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The direct observation and utilization of dynamical phase in convergent-beam electron diffraction

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Abstract. It is shown experimentally that significant structural phase information can be obtained by direct interference in the diffraction plane. Specifically, the intensity distributions of the {100} discs in the convergent-beam pattern of α(low)-quartz form, to within experimental accuracy, a hexagonal array about the c axis, but with suitable electron optics these beams can be made to interfere and the regions of overlap then form a trigonal array about the same axis. The relative phases and intensities thus determined are, of course, dynamical.

Introduction. Convergent-beam electron diffraction is now routinely used in the refinement of structures and for the determination of symmetry. The technique involves the measurement of the intensity of the scattered beams as a function of angle of incidence. High orders of interaction eliminate the ambiguities inherent in single scattering and enhance the sensitivity to structural detail. (Cowley & Moodie, 1962).

It is the purpose of this communication to show how the phases of the scattered beams can be incorporated into the above techniques and to demonstrate the resulting increase in sensitivity.

Theoretical. In the projection approximation, the scattering matrix appropriate to a plate can be written in the form (Hurley, Johnson, Moodie, Rez & Sellar, 1978)

$$S = \exp(iMz) = \sum_j P_j \exp(i\lambda_j z), \qquad (1)$$

where the P_j are projection operators, λ_j are the eigenvalues of the matrix M, assumed distinct, and z is the thickness of the plate.

As is shown in the *Appendix*, the necessary, but of course insufficient, condition that the N-beam wave function $U(g)$ should, excluding confluence, be of 'two-beam form' is that

$$\lambda_{N-1} + \lambda_N = \langle g|M^2|O\rangle/V_g. \qquad (2)$$

This is a generalization of the condition which, taken along with the first invariant of the characteristic equation of M, leads to the inversion of 'three-beam' scattering from a centrosymmetric crystal (Moodie, 1979).

Condition (2) cannot in general be satisfied for a noncentrosymmetric crystal because λ_{N-1} and λ_N are the eigenvalues of a Hermitian matrix and are therefore real, while $\langle g|M^2|O\rangle/V_g$ may be complex. For certain noncentrosymmetric space groups, however, there are reflexions for which this quantity can be real and for which the condition can therefore be satisfied. In particular, with α-quartz the condition can be satisfied for the {100} reflexions in the full 'seven-beam' approximation. This leads to a Niehrs' reduction (Niehrs, 1961; Blume, 1966; Fukuhara, 1966), so the intensity distributions in the first-order reflexions should exhibit a sixfold symmetry about the c axis although the overall symmetry is trigonal. Alpine (or Dauphine) twins, on the other hand, have a true sixfold axis about **c**.

Experimental. In an attempt to distinguish between single and microtwinned crystals of 'twisted quartz', convergent-beam electron diffraction patterns were taken about the c axis with a JEOL 2010 microscope. This instrument has a quadruple condensing system, so that with maximum excitation of the first condenser lens a small (< 3 nm) crossover can be obtained on the specimen plane when a 'good' and partially desaturated LaB_6 filament is fitted.

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A convergent-beam pattern taken under those conditions is shown in Fig. 1. The first-order reflexions show precise sixfold symmetry about the c axis while the {110} reflexions show threefold symmetry about the same axis. Therefore, the specimen is, at least on the microscale, a single crystal of α-quartz and not an Alpine twin. Because the crystal is fairly thin, quite careful comparison of the intensity distributions is required in order to detect this standard (Goodman & Johnson, 1977) N-beam result.

By contrast, the intensity distributions in the regions of angular overlap between the first-order reflexions exhibit a strong trigonal symmetry. In addition, the regions of overlap are very sharply defined.

These experimental results can be accounted for by the addition of the wave functions, as distinct from the squares of the moduli of these functions, in the regions of overlap. This can be seen, for instance, in terms of scattering diagrams. In Fig. 2, typical second-order diagrams for a first-order reflexion lie symmetrically about the line OV_2 while the neighbouring overlap lies about the line $OV_2{}^*$. When the squares of the moduli of the amplitudes are added, the intensities in the regions of overlap about OV_2 and $OV_2{}^*$ are equal, but when wave amplitudes are added the final intensities are unequal. In the case of α-quartz, the result is particularly striking because the structure amplitudes of the {100} reflexions are real and positive.

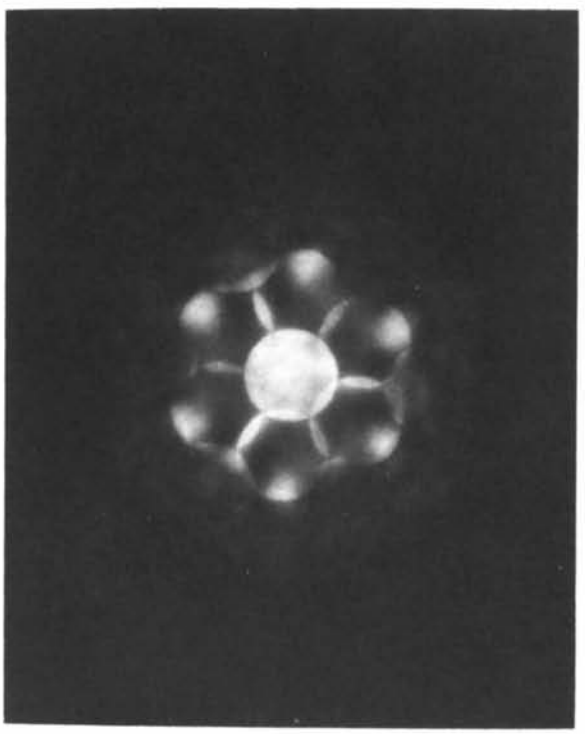

Fig. 1. Coherent convergent-beam pattern taken about the c axis of α-quartz. The effects of interference between the beams can be seen in, for instance, the trigonal symmetry about the zone axis of the regions of overlap between the {100} beams. Where there is no overlap these beams exhibit a hexagonal symmetry about the zone.

The phase effects that lead to the trigonal symmetry of the intensities within the regions of interference therefore result entirely from dynamical interaction. Cowley (1979) has pointed out that dynamical effects will always be present, and this constitutes an extreme example.

The utility of the technique is not, however, diminished by the circumstance that the measured phases are dynamical. At the very least, the regions of interference provide additional data that can be utilized in a variety of ways. In the present instance, an immediate application is found in an extension of the techniques for the determination of symmetry. Utilization in refinement, particularly of noncentrosymmetric structures, is clearly possible. It should be noted that complete coherence is not required in order to make the technique viable. The degree of coherence required for a given application may be estimated in terms of signal-to-noise ratio. For instance, in the present case, the ratio must be sufficient to lead to intensity distributions that are distinguishably trigonal to an adequate confidence level.

As can be seen from Fig. 1, phase effects are detectable in a considerable number of reflexions.

Phase distortion resulting from instrumental defects can clearly reduce the effectiveness of the technique. The only significant aberrations in a modern electron microscope are, however, radially symmetric, so that circumferential measurement of relative phase is practicable in an instrument of adequate quality, as can be seen from Fig. 1.

A more detailed account of these effects is in preparation. A preliminary account of the mineralogical aspects of this work has already been given (Fehlmann & Moodie, 1992).

Appendix. With the projection operators of (1) given by

$$P_j = \prod_{l=1}^{N} (l \neq j)(M - \lambda_l E)/(\lambda_j - \lambda_l),$$

with all eigenvalues distinct, and with

$$Q_j = \left\langle g \left| \prod^{N} (M - \lambda_l E) \right| O \right\rangle,$$

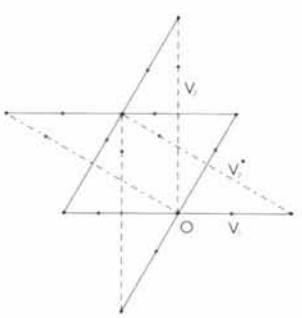

Fig. 2. Typical second-order diagrams about the c axis illustrating the origins of the phase effects.

a condition that the wave functions should have two-beam form is that

$$Q_1 = Q_2 = \ldots = Q_{N-2} = O.$$

Using $Q_1 = Q_2 = O$,

$$\left\langle g \left| (\lambda_1 - \lambda_2) \prod_{l=3}^{N} (M - \lambda_l E) \right| O \right\rangle = O.$$

Continuing this process,

$$\langle g|(M - \lambda_{N-1}E)(M - \lambda_N E)|O\rangle = O;$$

that is,

$$\langle g|M^2|O\rangle/V_g = \lambda_{N-1} + \lambda_N.$$

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