

phases (Bendersky, 1985) that have been shown to possess tenfold quasiperiodic symmetry in two dimensions, but yet are periodic in the third direction.

APPENDIX

The various Fibonacci pentagrids associated with the tilings discussed earlier are given in Fig. 7. The notation is the same as the corresponding sequences in Fig. 1, where the positive direction is to the right. The pentagrids are formed by orienting grids corresponding to a given sequence along the five principal directions in the plane, of which the first points towards the top of the page. The respective tilings, dual to these pentagrids, are similarly denoted, but capitalized.

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Quantitative Phase Determination from Three-Beam Diffraction with a Corrected Scaling Scheme

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Dedicated to Professor B. Post on his 80th birthday

Abstract

The scaling scheme in the quantitative phase-determination procedure proposed by Chang & Tang [*Acta Cryst.* (1988), **A44**, 1065–1072] is corrected by taking the average peak intensity of two centrosymmetrically related three-beam diffractions as the maximum kinematical intensity for the reconstruction of the phase-independent intensity profiles. By subtraction of these phase-independent profiles from the measured intensity distributions, more reliable information about phases can be obtained. This procedure is applied to the three-beam diffraction profiles of several organic crystals, reported by Hümmer, Weckert & Bondza [*Acta Cryst.* (1990), **A46**, 393–402], for quantitative phase analysis. The determined phase values are in good agreement with those calculated from the known structures.

1. Introduction

The phase δ of a structure-factor triplet can be determined qualitatively by analyzing the asymmetry of

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the profile tails of the diffracted intensity distribution of a simultaneous three-beam diffraction. That is, $\cos\delta$ can be determined (see, for example, Chang, 1982; Juretschke, 1982; Post, 1983; Gong & Post, 1983; Shen & Colella 1988; and many others). Recently, semiquantitative/quantitative determination of this phase has become feasible (Chang & Tang, 1988; Tang & Chang, 1988; Hümmer, Weckert & Bondza, 1989; Zuo, Spence & Hoier, 1989; Chang, Huang, Tang & Lee, 1989; Weckert & Hümmer, 1990; Hümmer, Weckert & Bondza, 1990) *via* the inspection and analysis of the entire diffraction profiles.

In the phase-determination procedure proposed by Chang & Tang (1988), a three-beam intensity profile is assumed to be composed of a dynamical (phase-dependent) part and a kinematical (phase-independent) part, which are related to the coherent and incoherent contributions, respectively, of this particular diffraction process. To extract phase information from the intensity distribution, the dynamical part ought to be delineated from the measured intensity profile. This can be done by first reconstructing the kinematical part, a Lorentzian, with its width equal to the experimental peak width and its maximum value determined by matching the

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experimental and theoretical kinematical intensities at the peak positions. Then the reconstructed kinematical profile is subtracted from the measured profile. The dynamical profile is thus obtained for phase analysis. During the intensity-matching process, a scale factor is introduced to accommodate errors due to crystal boundary, extinction and other effects. For real crystals, the extinction effects can be reduced to a minimum by determining the scale factor from weak three-beam diffractions (Chang, Huang, Tang & Lee, 1989). This situation, however, limits the applicability of the phase-determination procedure to weak three-beam cases. In the report of Hümmer, Weckert & Bondza (1990), two symmetry-related strong/medium-strong three-beam diffractions are used to determine semiquantitatively the associated triplet phases by inspection.

In principle, the scale factor, like extinction, depends on the structure factors involved. The use of the intensity ratio of two centrosymmetrically related three-beam diffractions for scaling can eliminate the extinction effect on a relative basis because almost the same sets of structure factors are involved. In addition, the triplet phases of this pair of diffractions have opposite signs to each other. The averaged peak intensity over the two cases is expected to be phase independent. This intensity is therefore most suited for the reconstruction of the kinematical profile. Adapting this idea we correct the scaling scheme of the phase-determination procedure previously reported and apply it to analyze the three-beam profiles of Hümmer, Weckert & Bondza (1990). The determined phase values are reported. In the following, we briefly outline the formalism involved in the phase-determination procedure.

2. Description of the phase-determination procedure

Consider a three-beam (O , G , L) diffraction, in which O is the incident diffraction and G and L are the primary and the secondary reflections, respectively. This diffraction is generated by first moving the reciprocal-lattice point G of the primary reflection onto the surface of the Ewald sphere and then, by rotating the crystal around the reciprocal-lattice vector \mathbf{OG} (the ψ scan), bringing the reciprocal-lattice point L onto the same surface. The relative intensity distribution, $I'_G(\Delta\psi)$, of the G reflection can be written as the sum of the dynamical intensity I_D and the kinematical intensity I_K as follows:

$$I'_G(\Delta\psi) = [I_G(3) - I_G(2)]/I_G(2) = I_D + I_K, \quad (1)$$

where $I_G(2)$ and $I_G(3)$ are the two-beam and three-beam intensities of the G reflection, ψ is the aximuthal angle of rotation around the reciprocal-lattice vector \mathbf{OG} of the G reflection and $\Delta\psi$ is the deviation from the exact three-beam diffraction position. I_D and I_K

are defined as

$$I_D = 2Pa_1Q[2(\Delta\psi)\cos\delta - \eta_T\sin\delta] \quad (2)$$

$$I_K = (\eta_T/\eta_i)k^2\Gamma^2L_F^2Q^2R \quad (3)$$

where

$$P = |\Gamma|kL_FQ|F_{G-L}||F_L||F_G| \quad (4)$$

$$Q = 1/[(\Delta\psi)^2 + (\eta_T/2)^2]^{1/2} \quad (5)$$

$$R = [a_2|F_{G-L}|^2|F_L|^2 - a_3|F_G|^2|F_L|^2 - a_4|F_G|^2|F_{G-L}|^2]/|F_G|^2. \quad (6)$$

The Lorentz factor L_F , the measured total peak width η_T at half-maximum, the intrinsic peak width η_i and the polarization factors a_1 , a_2 , a_3 and a_4 , which will not be used in the phase calculation, are defined in equations (6)–(20) of Chang, Huang, Tang & Lee (1989). The F 's are the structure factors and k is the modulus of the wave vector in vacuum. δ is the triplet phase of $F_{G-L}F_L/F_G$. $\Gamma = -r_e\lambda^2/\pi V$, where r_e , λ and V are the classical radius of the electron, the wavelength used and the volume of the crystal unit cell, respectively. It should be noted that the dynamical intensity I_D is phase dependent, while the kinematical intensity I_K is phase independent, as can be seen from (2) and (3). The expression for I_K can also be derived from the multibeam kinematical theory (Moon & Shull, 1964) using the power-transfer equations. To extract the phase information about δ from I_D , the kinematical part I_K , which is a Lorentzian, must be subtracted from the measured intensity profile I'_G . After this intensity subtraction, the associated phase δ can be calculated from I_D via the following relations for $a_1L_F > 0$:

$$\cos\delta - \sin\delta = I_+/(2Pa_1QW)|_{\Delta\psi = -\eta_T/2} \quad (7)$$

$$-\cos\delta - \sin\delta = I_-/(2Pa_1QW)|_{\Delta\psi = \eta_T/2} \quad (8)$$

where

$$I_{\pm} = I_D(\Delta\psi = \pm\eta_T/2) \quad (9)$$

$$W = k/L_F. \quad (10)$$

For $a_1L_F < 0$, 180° should be added to the determined δ .

Equation (8) can be simplified as

$$\tan\delta = -(I_+ + I_-)/(I_+ - I_-) \quad (11)$$

where the signs of the numerator and denominator of (11) determine to which quadrant δ belongs.

3. Corrected scaling procedure for determining I_K

The kinematical intensity distribution I_K , given in (3), is an approximate expression. To account for the actual intensity distribution $I_{K,E}$, a scale factor is introduced such that

$$I_{K,E} = CI_K. \quad (12)$$

In principle, the factor C depends on the diffraction strength of the three-beam case, extinctions and crystal boundary effects.

If we consider two symmetry-related three-beam cases, (a) (O, G, L) and (b) ($O, -G, -L$), the two triplet phases are related, if the anomalous dispersion is not important, by

$$\delta(a) = -\delta(b),$$

where

$$\delta(a) = \delta_{-G} + \delta_L + \delta_{G-L}$$

$$\delta(b) = \delta_G + \delta_{-L} + \delta_{L-G}.$$

According to (2), $I_D(a) = -I_D(b)$ at the peak positions, $\Delta\psi = 0$. Therefore, the kinematical intensity at the peak is the average of the measured peak intensities, $I'_G(a)$ and $I'_G(b)$, i.e.

$$I_K(0) = [I'_G(a) + I'_G(b)]/2. \quad (13)$$

With this $I_K(0)$ as the peak value and the experimental η_T as the width, the kinematical intensity distribution can be constructed as follows:

$$I_K(\Delta\psi) = I_K(0)\mathcal{L}(\Delta\psi), \quad (14)$$

where \mathcal{L} is a Lorentzian defined as

$$\mathcal{L}(\Delta\psi) = 1/[(\Delta\psi)^2 + (\eta_T/2)^2]. \quad (15)$$

The phase-dependent I_D can be obtained by subtracting the $I_K(\Delta\psi)$ from the measured I'_G for cases a and b . The triplet phases can then be determined according to (11). In this scaling scheme, the phases can be analyzed without invoking the structure-factor moduli. This greatly simplifies the quantitative phase-determination procedure.

4. Results

The phase-determination procedure described above is applied to the experimental data reported by Hümmel, Weckert & Bondza (1990). Figs. 1-5 show the smoothed experimental profiles (the solid curves), the kinematical profiles (the dashed curves) constructed according to (14) and the dynamical profiles (the dash-dotted curves) for the three-beam pairs $\bar{3}21/00\bar{1}$ and $\bar{3}2\bar{1}/00\bar{1}$ of L-ascorbic acid, $\bar{3}1\bar{2}/\bar{1}0\bar{7}$ and $312/107$ of raffinose pentahydrate, $01\bar{1}/\bar{1}23$ and $0\bar{1}\bar{1}/1\bar{2}\bar{3}$ of mezanon, $020/\bar{3}1\bar{1}$ and $020/311$ and $04\bar{2}/\bar{1}2\bar{1}$ and $04\bar{2}/12\bar{1}$ of L-glutamic acid, respectively. The Miller indices before and after the slashes indicate the primary and secondary reflections. The experimentally determined phases δ_E and the calculated phases δ_T are indicated in the figures. Clearly, the experimental phases δ_E determined from the well defined smooth dynamical curves are in good agreement with the theoretical phases δ_T , with a less than 30° difference. The same analysis has also been applied to the three-beam pairs, $\bar{3}1\bar{1}/\bar{1}2\bar{3}$ and $31\bar{1}/12\bar{3}$ of L-glutamic acid

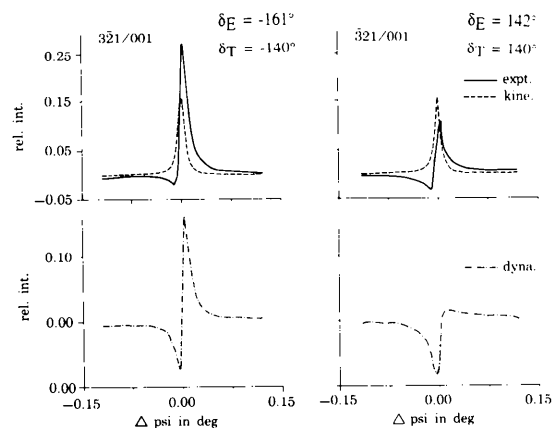


Fig. 1. The experimental, kinematical and dynamical profiles of the $\bar{3}21/00\bar{1}$ and $\bar{3}2\bar{1}/00\bar{1}$ pair of L-ascorbic acid for $\lambda = 1.632 \text{ \AA}$.

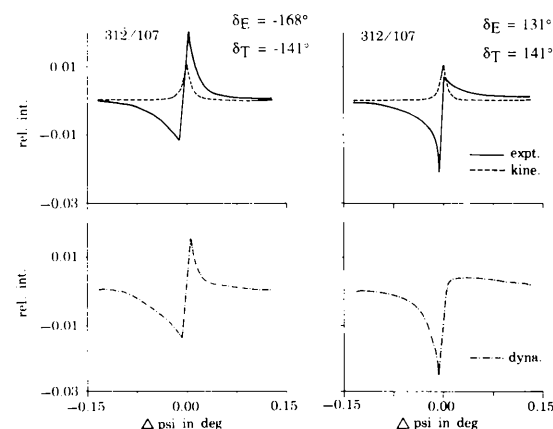


Fig. 2. The experimental, kinematical and dynamical profiles of the $\bar{3}1\bar{2}/\bar{1}0\bar{7}$ and $312/107$ pair of raffinose pentahydrate for $\lambda = 1.8300 \text{ \AA}$.

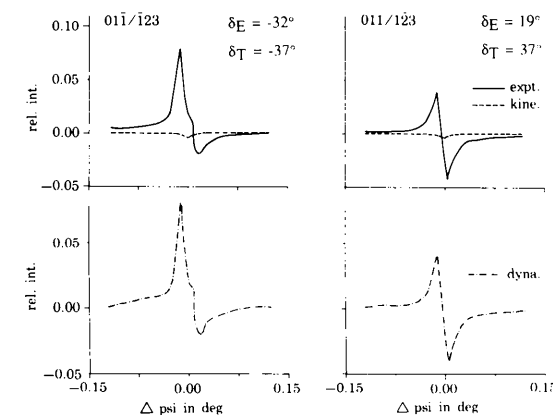


Fig. 3. The experimental, kinematical and dynamical profiles of the $01\bar{1}/\bar{1}23$ and $0\bar{1}\bar{1}/1\bar{2}\bar{3}$ pair of mezanon for $\lambda = 1.9115 \text{ \AA}$.

and $\bar{2}1\bar{3}/0\bar{1}\bar{3}$ and $\bar{2}13/013$ of benzil, respectively. (The intensity profiles are not shown here.) The phases determined are -90° for $\bar{3}1\bar{1}/\bar{1}\bar{2}\bar{3}$ and $\bar{2}1\bar{3}/0\bar{1}\bar{3}$ and 90° for $31\bar{1}/1\bar{2}\bar{3}$ and $\bar{2}13/013$. The theoretical δ_T are -94 and 94° for $\bar{3}1\bar{1}/\bar{1}\bar{2}\bar{3}$ and $31\bar{1}/1\bar{2}\bar{3}$ and -95 and 95° for $\bar{2}1\bar{3}/0\bar{1}\bar{3}$ and $\bar{2}13/013$, respectively. This procedure has also been applied to cases involving macromolecular crystals with large errors in the determined phase values (Chang, King, Huang & Gao, 1991).

The sources of error are mainly the uncertainties in the peak positions and the kinematical peak intensity I_K . The former is due to the backlash of the motor gear for the ψ scan; the latter is attributed partly to the experimental error in determining the peak positions and partly to the theoretical approximation used in the derivation of I_K .

The error due to the experimental factors was analyzed by determining the variation of phase values, when the uncertainty in peak position was

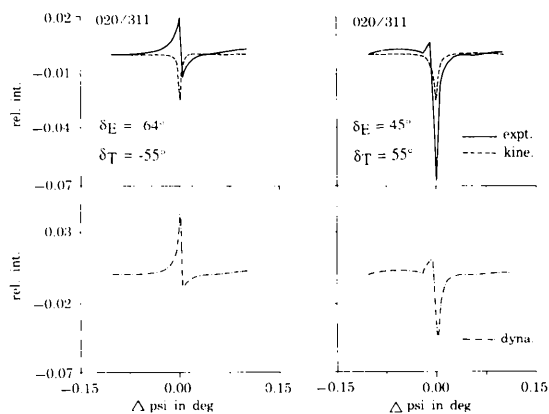


Fig. 4. The experimental, kinematical and dynamical profiles of the $020/\bar{3}1\bar{1}$ and $020/311$ pair of L-glutamic acid for $\lambda = 2.0431 \text{ \AA}$.

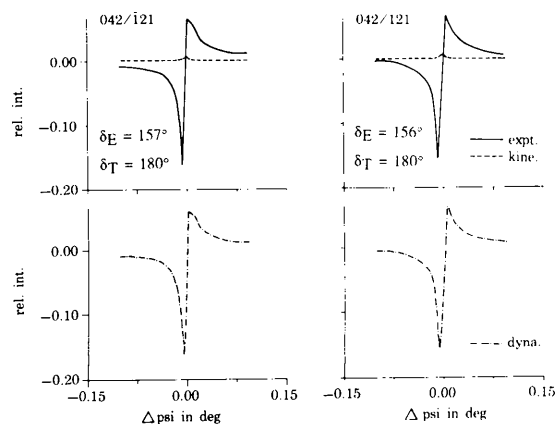


Fig. 5. The experimental, kinematical and dynamical profiles of the $042/\bar{1}2\bar{1}$ and $042/12\bar{1}$ pair of L-glutamic acid for $\lambda = 1.7610 \text{ \AA}$.

considered to be one step, 0.001, of the ψ scan. The maximum error in δ of these ten three-beam diffractions was estimated to be $\pm 15^\circ$, which is smaller than the difference between the calculated and the determined δ values. This difference probably comes from the error introduced by the theoretical approximation, which, however, is difficult to estimate without knowing the correct phases beforehand. Nevertheless, from the statistics of the determined phase values of these ten diffractions, the uncertainty in δ is about 30° .

5. Discussion and concluding remarks

We have proposed a corrected scheme for defining the kinematical intensity distribution for quantitative phase analysis and demonstrated that with this analysis procedure the triplet phases of three-beam diffractions from several organic crystals can be determined within the accuracy of about 30° for the cases studied.

It is worth noting that the peak intensity of the kinematical profile defined in (13) is equal to the maximum value of the ideal profile ΔI of Weckert & Hümmer (1990). The intensity distribution $I_K(\Delta\psi)$ of (14) is, however, different from the ideal profile in taking a symmetric function of $\Delta\psi$. This approach seems to provide a phase value with a better accuracy than using the ideal profile determined from the measured three-beam intensity distributions, because the symmetric profile is not affected by the errors in intensity measurements.

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