjugate reflections. In the electron diffraction literature, examples of the determination of hand using multiple scattering are given by Goodman & Secomb (1977) for dextrorotatory quartz and Tanaka, Takayoshi, Ishida & Endoh (1985) for MnSi. Depending on crystal thickness and beam energy, transmission electron diffraction patterns may show single scattering, multiple scattering without absorption or multiple scattering with absorption.

In general, an enantiomorphous pair A and B are distinguishable by dynamical diffraction if, for one orientation of A, no orientation for B exists that generates the same diffracted intensities produced by crystal A. The hand of a particular sample of known structure but unknown hand can

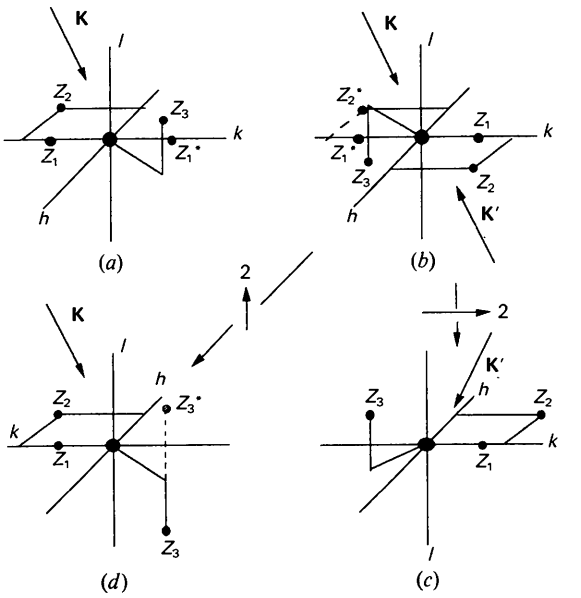

Fig. 1. Reciprocal lattices for enantiomorphs (*a*) A and (*b*) B generated by inversion. The geometric lattice has inversion symmetry. (*c*) B rotated by 180° about a horizontal axis. (*d*) Rotation of B about a vertical axis. (*a*) and (*c*) are related by mirror symmetry (BM). (*a*) and (*d*) have identical ZOLZ structure factors and projections along l (BP). The relationships do not depend on the use of orthogonal axes.

then be determined uniquely from a given experimental pattern by comparing experimental and calculated intensities for the two forms if the differences exceed experimental errors. The existence of a *single* orientational relationship between A and B that gives identical dynamical intensities is sufficient to establish the indistinguishability of the enantiomorphs. We now consider in detail the four orientations of crystal B shown in Fig. 1 that produce patterns most similar to those of A.

Fig. 1(*a*) shows the reciprocal lattice for an enantiomorph A, weighted by complex structure factors Z_i, with beam direction $\mathbf{K}$ in a general orientation. 'Same' (B), 'same' with reversed beam (B, $-\mathbf{K}$), mirror (BM) and projection (BP) orientational relationships for crystal B are also shown. The dynamical diffracted intensities depend (ideally) only on the complex structure factors and beam direction for crystals of equal thickness. The B form shown in Fig. 1(*b*) is generated equivalently by reversing the signs of all atom coordinates, conjugating structure factors or inverting the Z_i through the origin. Since the inversion of the three complex points Z_i reverses their hand and since the complex lattice does not possess a center of symmetry, no rotation of them can bring them into coincidence with points in A's lattice. In general, then, provided these three points and the origin do not lie in a plane, four-beam dynamical diffracted intensities will always distinguish enantiomorphs in principle. Four noncoplanar points are the minimum number needed to *distinguish* the hand of objects in real or reciprocal space (the *definition* of left and right is arbitrary); three-dimensional dynamical diffraction then preserves the hand of an object.

That three-beam interactions are insufficient to distinguish enantiomorphs follows immediately from the projection theorem and from symmetry. Any three reciprocal-lattice points (including the origin) define a plane, onto which the structure may be projected. As shown in Figs. 1(*a*), (*b*) and (*d*), a rotation of B by 180° about *any* common axis l brings the zero-order Laue zone (ZOLZ) ($l = 0$ plane) into coincidence with A, so that the structures may not be distinguished using these reflections alone. The projections of the real-space structures onto this plane are identical. Given experimental intensities from a crystal of known structure but unknown hand, it is impossible to determine whether one has the right-handed form in orientation A or the left-handed form in orientation BP, regardless of the number of dynamically interacting beams in the zero-order Laue zone. As was understood at an early stage in electron diffraction, three-dimensional dynamical interactions are required in order to distinguish enantiomorphs (Goodman & Secomb, 1977).

We note that the kinematic intensities from the orientations shown in Figs. 1(*a*) and (*b*) are identical, whereas [contrary to previous work (Shen & Colella, 1986)] we find that the *three-beam* dynamical intensities (Z_1, Z_2, 0, $\mathbf{K}$) in Fig. 1(*a*) and (Z_1^*, Z_2^*, 0, $\mathbf{K}$) in Fig. 1(*b*) differ, owing to the reversal in sign of the three-phase invariant Ψ [see Marthinsen (1993) for details]. Both the Kambe and the Bethe approximations give the (incorrect) result that the three-beam intensity is independent of the sign of the three-phase invariant Ψ. The approximations of Bird, James & Preston (1987) show a dependence on $\sin\Psi$. Exact computations show that three-beam dynamical intensities *are* sensitive to the sign of Ψ, which may therefore be determined (Marthinsen, 1993). Dynamical interactions are therefore necessary to distinguish these possibilities. Instead of crystal A in the orientation of Fig. 1(*a*), one might unwittingly be dealing with crystal B in the BP orientation. Then, the three-beam intensities are identical; however, the position of the higher-order Laue zone (HOLZ) reciprocal-lattice point Z_3 distinguishes these arrangements. Only the position of this lattice point need be identified. A rotation axis may lie normal to the plane containing the reflections used. For a two- or fourfold axis along l, all structure factors in the ZOLZ normal to this axis are real and the projection is centrosymmetric. The three-beam intensities using Z_1, Z_2 and (000) in Figs. 1(*a*) and (*d*) remain identical but can no longer be distinguished by the position of the lattice point Z_3 because of the point Z_3^* (shown dashed in Fig. 1*d*) generated by symmetry. Then, four-beam interactions, which are sensitive to the phase of Z_3, are required to distinguish the enantiomorphs.

By reversal of the beam direction and rotation of the B crystal and beam about a horizontal axis, the mirror-related arrangement BM is created (Figs. 1*a*, *b* and *c*), since the inversion operation is equal to a twofold rotation followed by a mirror. Thus, three-dimensional zone-axis convergent-beam electron diffraction patterns from a pair of enantiomorphous crystals can be obtained that are mirror-related, as shown experimentally by Tanaka & Terauchi (1985).

It is necessary to reconcile these results with theoretical predictions for few-beam X-ray and electron diffraction and to estimate their magnitude. The X-ray literature is reviewed by Chang (1987) and the electron literature by Spence & Zuo (1992). We have therefore performed four-beam dynamical computations for the $Z_1 = \bar{1}1\bar{1}$, $Z_2 = 03\bar{2}$ and $Z_3 = 3\bar{4}4$ reflections of two enantiomorphs of cubic FeSi (space group $P2_13$). The relative positions of these reflections are given very approximately by Z_1, Z_2 and Z_3, respectively, in Fig. 1(*a*). We define the A form by an Fe atom at $x = y = z = 0.1358$ and an Si atom at $x = y = z = 0.844$ with respect to a right-handed orthogonal coordinate system. The B form was created by reversing the signs of all atom coordinates. We use the exact results of the Bloch-wave formulation of the dynamical diffraction problem without absorption (Marthinsen, 1993) for transmission convergent-beam electron diffraction at 73 kV. The intensity of beam $\mathbf{h}$ in electron diffraction for a thin slab of noncentrosymmetric crystal of thickness z without absorption is

$$I_{\mathbf{h}}(z) = \sum_i \sum_j |C_0^{i^*} C_{\mathbf{h}}^i C_0^j C_{\mathbf{h}}^{j^*}| \exp[(\gamma^i - \gamma^j)z + \varphi^{ij}], \quad (1)$$

while the corresponding expression for the electric displacement field $\mathbf{D}$ in X-ray diffraction is of similar form (Pinsker, 1978):

$$\begin{aligned} |\mathbf{D}_{\mathbf{h}}(z)|^2 = \sum_i \sum_j \big| & (D_{0\sigma}^i D_{0\sigma}^{j^*} + D_{0\pi}^i D_{o\pi}^{j^*}) \\ & \times (D_{\mathbf{h}\sigma}^{i^*} D_{\mathbf{h}\sigma}^j + D_{\mathbf{h}\pi}^{i^*} D_{\mathbf{h}\pi}^j) \\ & \times \exp[2\pi(\gamma^i - \gamma^j)z + \varphi^{ij}] \big| . \end{aligned} \quad (2)$$

Here, σ and π are orthogonal unit vectors specifying the directions of polarization, while φ^{ij} is the phase of the eigenvector. The effect of enantiomorphism is to conjugate the eigenvectors of the dispersion equations C_g^i (D^i) but leave its eigenvalues γ^i unchanged (Marthinsen, 1993). In general, this can lead to large changes in intensity for the 'same' orientation of the two enantiomorphs. Fig. 2(*a*) ('A above') shows two-dimensional rocking curves for the A form around the simultaneous Bragg conditions (which occur at the center

of every disc) for the four reflections. Fig. 2(*c*) shows the *B* form for the 'same' orientation as Fig. 1(*a*) ('*B* above'). Fig. 2(*b*) shows the *B* form as for Fig. 1(*c*) but with reversed beam direction ('*B* below'). Fig. 2(*d*) shows the *A* form as for Fig. 1(*a*) with reversed beam ('*A* below'). We note the small differences in the $\bar{1}1\bar{1}$ discs in Figs. 2(*a*) and (*c*). The equations appear to predict the same dynamical intensities for Figs. 2(*a*) (*A* above) and (*b*) (*B* below). The three-dimensional arrangement of reciprocal-lattice points (see Fig. 1), however, shows that the patterns are in fact mirror-related, as shown. According to (1) and (2), similar symmetries and differences will be observed in X-ray diffracted intensities although, for experimental reasons, these data are not normally presented in the same way.

The sensitivity of the method depends on the diffraction conditions and particular reflections used. Sensitivity is greatest when the three-phase invariant is close to 90°. Many other experimental uncertainties may influence these general predictions, particularly in X-ray work. Data may be collected in different ways, the effects of crystal thickness may be incorporated differently and computer programs may make different approximations. As a practical matter, it is probably impossible to find a rotation axis about which to collect angle-integrated X-ray data for four simultaneous noncoplanar reflections except in very special cases. Thus, for X-rays, the only method requires three dynamically interacting beams together with the relative orientation of a fourth noncoplanar indexed reflection.

In summary, we find that the minimum strategy for identifying hand by dynamical diffraction requires the indexing of four noncoplanar reflections, three of which (at least) must show observable dynamical interactions. These three should not lie in a plane normal to a symmetry axis.

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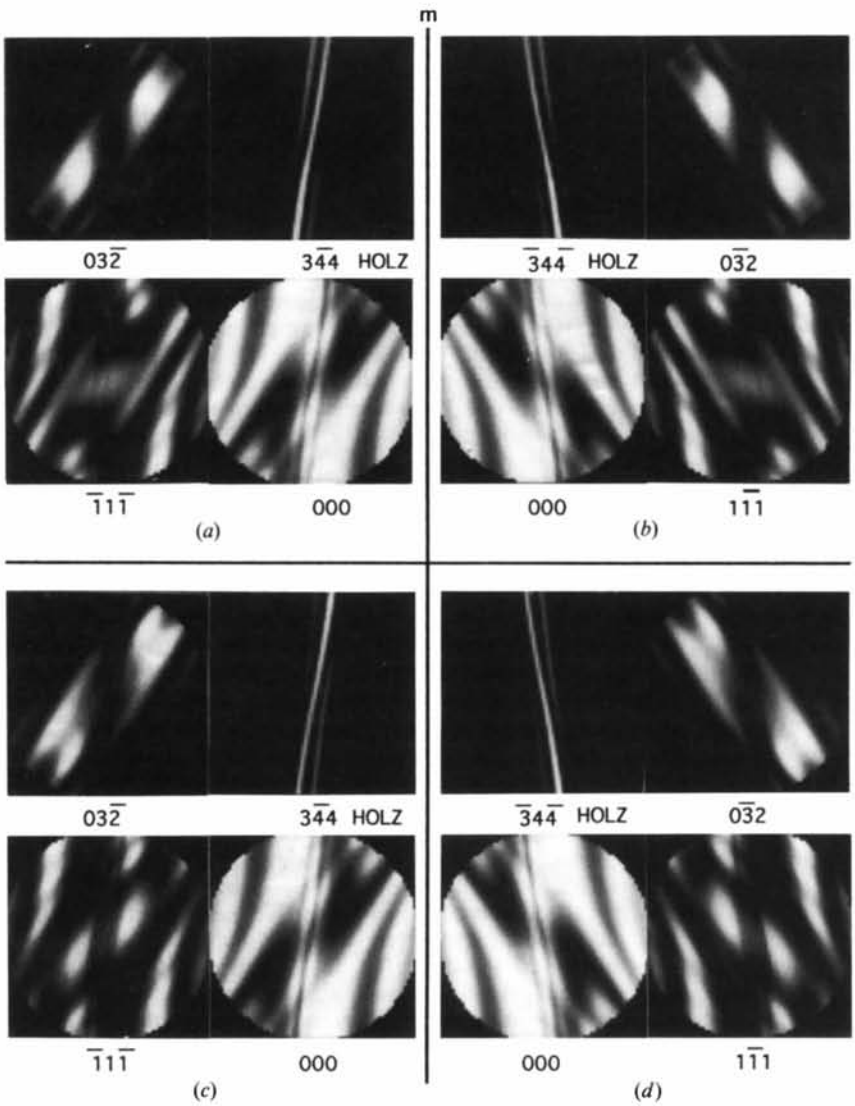

Fig. 2. Computed four-beam diffraction patterns from enantiomorphs *A* and *B* of FeSi at 73 kV with beam directions **K** ('above') and $-\mathbf{K}$ ('below'). (*a*) *A* above. (*b*) *B* below. (*c*) *B* above. (d) *A* below. The reflections $Z_1 = \bar{1}1\bar{1}$, $Z_2 = 03\bar{2}$ and $Z_3 = 3\bar{4}4$ shown in Fig. 1 are used. Here, (*a*) and (*c*) show slight differences in $\bar{1}1\bar{1}$ owing to the change in the sign of the phase invariant. Note that (*a*) and (*b*) [and (*c*) and (*d*)] are mirror-related.

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The maximum-entropy method in charge-density studies. II. General aspects of reliability.

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Abstract

Several general properties of maximum-entropy maps are reviewed that substantiate previous results from selected applications. In particular, the maximum-entropy method (MEM) is depicted as a smoothing scheme and the intrinsic bias introduced by this procedure is pointed out. It is argued that the MEM is not well suited for accurate charge-density mapping.

1. Introduction

In a previous note (Jauch & Palmer, 1993; hereafter referred to as paper I), several unsatisfactory features of the maximum-entropy method (MEM) have been found empirically. The observed peculiarities can be traced back to general properties of MEM images, which were deduced earlier in the field of astronomy (Nityananda & Narayan, 1982; Narayan & Nityananda, 1986). These results have remained unnoticed in the crystallographic literature. As there is a growing interest in using the MEM in charge-density studies (*e.g.* Kumazawa, Kubota, Takata & Sakata, 1993), some aspects relevant to this context will be pointed out in the present note.

2. A smoothing scheme

Entropy maximization was originally introduced (Jaynes, 1957) as a plausible scheme for constructing probability distributions: from the set of all distributions compatible with the available information, the one that maximizes Shannon's entropy is chosen. Well known properties and familiar special cases of probability distributions can thus be generated by a unified variational treatment. *Via* an axiomatic approach, Shore & Johnson (1980) have established that the maximum-entropy criterion is the only consistent way to determine an underlying probability distribution.

When applied to nonprobabilistic problems, the conceptual foundations for the choice of entropy maximization become controversial. Here, it has been argued that the MEM is to be preferred solely on grounds of consistency, without the corresponding map being more likely than others (*e.g.* Livesey & Skilling, 1985). A different view rests on the belief that the MEM map must correspond to the most probable one (*e.g.* Gull & Daniell, 1978). Electron-density reconstruction from incomplete Fourier data represents an example where the MEM is used as a statistical analogue for the evaluation of a continuous function that happens to be restricted to non-negative values, thus allowing a formal identification with a probability distribution. From a pragmatic point of view, the ME principle can be interpreted as a smoothness criterion. Following Titterington (1985), MEM image reconstruction is then regarded merely as one particular case of a very general scheme aiming at a compromise between smoothness and agreement to the data (χ^2 deviation), the relative weight between the two being adjusted to yield a desired value of χ^2.

In actual practice of the MEM, the local contribution to the smoothness functional is chosen as $h(\rho_x) = -\rho_x \ln(\rho_x/\tau_x)$, where ρ_x represents the calculated scattering density located at $\mathbf{x}$ and τ_x denotes the prior distribution. For the usual assumption of a uniform prior, the local contribution reduces to $-\rho_x \ln \rho_x$. Nityananda & Narayan (1982) have shown that, in the context of incomplete Fourier image reconstruction, the detailed form of the smoothness functional is not critical but can be chosen rather arbitrarily as long as certain general restrictions are satisfied. Of crucial importance are the signs of the second and third derivatives of $h(\rho_x)$ with respect to ρ_x: $h''(\rho_x) < 0$ (required for the uniqueness of the solution) and $h'''(\rho_x) > 0$ (necessary sign for nonlinearity in order to generate nonzero Fourier coefficients of higher orders). This contrasts with the view according to which MEM maps are 'better' than all other maps. In fact, the above authors have even recommended that the entropy