

Table 4. *The slopes of the normalized lattice parameters*

The first two rows are experimental results, the last two are calculated values. Units are  $\text{GPa}^{-1}$ .

$-(da/dp)/a$	$-(db/dp)/b$	$-(dc/dp)/c$	Comments
0.058	0.027	0.035	Experimental data 300 K
0.036	0.017	0.022	Extrapolated data 0 K
0.033	0.025	0.020	Williams parameter
0.035	0.023	0.015	Kitaigorodski parameter

with  $W = 1.61$ . The asterisk means 'measured values', whereas the right-hand side means 'calculated values at 0 K'. Surprisingly, it is found that this correction of measured values reproduces the calculated slopes of the normalized lattice parameters quite reasonably (see Table 4). But on the basis of these experimental results we cannot find a clear decision in favour of one of the two parameter sets. We have to mention here that the lattice constants (see Table 3) seem to favour the Williams set of parameters.

To explain the pressure dependence of the structure factor, different aspects must be considered. For example, some reflection intensities increase while others decrease in intensity when pressure is applied. Under pressure, the reflections are shifted to higher scattering angles. In this case the atom form factor and the Debye-Waller factor decrease. Under pressure, however, the amplitudes of the oscillating atoms become smaller and the drop in magnitude of the Debye-Waller factor is therefore reduced. The change of the phases with pressure occurs in both directions. Depending on these effects, the structure factor can increase, remain constant or decrease with pressure.

The Euler angles display only a linear pressure dependence within the pressure range of the present experiment. If we compare this with the calculated Euler angles the dependence is the same, but neither the sign nor the magnitude of the pressure dependences are reproduced correctly by the calculations.

*Acta Cryst.* (1988). **A44**, 1065–1072

## Quantitative Determination of Phases of X-ray Reflections from Three-Beam Diffraction. I. Theoretical Considerations

BY SHIH-LIN CHANG AND MAU-TSU TANG

*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30043*

(Received 22 March 1988; accepted 22 June 1988)

*Dedicated to Professor Dr Ulrich Bonse on the occasion of his 60th birthday*

### Abstract

A method of quantitative determination of X-ray reflection phases using three-beam multiple diffraction is described. This method is derived from the

This discrepancy is especially large for the Euler angle  $\varphi$  whereas the slopes of  $\psi$  and  $\theta$  nevertheless remain small. It seems to us that the crystal structure depends to some extent on electrostatic long-range interactions, as already discussed by Murthy, O'Shea & McDonald (1983). Such interactions are not taken into account in our model calculations.

### References

- ALT, H. & KALUS, J. (1982). *Acta Cryst.* **B38**, 2595–2600.  
 BLOCH, D., PAUREAU, J., VOIRON, J. & PARISOT, G. (1976). *Rev. Sci. Instrum.* **47**, 296–298.  
 BOKHENKOV, E. L., KOLESNIKOV, A. I., MAIER, I. & FEDOTOV, V. G. (1986). Private communication.  
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 915–923.  
 DORNER, B., BOKHENKOV, E. L., CHAPLOT, S. L., KALUS, J., NATKANIEC, I., PAWLEY, G. S., SCHMELZER, U. & SHEKA, E. F. (1982). *J. Phys. C*, **15**, 2353–2365.  
 HÄFNER, W. & KIEFER, W. (1987). *J. Chem. Phys.* **86**, 4582–4596.  
 JINDAL, V. K. & KALUS, J. (1986). *Phys. Status Solidi B*, **133**, 89–99.  
 KITAIGORODSKI, A. I. (1966). *J. Chim. Phys. Phys. Chim. Biol.* **63**, 9–16.  
 KOZHIN, V. M. & KITAIGORODSKI, A. I. (1953). *Zh. Fiz. Kim.* **27**, 1676–1681.  
 LEHMANN, M. S. & PAWLEY, G. S. (1972). *Acta Chim. Scand.* **26**, 1996–2004.  
 MASON, R. (1964). *Acta Cryst.* **17**, 547–555.  
 MATHIESON, A. McL., ROBERTSON, J. M. & SINCLAIR, V. C. (1950). *Acta Cryst.* **3**, 245–250.  
 MURTHY, C. S., O'SHEA, S. F. & McDONALD, I. R. (1983). *Mol. Phys.* **50**, 531–541.  
 PAWLEY, G. S. (1967). *Phys. Status Solidi*, **20**, 347–360.  
 PAWLEY, G. S. & MIKA, K. (1974). *Phys. Status Solidi B*, **66**, 679–686.  
 RIETVELD, H. M. (1967). *Acta Cryst.* **22**, 151–152.  
 RYZHENKOV, A. I. & KOZHIN, V. M. (1967). *Kristallografiya*, **12**, 1079–1086.  
 SCHMELZER, U., BOKHENKOV, E. L., DORNER, B., KALUS, J., MACKENZIE, G. A., NATKANIEC, I., PAWLEY, G. S. & SHEKA, E. F. (1981). *J. Phys. C*, **14**, 1025–1041.  
 WILES, D. B. & YOUNG, R. A. (1981). *J. Appl. Cryst.* **14**, 149–151.  
 WILLIAMS, D. E. (1967). *J. Chem. Phys.* **47**, 4680–4684.

instrumental broadening and crystal mosaicity are included in calculating the diffraction intensity profiles. It is found that in the theoretical formulation the phase-dependent (dynamical) diffraction distribution can be separated from the phase-independent (kinematical) diffraction background. This makes possible the quantitative determination of reflection phases.

### I. Introduction

The X-ray phase problem is one of the central research subjects in crystallography. Although there are several well established methods for phasing, such as direct methods, heavy-atom methods, isomorphous replacement, molecular replacement and anomalous scattering and so on, multiple diffraction has recently been demonstrated as a potential technique for solving the phase problem. [See, for example, Chang (1987) for detailed references.]

Phase is a relative physical quantity. In order to determine this quantity, internal or external references may have to be established in the analysis procedures or set into the crystal sample itself. As a matter of fact, multiple diffraction involves several reflections simultaneously. One of the diffracted beams can be treated as a reference for the other beams. The interference among these beams modifies the intensity of the reference beam. The intensity variation thus provides information about the relative phase involved in the multi-beam process. Recent progress on the use of this particular diffraction technique for phase determination has focused on the determination of the signs of sine and cosine of the relative phase  $\delta$ . For non-centrosymmetric crystals, the reflection phases have values between 0 and 360°. Quantitative determination of these phases is usually desired. This goal, however, has not been reached by the present state of the art of the reported multiple-beam experiments. Recently, Chang & Tang (1988) proposed a method for quantitative determination of X-ray phases using the multiple diffraction technique. It is the purpose of this paper to give a rather complete theoretical formulation for the proposed quantitative phase-determination method within the framework of the dynamical and kinematical theories of X-ray diffraction. In subsequent papers we will report phase-determination experiments for perfect and imperfect crystals.

### II. Geometry of multiple diffraction

Multiple diffraction occurs when several sets of atomic planes are simultaneously aligned to diffract an incident X-ray beam. According to Renninger (1937), multiple diffraction can be obtained systematically by the following procedures. A crystal is first aligned by adjusting the Bragg angle  $\theta_G$  for a preselected reflection  $G$ , the primary reflection. The

crystal is then rotated (the azimuthal rotation) around the corresponding reciprocal-lattice vector  $\mathbf{g}$  to bring an additional reciprocal-lattice point  $L$  (the secondary reflection) onto the surface of the sphere. Thus, multiple diffraction takes place. The interaction between the diffracted beams modifies the intensity of the primary reflection  $I_G$ . The distribution of  $I_G$  versus the azimuthal rotation angle  $\varphi$  forms a multiple diffraction profile.

Fig. 1(a) shows the geometry of a three-beam multiple diffraction in reciprocal space. Points  $O$ ,  $G$  and  $L$  are the reciprocal-lattice points of the incident, the primary and the secondary reflections, respectively.  $\mathbf{l}$  ( $=\mathbf{OL}$ ) is the reciprocal-lattice vector of the  $L$  reflection. The vectors from the center  $C$  of the Ewald sphere to  $O$ ,  $G$  and  $L$  are the wave vectors  $\mathbf{k}_O$ ,  $\mathbf{k}_G$  and  $\mathbf{k}_L$  for the  $O$ ,  $G$  and  $L$  reflections in vacuum, where  $k_O = k_G = k_L = k = 1/\lambda$ .  $\lambda$  is the wavelength of the X-rays used. During the azimuthal rotation, there are two positions for the  $L$  point touching the surface of the Ewald sphere, i.e.  $\varphi_-$  (in) and  $\varphi_+$  (out) positions, depending on whether the  $L$  point is initially outside or inside the Ewald sphere. According to Cole, Chambers & Duun (1962),

$$\varphi_{\pm} = \varphi_0 \pm \beta,$$

where  $\varphi_0$  is the initial azimuthal position of the reciprocal-lattice point  $L$  with respect to the plane of incidence of the  $G$  reflection (see Fig. 1b). The angle  $\beta$  is the angle between the vector component  $\mathbf{l}_{\perp}$  and the plane of incidence.  $\mathbf{l}_{\perp}$  is the component of the reciprocal-lattice vector perpendicular to  $\mathbf{g}$ .

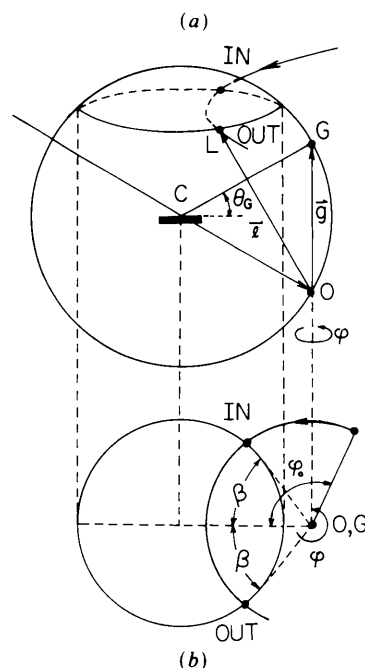


Fig. 1. (a) Geometry of multiple diffraction. (b) Top view of (a).

### III. Theoretical considerations

#### (a) Fundamental equations of wave fields

In the dynamical theory of X-ray diffraction of Ewald (1917) and Laue (1931), the interaction of X-rays with the periodic array of electron density under the diffraction conditions is described by Maxwell's equations. The assumed solutions of these equations are of the form of a Bloch function, with the involved wave vectors  $\mathbf{K}$  satisfying Bragg's law, *i.e.*  $\mathbf{K}_O + \mathbf{G} = \mathbf{K}_G$ .  $\mathbf{K}_O$  and  $\mathbf{K}_G$  are the wave vectors of the incident beam  $O$  and the diffracted beam  $G$  inside the crystal. The moduli  $D$  of the Bloch functions, representing the wave field amplitudes, are governed by the fundamental equation of wave fields

$$(k^2 - K_G^2)\mathbf{D}_G = \sum_L \chi_{G-L} [\mathbf{K}_G \times (\mathbf{K}_G \times \mathbf{D}_L)]. \quad (1)$$

The quantity  $\chi_{G-L}/4\pi$  is the electric susceptibility of the  $G-L$  reflection, which is proportional to the structure factor  $F_{G-L}$ :

$$\chi_{G-L} = -(r_e \lambda^2 / \pi V) F_{G-L} = \Gamma F_{G-L}. \quad (2)$$

$r_e$  is the classical radius of the electron,  $V$  is the volume of the crystal unit cell. The summation in (1) is taken over all the reflections involved, including the incident reflection  $O$ . For a simple Bragg diffraction, the two-beam ( $O, G$ ) case, the fundamental equations take the form

$$(k^2 - K_O^2)\mathbf{D}_O = \chi_{O-O}\mathbf{K}_O \times (\mathbf{K}_O \times \mathbf{D}_O) + \chi_{O-G}\mathbf{K}_O \times (\mathbf{K}_O \times \mathbf{D}_G) \quad (3a)$$

$$(k^2 - K_G^2)\mathbf{D}_G = \chi_{G-O}\mathbf{K}_G \times (\mathbf{K}_G \times \mathbf{D}_O) + \chi_{O-O}\mathbf{K}_G \times (\mathbf{K}_G \times \mathbf{D}_O). \quad (3b)$$

The above two equations can be combined as

$$\mathbf{D}_G = \chi_{G-O}\mathbf{K}_G \times (\mathbf{K}_G \times \mathbf{D}_O) / [(k^2 - K_G^2) + K_G^2\chi_{O-O}], \quad (4)$$

where the relation  $\mathbf{K}_G \times (\mathbf{K}_G \times \mathbf{D}_G) = -K_G^2\mathbf{D}_G$  (because  $\mathbf{K}_G$  is perpendicular to  $\mathbf{D}_G$ ) has been employed.

For a three-beam ( $O, G, L$ ) case, there are three fundamental equations of the wave fields  $\mathbf{D}_O$ ,  $\mathbf{D}_G$  and  $\mathbf{D}_L$ . Expressing  $\mathbf{D}_G$  in terms of  $\mathbf{D}_O$  and  $\mathbf{D}_L$ , we obtain

$$\mathbf{D}_G = A_G [\chi_{G-O}\mathbf{K}_G \times (\mathbf{K}_G \times \mathbf{D}_O) + \chi_{G-L}\mathbf{K}_G \times (\mathbf{K}_G \times \mathbf{D}_L)], \quad (5)$$

where

$$A_G = 1 / [(k^2 - K_G^2) + K_G^2\chi_{O-O}]. \quad (6)$$

Similarly, the wave field  $\mathbf{D}_L$  can be expressed as

$$\mathbf{D}_L = A_L [\chi_{L-O}\mathbf{K}_L \times (\mathbf{K}_L \times \mathbf{D}_O) + \chi_{L-G}\mathbf{K}_L \times (\mathbf{K}_L \times \mathbf{D}_G)], \quad (7)$$

where

$$A_L = 1 / [(k^2 - K_G^2) + K_L^2\chi_{O-O}]. \quad (8)$$

Substituting (7) into (5), we obtain

$$\begin{aligned} \mathbf{D}_G = & A_G \chi_{G-O} \mathbf{K}_G \times \mathbf{K}_G \\ & \times \{ \mathbf{D}_O + A_L (\chi_{G-L} / \chi_{G-O}) [\chi_{L-O} \mathbf{K}_L \times (\mathbf{K}_L \times \mathbf{D}_O) \\ & + \chi_{L-G} \mathbf{K}_L \times (\mathbf{K}_L \times \mathbf{D}_G)] \}. \end{aligned} \quad (9)$$

Equation (9) is an exact expression of the recurrent relationship between  $\mathbf{D}_G$  and  $\mathbf{D}_O$  in the three-beam regime. If, however, an approximate expression of  $\mathbf{D}_G$  in terms of the explicit  $\mathbf{D}_O$  is desired, the  $\mathbf{D}_G$  in the last term of (9) may be substituted by its two-beam form, (4). In comparison with the second term of (9), the substituted term is one order of  $\chi$  higher than the second term. To a first-order approximation, the third term can be dropped from (9), to give

$$\begin{aligned} \mathbf{D}_G \approx & A_G \chi_{G-O} \mathbf{K}_G \times \mathbf{K}_G \\ & \times \{ \mathbf{D}_O + A_L (\chi_{G-L} \chi_{L-O} / \chi_{G-O}) \mathbf{K}_L \times (\mathbf{K}_L \times \mathbf{D}_O) \}. \end{aligned} \quad (10)$$

The first term of (10) is nothing more than the two-beam  $\mathbf{D}_G$  [see (4)]. The second term represents the contribution from the presence of the secondary reflection  $L$  in the diffraction process.

#### (b) Phases, wave vectors and the polarizations

Considering the structure factor amplitudes and the phases, one can write (10) as

$$\mathbf{D}_G = B_1 \hat{\mathbf{K}}_G \times \hat{\mathbf{K}}_G \times [\hat{\mathbf{D}}_O - B_2 \hat{\mathbf{K}}_L \times (\hat{\mathbf{K}}_L \times \hat{\mathbf{D}}_O)] \quad (11)$$

or

$$\mathbf{D}_G = B_1 \hat{\mathbf{K}}_G \times \hat{\mathbf{K}}_G \times [(1 + B_2) \hat{\mathbf{D}}_O - B_2 (\hat{\mathbf{K}}_L \cdot \hat{\mathbf{D}}_O) \hat{\mathbf{K}}_L], \quad (12)$$

where

$$B_1 = A_G \chi_{G-O} K_G^2 D_O$$

$$B_2 = P_O \exp(iu)$$

$$P_O = \Gamma (|F_{G-L}| |F_{L-O}| / |F_{G-O}|) K_L^2 / [(k^2 - K_L^2)^2 + (K_L^2 \chi''_{O-O})^2]^{1/2} \quad (13)$$

$$u = \delta + \arctan [\chi''_{O-O} K_L^2 / (k^2 - K_L^2)].$$

Here, the approximation of small imaginary part has been employed. That is, the term  $K^2 - K_L^2$  is real, which is equal to  $k^2(1 + \chi'_{O-O})$ .  $\delta$  is the invariant phase, *i.e.*  $\delta = \psi_{L-O} + \psi_{O-G} + \psi_{G-L}$ .  $\psi_G$  is the phase of the  $G$  reflection.  $\chi'_{O-O}$  and  $\chi''_{O-O}$  are the real and imaginary parts of  $\chi_{O-O}$ .  $B_1$  is the modulus of the two-beam wave field  $\mathbf{D}_G$ , *i.e.*  $D_G = B_1$ .  $\hat{\mathbf{K}}$  and  $\hat{\mathbf{D}}_O$  are the unit vectors of  $\mathbf{K}$  and  $\mathbf{D}_O$ . The coordinates of the wave vectors  $\mathbf{K}$  and the reciprocal-lattice vectors  $\mathbf{g}$  and  $\mathbf{l}$  are shown in Fig 2.  $C$  is the center of the Ewald sphere. The  $XZ$  plane is the plane of incidence of the

$G$  reflection.  $\mathbf{OG}$  and  $\mathbf{OL}$  are the reciprocal-lattice vectors  $\mathbf{g}$  and  $\mathbf{l}$ . The angle between  $\mathbf{g}$  and  $\mathbf{l}$  is  $\alpha$ . From Fig. 2, the wave vectors  $\mathbf{K}$  can be expressed as

$$\begin{aligned}\mathbf{K}_O &= K(-\cos \theta_G, 0, -\sin \theta_G) \\ \mathbf{K}_G &= K(-\cos \theta_G, 0, \sin \theta_G)\end{aligned}\quad (14)$$

$$\mathbf{K}_L = (l \sin \alpha \cos \beta - K \cos \theta_G, l \sin \alpha \sin \beta, l \cos \alpha - K \sin \theta_G),$$

where  $K = nk$ , with the refractive index  $n = 1 + \chi'_{o-o}/2$ .

In (12), the values of the scalar and vector products depend on the polarizations of the incident and diffracted wave fields. In multi-beam cases, it is known (e.g. Chang, 1984) that a given  $\sigma$ -polarized incident wave,  $\mathbf{D}_{\sigma O}$  can excite both  $\sigma$ - and  $\pi$ -polarized diffraction wave fields, for example, say,  $D_{\sigma G}(\sigma)$  and  $D_{\pi G}(\sigma)$ . Similarly, a given  $\mathbf{D}_{\pi O}$  can generate  $D_{\sigma G}(\pi)$  and  $D_{\pi G}(\pi)$ . This can be understood directly from the second term of (12). For simplicity, let us define that the  $\mathbf{D}_{\sigma O}$  and  $\mathbf{D}_{\sigma G}$  are perpendicular to the plane of incidence of the  $G$  reflection (the  $XZ$  plane) and that  $\mathbf{D}_{\pi O}$  and  $\mathbf{D}_{\pi G}$ , satisfying the conditions  $\hat{\mathbf{D}}_{\pi} = \hat{\mathbf{D}}_{\sigma} \times \hat{\mathbf{k}}$ , lie in that plane. Thus  $\hat{\mathbf{D}}_{\sigma O} \cdot \hat{\mathbf{D}}_{\sigma G} = 1$ ,  $\hat{\mathbf{D}}_{\pi O} \cdot \hat{\mathbf{D}}_{\pi G} = \cos 2\theta_G$ ,  $\hat{\mathbf{D}}_{\sigma O} \cdot \hat{\mathbf{D}}_{\pi O} = \hat{\mathbf{D}}_{\sigma O} \cdot \hat{\mathbf{D}}_{\pi G} = \hat{\mathbf{D}}_{\sigma G} \cdot \hat{\mathbf{D}}_{\pi O} = 0$ .

First, let us consider only the  $\sigma$ -polarized incident beam, i.e.  $\mathbf{D}_{\sigma O}$ .  $\mathbf{D}_{\sigma O}$  is perpendicular to the  $XZ$  plane and parallel to the  $XY$  plane (Fig. 2). According to (11), the excited  $\sigma$  and  $\pi$  components of the  $G$  wave field are

$$D_{\sigma G}(\sigma) = -B_1[1 + B_0 B_2] \quad (15)$$

$$D_{\pi G}(\sigma) = B_1 B_2 B_3, \quad (16)$$

where

$$B_0 = 1 - (l/K)^2 \sin^2 \alpha \sin^2 \beta$$

$$\begin{aligned}B_3 &= (l/K) \sin \alpha \sin \beta [(l/K) \sin \alpha \cos \beta \sin \theta_G \\ &\quad + (l/K) \cos \alpha \cos \theta_G - \sin 2\theta_G].\end{aligned}$$

The  $G$  reflected intensity is equal to

$$\begin{aligned}I_G(\sigma) &= |D_{\sigma G}(\sigma)|^2 + |D_{\pi G}(\sigma)|^2 \\ &= B_1^2 [1 + 2P_O B_0 \cos u + P_O^2 (B_0^2 + B_3^2)].\end{aligned}\quad (17)$$

Similarly, for a  $\pi$ -polarized incident wave,  $\mathbf{D}_{\pi O}$ , the excited  $\sigma$  and  $\pi$  components of the  $G$  wave field take the form

$$D_{\sigma G}(\pi) = B_1 B_2 B_4 \quad (18)$$

$$D_{\pi G}(\pi) = B_1 (-\cos 2\theta_G - B_2 B_5), \quad (19)$$

where

$$\begin{aligned}B_4 &= (l/K)^2 (\cos \alpha \cos \theta_G \\ &\quad - \sin \alpha \cos \beta \sin \theta_G) \sin \alpha \sin \beta\end{aligned}$$

$$B_5 = \cos 2\theta_G - (B_3 B_4) / [(l/K) \sin \alpha \sin \beta]^2.$$

The corresponding  $G$  reflection intensity is

$$\begin{aligned}I_G(\pi) &= |D_{\sigma G}(\pi)|^2 + |D_{\pi G}(\pi)|^2 \\ &= B_1^2 [\cos^2 2\theta_G + 2P_O B_5 \cos 2\theta_G \cos u \\ &\quad + P_O^2 (B_4^2 + B_5^2)].\end{aligned}\quad (20)$$

For an unpolarized incident wave,  $D_{\sigma O} = D_{\pi O}$ . The intensity of the  $G$  reflection can be expressed in a kinematical approach as

$$\begin{aligned}I_G &= [I_G(\sigma) + I_G(\pi)]/2 \\ &= B_1^2 (1 + \cos^2 2\theta_G)/2 \\ &\quad + B_1^2 P_O \cos u [B_0 + B_5 \cos 2\theta_G] \\ &\quad + B_1^2 P_O^2 (B_0^2 + B_3^2 + B_4^2 + B_5^2)/2,\end{aligned}\quad (21)$$

or in a dynamical approach as

$$\begin{aligned}I_G &= [|D_{\sigma G}(\sigma) + D_{\sigma G}(\pi)|^2 + |D_{\pi G}(\sigma) + D_{\pi G}(\pi)|^2]/2 \\ &= B_1^2 (1 + \cos^2 2\theta_G)/2 \\ &\quad + B_1^2 P_O \cos u [B_0 + (B_5 - B_3) \cos 2\theta_G] \\ &\quad + B_1^2 P_O^2 [(B_0 - B_4)^2 + (B_5 - B_3)^2]/2.\end{aligned}\quad (22)$$

It is known that diffraction from an ideally perfect crystal is dynamical and diffraction from an ideally imperfect crystal is kinematical. Since the usual crystals lie in between the categories of ideally perfect and imperfect crystals and the dynamical effect has been considered in the fundamental equations of the wave field during the course of the derivation, we will adopt hereafter the kinematical intensity expression, (21), to take care of the effects from kinematical diffraction. It should, however, be noted that the subsequent considerations on intensity profiles can also be adopted for the dynamical  $I_G$  given in (22).

### (c) Intensity versus $\Delta\varphi$ -diffraction intensity profile

Referring to Figs. 1 and 2, we see that during azimuthal rotation, the distance  $CL$  varies as  $\beta$  varies. Thus, the magnitude of the wave vector  $\mathbf{K}_L$  is a

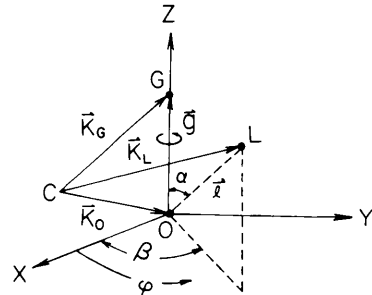


Fig. 2. The coordinate system for wave vectors and reciprocal-lattice vectors.

function of  $\beta$ :

$$K_L(\beta) = [(K \cos \theta_G - l \sin \alpha \cos \beta)^2 + (K \sin \theta_G - l \cos \alpha)^2 + (l \sin \alpha \sin \beta)^2]^{1/2}. \quad (23)$$

When  $\beta = \beta_0$ , multiple diffraction takes place, *i.e.*  $K_L(\beta_0) = K$ . When  $\beta$  is very close to  $\beta_0$ , the magnitude of the wave vector can be expressed as a Taylor series of  $(\beta - \beta_0)$ :

$$K(\beta) = K(\beta_0) + (dK/d\beta)|_{\beta_0}(\beta - \beta_0) = K - (W/K)\Delta\varphi, \quad (24a)$$

where

$$W = Kl \sin \alpha \sin \beta \cos \theta_G \\ \Delta\varphi = \beta - \beta_0. \quad (24b)$$

Hence

$$K^2 - K_L^2 = 2W\Delta\varphi. \quad (24c)$$

$\beta_0$  can be derived from (23) by letting  $K_L(\beta_0) = K$ . Then

$$\cos \beta_0 = (l/2K - \sin \theta_G \cos \alpha) / (\sin \alpha \cos \theta_G). \quad (25)$$

Substituting (24) into (21), we obtain an expression for the multiple diffraction intensity profile:

$$I'_G = I_G/I_2 = 1 + 2Pa_1 \cos u + a_2P^2, \quad (26)$$

where

$$I_2 = B_1^2(1 + \cos^2 2\theta_G)/2 \\ P = \Gamma(|F_{G-L}||F_{L-O}||F_{G-O})K^2Q \\ \cos u = [2(\Delta\varphi) \cos \delta - \eta_i \sin \delta]QW \\ a_1 = (B_0 + B_5 \cos 2\theta_G)/(1 + \cos^2 2\theta_G) \quad (27) \\ a_2 = (B_0^2 + B_3^2 + B_4^2 + B_5^2)/(1 + \cos^2 2\theta_G) \\ Q = 1/[(\Delta\varphi)^2 + (\eta_i/2)^2]^{1/2} \\ \eta_i = |K^2\chi''_{O-O}/W|.$$

$I_2$  is the intensity of the two-beam  $G$  reflection.  $\eta_i$  is defined here as the intrinsic kinematical diffraction width. In (26) only the second term is phase dependent. This intensity distribution is called the dynamical diffraction profile. The last term,  $a_2P^2$ , which is phase independent, is denoted as the intrinsic kinematical diffraction intensity profile (a Lorentzian). In order to reveal clearly the phase effect on the diffraction intensity  $I'_G$ , Fig. 3 shows the calculated total intensity profiles  $I'_G$  versus  $\Delta\varphi$  (the dotted curves), the kinematical profiles (the dashed curves) and the dynamical profiles for various  $\delta$  values (the solid curves). The parameters used are  $P/Q = 6.24 \times 10^{-5}$ ,  $a_1 = 0.883$ ,  $a_2 = 0.872$ ,  $\eta_i = 7.19 \times 10^{-5}$  and  $W = 0.16$ . As can be seen from this figure, the dynamical profiles provide most phase information. For example, in the cases of  $\delta = 90$  and  $270^\circ$ , even though the total intensity curves for both cases are alike, *i.e.* almost

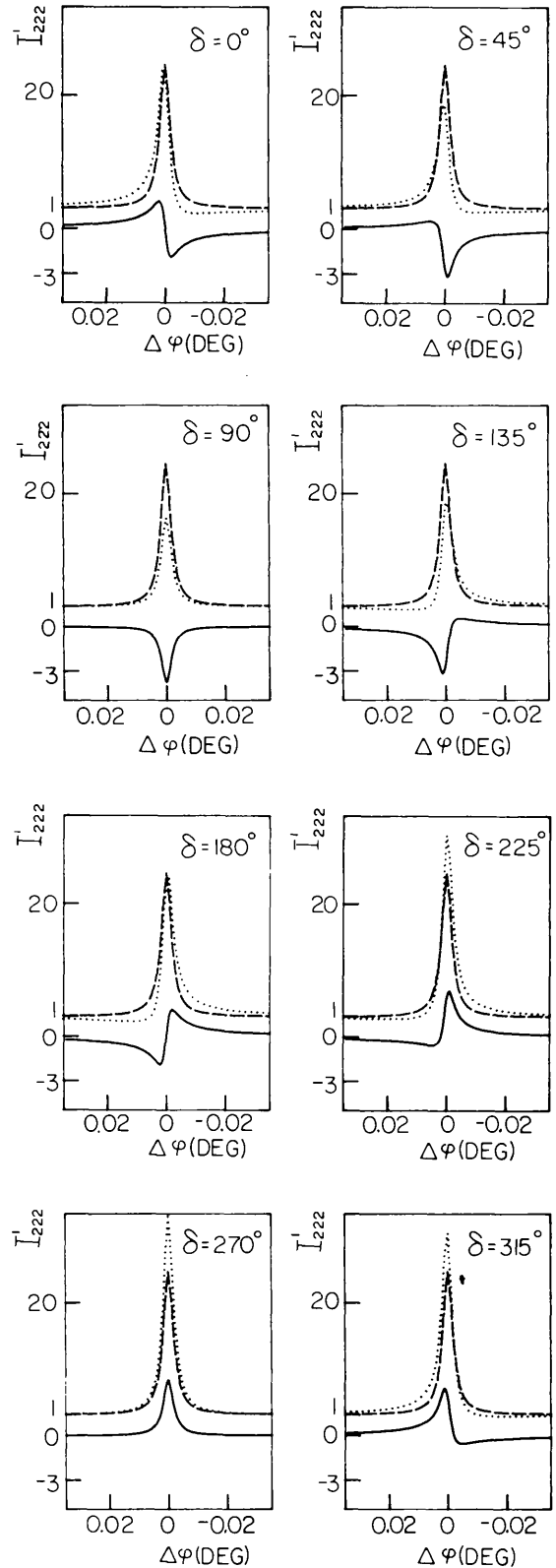


Fig. 3. Calculated total intensity profiles (the dotted curves), kinematical profiles (the dashed curves) and dynamical profiles (the solid curves) for various phases.

symmetric about  $\Delta\varphi = 0$ , the dynamical profiles are quite different. If the dynamical profiles can be obtained experimentally, quantitative phase information may be extracted from the second term of (26). In practice, the dynamical profile can be obtained by subtracting the kinematical Lorentzian profile from the total diffraction profile, provided that the kinematical profile takes the experimental conditions into account.

(d) *Instrumental broadening and crystal mosaicity*

In actual experimental situations, the instrumental broadening and crystal mosaicity greatly affect the kinematical diffraction profile. In reality, the actual kinematical profile can be considered as the convolution of the intrinsic intensity profile, the mosaic distribution, and the instrumental broadening function. Since the crystal mosaicity and the instrumental broadening are usually considered as distributions in between Lorentzians and Gaussians, for mathematical simplicity, we assume here that they all behave as a Lorentzian, as does the  $Q$  function. Thus, the intrinsic kinematical profile  $I_i$  may be written as

$$I_i = \frac{a_2(K^4/4W^2)(\Gamma|F_{G-L}||F_{L-O}||F_{G-O}|)^2}{(\Delta\varphi)^2 + (\eta_i/2)^2}, \quad (28)$$

the mosaic distribution  $I_M$  with mosaic spread  $\eta_M$ : as

$$I_M = \frac{(\eta_M/2\pi)}{(\Delta\varphi)^2 + (\eta_M/2)^2} \quad (29)$$

and the instrumental broadening function  $I_B$  with instrumental spread  $\eta_B$  as

$$I_B = \frac{(\eta_B/2\pi)}{(\Delta\varphi)^2 + (\eta_B/2)^2}. \quad (30)$$

The convolution  $I_i * I_M * I_B$  leads to the actual kinematical diffraction profile:

$$I_K = C_0(|F_{G-L}||F_{L-O}||F_{G-O}||F''_{O-O}|)^2 \times (\eta_i/\eta_M)a_2/[(\Delta\varphi)^2 + (\eta_T/2)^2], \quad (31)$$

where the total diffraction width  $\eta_T = \eta_i + \eta_B + \eta_M$ .  $C_0$  is a scaling factor for matching the experimental and the calculated kinematical intensities.  $C_0$  and  $\eta_T$  can be determined experimentally.

It should be noted that the convolution should, in principle, be carried out for  $I'_G$  with respect to both  $\Delta\varphi$  and  $\Delta\theta$ , the angular deviation from  $\theta_G$  (see Appendix A). However, referring to (26) and the first-order approximation, we see that the two-beam intensity distribution  $I_2$  is a function of  $\Delta\theta$  only. The convolution of  $I_2$  with respect to  $\Delta\theta$  leads only to the general background for multiple diffraction profiles. This would not affect the final results of  $I_K$ .

(e) *Quantitative determination of the phase*

When the actual kinematical intensity profile is constructed *via* (31), the phase-dependent (dynamical) profile can be obtained by subtracting  $I_K$  from the total profile obtained experimentally. According to (26), the values of  $\cos \delta$  and  $\sin \delta$  can be determined from the second term  $2Pa_1 \cos u$ , where the  $\eta_i$  should be replaced by the actual diffraction width  $\eta_T$ . Suppose that the dynamical intensities are  $I_{\pm}$  at  $\Delta\varphi = \pm \eta_T/2$ . From (26), the phase  $\delta$  is determined from the relations

$$\cos \delta - \sin \delta = I_+/(2Pa_1QW) \quad (32)$$

$$-\cos \delta - \sin \delta = I_-/(2Pa_1QW). \quad (33)$$

#### IV. Discussion and concluding remarks

In the derivation of the expression for the diffraction intensity, the first-order approximation has been employed. This approximation will, of course, introduce errors in the quantitative phase determination. However, detailed error analysis for some actual cases, which will be given in paper II (Tang & Chang, 1988), shows that this error for *Umweganregung* three-beam diffraction (Renninger, 1937) is small in calculating the dynamical diffraction intensity. This turns out to cause much smaller errors in phase determination. It should, however, be noted that for *Aufhellung* three-beam diffraction (Renninger, 1937), where the primary reflection is not weak, the second-order approximation should be employed in order to have small errors in the intensity calculation. The intensity expressions of this approximation are given in Appendix B.

From (15), (16), (18) and (19), it can be clearly seen that the phase  $\delta$  takes part only in the excited wave fields  $\mathbf{D}_{\sigma G}(\sigma)$  and  $\mathbf{D}_{\pi G}(\pi)$ . This implies that only the cross-excited wave fields  $\mathbf{D}_{\sigma G}(\pi)$  and  $\mathbf{D}_{\pi G}(\sigma)$  provide no coherent phase relation between the  $\sigma$ - and  $\pi$ -polarized waves. These two terms therefore contribute only to the kinematical profile.

In (27), the intrinsic diffraction width  $\eta_i$  is defined as  $k^2\chi''_{O-O}/W$ . This is, however, one or two orders of magnitude smaller than the usual two-beam intrinsic width, *i.e.*  $k^2|\chi_{G-O}|/W$  (e.g. Cowley, 1964). This difference comes from the boundary conditions. In the derivation of (27), no boundary conditions have been introduced. The formulation can be used for crystals of arbitrary shape. This, of course, introduces errors, which, however, can be remedied by the profile convolution with crystal mosaic spread and instrumental broadening.

If the boundary conditions are considered for a three-beam symmetric Bragg diffraction, of which the primary  $G$  reflection is a symmetric Bragg reflection, the terms  $\Delta\varphi$  and  $\eta_i$  in (27) should be replaced

respectively by (the derivation is given in Appendix A)

$$\Delta\varphi \rightarrow \Delta\varphi + K^2\chi''_{O-O}/2W \quad (34)$$

$$\eta_i \rightarrow |K^2\chi''_{O-O}/W + G_2|q|^{1/2}/W|, \quad (35)$$

where  $G_2$  is a geometric factor which is defined in Appendix A.  $\chi''_{O-O}$  is a small quantity compared with  $|q|^{1/2}$ . Moreover, because  $|q|^{1/2}$  is the effective electric susceptibility of the three-beam interaction (see Appendix A), it is also phase dependent. Without knowing the triplet phase  $\delta$ , the modulus of  $q$  is unknown. This, in turn, will lead to indeterminate kinematical intensities. To suppress this indeterminacy, the term  $|q|^{1/2}$  may be replaced by  $|\chi_{O-O}|$  as an approximation, *i.e.*

$$\eta_i \rightarrow k^2\chi''_{O-O}/W + G_2|\chi_{O-O}|/W. \quad (36)$$

This approximation is based on the fact that at maximum the effective  $|q|^{1/2}$  could not exceed the electric susceptibility  $\chi_{O-O}$  of the direct reflection. Similarly,  $\eta_i$  in (36) is approximately equal to  $k^2|\chi_{O-O}|/W$ , which is comparable in order of magnitude with the usual two-beam diffraction peak width. Evidently, the actual multiple diffraction width will not be affected much by this approximation after the convolution procedures, because after all the errors caused are absorbed in the scaling factor  $C_0$ .

The  $W$  factor defined in (24b) can be written as

$$K/W = \Delta\varphi/\Delta K. \quad (37)$$

This is the Lorentz factor of multi-beam diffraction, namely,  $L_F = k/W = (\Delta\varphi)/(\Delta K)$ . According to Chang (1982a, b), the sign of  $L_F$  is the sign of rotation  $S_R$ , which is defined as

$$S_R = -\text{sign} [\Delta\varphi/\Delta(1/\lambda)] = S_{\pm}S(I^2 - \mathbf{l} \cdot \mathbf{g}), \quad (38)$$

where  $S_{\pm}$  is positive for the position (in) and negative for the position (out).  $S(I^2 - \mathbf{l} \cdot \mathbf{g})$  is positive for  $I^2 - \mathbf{l} \cdot \mathbf{g} > 0$  and negative for  $I^2 - \mathbf{l} \cdot \mathbf{g} < 0$ . It has been demonstrated (Chang, 1981, 1982a, b) that the sign of  $\cos \delta$  is the product of the sign  $S_L$  of the asymmetry of the multiple diffraction intensity profile and the sign of rotation  $S_R$ . In quantitative phase analysis, the sign  $S_R$  should be considered for unambiguous phase determination. The simplest way to do this is to reverse the intensity profile with respect to  $\Delta\varphi$  for negative  $S_R$ .

In conclusion, we have given some theoretical considerations on the method of quantitative determination of reflection phases. This method separates the phase-dependent (dynamical) intensity from the kinematical (phase-independent) intensity. The phase information, immersed in the kinematical intensity background caused by instrumental broadening and crystal mosaicity, may now be brought out for analysis. This method may therefore be used for phase determination in both centro- and non-centrosymmetric crystals.

The authors thank the National Science Council for financial support under the grant NSC77-0208-M007-71. MTT is indebted to the same organization for a graduate fellowship.

## APPENDIX A

### Expression of $K^2 - K_L^2$ for a three-beam symmetric Bragg diffraction

Consider a three-beam ( $O, G, L$ ) case in which the primary reflecting planes  $G$  are parallel to the crystal surface. For simplicity, the crystal is assumed to be infinitely thick. The geometric relation among the incident  $O$ , the primary  $G$ , and the secondary reflection  $L$  are shown in Fig. 1. From Chang (1984), the scalar product  $\mathbf{K}_L \cdot \mathbf{K}_L$  can be expressed as

$$K_L^2 = \mathbf{K}_L \cdot \mathbf{K}_L = k^2 - 2W(\Delta\varphi) + 2(l \cos \alpha - g/2)k\zeta, \quad (A1)$$

where  $k\zeta$  is the accommodation (Ewald, 1917) along the crystal-surface normal, which is defined as

$$2\xi_O = \chi_{O-O} + 2\zeta\gamma_O \quad (A2)$$

with

$$\xi_O = [z \mp (z^2 + q)^{1/2}]/2 + a|\chi_{O-L}|^2/4. \quad (A3)$$

$\gamma_O$  is the direction cosine of  $\mathbf{K}_O$  with respect to the downward crystal surface normal,  $\hat{\mathbf{n}}$ . In (A3), the approximation of small imaginary part has been employed. The parameters  $z$  and  $q$  are defined as

$$z = \chi_{O-O} + (\Delta\theta) \sin 2\theta_G - \frac{1}{4}a'|\chi_{G-L}|^2 - \frac{1}{4}a|\chi_{O-L}|^2 \quad (A4)$$

$$q = -\chi_{G,L}\chi_{L,G}, \quad (A5)$$

where  $\chi_{G,L}$  is the effective electric susceptibility near the exact three-beam point, defined as

$$\chi_{G,L} = p\chi_{G-O} - (a_0/2)\chi_{L-O}\chi_{G-L}. \quad (A6)$$

The terms  $a$ ,  $a'$  and  $a_0$  are inversely proportional to the resonance failure  $\xi_O$ .  $p$  is a polarization factor. Since  $G$  is a symmetric Bragg reflection and multiple diffraction takes place at the peak position in the range of total reflection, it is justified to assume that  $|q| > |z^2|$ . Thus, with approximation,  $\xi_O$  can be written as

$$\xi_O = (z - i|q|^{1/2}) + a|\chi_{O-L}|^2/4. \quad (A7)$$

Note that the plus and minus signs in (A3) are referred to the two possible modes of propagation. In the two-beam approximation for three-beam diffraction, only the mode with the minus sign is effective for very thick crystals. This fact has been taken care of in (A7).

With a few steps of manipulation, the accommodation  $k\zeta$  takes the form

$$2k\zeta = k[(\Delta\varphi) \sin 2\theta_G + S - i|q|^{1/2}]/\gamma_O, \quad (A8)$$

where

$$S = (a/4)|\chi_{O-L}|^2 - (a'/4)|\chi_{G-L}|^2. \quad (A9)$$

By substituting (A8) into (A1), we obtain the expression

$$\begin{aligned} K^2 - K_L^2 &= k^2(1 + \chi_{G-O}) - K_L^2 \\ &= k^2\chi'_{O-O} + 2W(\Delta\varphi) - G_2(\Delta\theta)\sin 2\theta_G - SG_2 \\ &\quad + i[k\chi''_{O-O} + G_2|q|^{1/2}] \end{aligned} \quad (A10)$$

where

$$G_2 = k(l \cos \alpha - g/2)/\gamma_O. \quad (A11)$$

Following the same procedures in deriving (27), the quantities,  $\Delta\varphi$  and  $\eta_i$  in (27) should now be replaced by

$$\Delta\varphi \rightarrow \Delta\varphi + [k^2\chi'_{O-O} - G_2(\Delta\theta)\sin 2\theta_G - SG_2]/2W \quad (A12)$$

$$\eta_i \rightarrow k^2\chi''_{O-O}/W + G_2|q|^{1/2}/W. \quad (A13)$$

In (A12), the last two terms are small compared with  $k^2\chi'_{O-O}$ . Therefore, (A12) can be simplified as

$$\Delta\varphi \rightarrow \Delta\varphi + k^2\chi'_{O-O}/2W. \quad (A14)$$

With this approximation in mind, the derivation of (26) in the text, where  $\mathbf{D}_L$  is considered as a function independent of  $\Delta\theta$ , is justified.

## APPENDIX B

### Second-order approximation for the diffraction intensity $I$

The expression for the wave field  $\mathbf{D}_G$ , in the second-order approximation, can be obtained by substituting the two-beam  $\mathbf{D}_G$ , given in (4), into the last term of (9):

$$\begin{aligned} \mathbf{D}_G &= B_1 \hat{\mathbf{K}}_G \times \hat{\mathbf{K}}_G \\ &\quad \times [\hat{\mathbf{D}}_O - (B_2 + B'_2) \hat{\mathbf{K}}_L \times (\hat{\mathbf{K}}_L \times \hat{\mathbf{D}}_O)], \end{aligned} \quad (B1)$$

where

$$B'_2 = A_G A_L K^4 \chi_{G-L} \chi_{L-G} D_O. \quad (B2)$$

For a weak primary reflection ( $|\chi_{G-O}|$  is small), the modulus of  $B_2$  is much larger than that of  $B'_2$ . For a strong primary,  $|B'_2|$  is comparable with  $|B_2|$ . The second-order term  $B'_2$  should be included in the wave field calculation.

Following the same consideration on polarization as given in the text, we obtain

$$D_{\sigma G}(\sigma) = -B_1[1 + B_0(B_2 + B'_2)] \quad (B3)$$

$$D_{\pi G}(\sigma) = B_1 B_3 (B_2 + B'_2) \quad (B4)$$

$$D_{\sigma G}(\pi) = B_1(B_2 B_4 + B'_2 B'_4) \quad (B5)$$

$$D_{\pi G}(\pi) = B_1(-\cos 2\theta_G - B_2 B_5 - B'_2 B'_5) \quad (B6)$$

where

$$\begin{aligned} B'_4 &= B_4 + (l/K) \sin \alpha \sin \beta \sin 2\theta_G \\ &\quad \times [(l/K) \sin \alpha \cos \beta \cos \theta_G \\ &\quad - (l/K) \cos \alpha \sin \theta_G - 2 \cos 2\theta_G] \end{aligned} \quad (B7)$$

$$B'_5 = \cos 2\theta_G - B_3 B'_4 / [(l/K) \sin \alpha \sin \beta]^2. \quad (B8)$$

The corresponding intensities  $I_G(\sigma)$ ,  $I_G(\pi)$  and  $I_G$  are

$$\begin{aligned} I_G(\sigma) &= B_1^2 \{1 + 2P_O \cos u \\ &\quad \times [B_0(1 - B_0 B'_2) + 2B'_2 B_3^2] + P_O^2 (B_0^2 + B_3^2) \\ &\quad + B'_2 (B_0^2 + B_3^2) - 2B_0 B'_2\} \end{aligned} \quad (B9)$$

$$\begin{aligned} I_G(\pi) &= B_1^2 \{\cos^2 2\theta_G + 2P_O \cos u \\ &\quad \times [B_5(\cos 2\theta_G - B'_2 B'_5) + B'_2 B_4 B'_4] \\ &\quad + P_O^2 (B_4^2 + B_5^2) + B_2'^2 (B_4'^2 + B_5'^2) \\ &\quad - 2B_2' B_5' \cos 2\theta_G\} \end{aligned} \quad (B10)$$

$$\begin{aligned} I_G &= [I_G(\sigma) + I_G(\pi)]/2 \\ &= B_1^2 (1 + \cos^2 2\theta_G)/2 \\ &\quad + B_1^2 P_O \cos u [B_0(1 - B_0 B'_2) \\ &\quad + B'_2 B_3^2 + B_5(\cos 2\theta_G - B'_2 B'_5) + B'_2 B_4 B'_4] \\ &\quad + B_1^2 \{P_O^2 (B_0^2 + B_3^2 + B_4^2 + B_5^2) \\ &\quad + B_2'^2 (B_0^2 + B_3^2 + B_4'^2 + B_5'^2) \\ &\quad - 2B_2'^2 (B_0 + B_5' \cos 2\theta_G)\}/2. \end{aligned} \quad (B11)$$

By letting  $B'_2$ ,  $B'_4$  and  $B'_5$  equal zero, we find that  $I_G(\sigma)$ ,  $I_G(\pi)$  and  $I_G$  reduce to their first-order expressions, i.e. (17), (20) and (21), respectively.

### References

- CHANG, S. L. (1981). *Appl. Phys.* **A26**, 221-226.  
 CHANG, S. L. (1982a). *Phys. Rev. Lett.* **48**, 163-166.  
 CHANG, S. L. (1982b). *Acta Cryst.* **A38**, 516-521.  
 CHANG, S. L. (1984). *Multiple Diffraction of X-rays in Crystals*. Berlin, Heidelberg, New York, Tokyo: Springer-Verlag.  
 CHANG, S. L. (1987). *Crystallogr. Rev.* **1**, 85-189.  
 CHANG, S. L. & TANG, M. T. (1988). Unpublished.  
 COLE, H., CHAMBERS, F. W. & DUUN, H. M. (1962). *Acta Cryst.* **15**, 138-144.  
 COWLEY, J. M. (1964). *Acta Cryst.* **17**, 33-40.  
 EWALD, P. P. (1917). *Ann. Phys. (Leipzig)*, **54**, 519-597.  
 LAUE, M. VON (1931). *Ergeb. Exakten Naturwiss.* **10**, 133-158.  
 RENNINGER, M. (1937). *Z. Phys.* **106**, 141-176.  
 TANG, M.-T. & CHANG, S.-L. (1988). *Acta Cryst.* **A44**, 1073-1078.