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Three-wave X-ray diffraction: an analysis scheme of the sensitivity in determining triplet phase invariants

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Abstract

A model for analysing the phase sensitivity of the reflection coefficients of a diffracted wave in the case of three-wave X-ray diffraction is proposed. This model considers three-wave diffraction as the interference of the directly excited and the *Umweg*-excited diffracted waves and seems to account properly for the phase sensitivity as well as the behaviour of an involved diffracted wave as a function of the triplet phase invariant, the polarization state of the incident wave and the diffraction geometry. The practical issues for phase determination are also considered.

1. Introduction

X-ray crystal structure analysis is usually based on the data obtained from two-wave diffraction. In this case, the intensity of the diffracted wave is determined solely by the absolute magnitude of the structure factor, which is independent of its phase. Thus, the phase cannot be determined from a single two-wave experiment. This phase problem does not, however, arise for multiple-wave diffraction since the intensity of the diffracted wave depends on both the absolute magnitude and the phases of the structure factors involved. This observation was first reported in the literature by Lipscomb (1949). Since then the problem of obtaining the phase information has been tackled by several investigators (Miyake & Kambe, 1954; Kambe, 1957; Kambe & Miyake, 1954; Hart & Lang, 1961). But no marked progress in the development of a useful method for X-ray diffraction analysis had been achieved. During the past two decades, a number of studies (Collella, 1974; Post, 1977; Chapman *et al.*, 1981; Hoier & Aanestad, 1981; Chang, 1982, 1984, 1998; Hümmer & Billy, 1982, 1986; Juretschke, 1982*a*,*b*; Chang & Valladares, 1985; Juretschke, 1986; Kshevetskiy *et al.*, 1987; Sheludko, 1987; Shen & Colella, 1988; Mo *et al.*, 1988; Chang & Tang, 1988; Hümmer *et al.*, 1989; Stetsko, 1990; Tseng & Chang, 1990; Weckert & Hümmer, 1997; Chang *et al.*, 1998; Shen, 1998; Stetsko & Chang, 1999) have been devoted to the investigation of the effect of X-ray reflection phases on the behaviour of multiple-wave diffraction, and methods for directly measuring the magnitude of the triplet phase invariant have been developed.

Hümmer & Billy (1986) have made possible the physical interpretation of the phase sensitivity of multiple-wave diffraction in terms of the interference of electromagnetic waves inside a crystal using the one-coordinate angular (the azimuthal angle of a given primary reflection) distributions of waves. A more preferable interpretation of phase sensitivity seems to be the approach given by Sheludko (1987), where the two-coordinate (the azimuthal and Bragg angles of a given primary reflection) angular distributions of phases of all the waves excited in the multiple-wave diffraction are considered. Very recently, Weckert & Hümmer (1997) and Chang (1998) have reviewed the current status of the problem under consideration. The purpose of the present contribution is to discuss some general features of phase sensitivity of three-wave diffraction and, of equal importance, to derive the diffraction conditions under which high phase sensitivity, for the accurate determination of the values of triplet phase invariants, can be achieved.

2. The triplet phase invariant

The problem of finding the amplitudes of diffracted waves is known to have no analytical solution for a general case of three-wave dynamic X-ray diffraction. Therefore, to illustrate the proposed technique for analysing the phase sensitivity of the three-wave diffraction, numerical calculations need to be employed (see, for example, Kohn, 1979; Stetsko & Chang, 1997). In fact, when considering the phase sensitivity, the proper presentation of a triplet phase invariant value in the numerical calculations is nontrivial. In the following, we discuss this in some detail.

The structure factor of a reflection H with the diffraction vector $\mathbf{H}$ is

$$F_H = \sum_j f_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) = |F_H| \exp(i\Phi_H), \qquad (1)$$

where f_j is the atomic scattering factor for the jth atom of the unit cell, $\mathbf{r}_j$ is the position vector of this atom with respect to an arbitrary origin, and Φ_H is the phase of the structure factor. In real space, the loci of equal phase Φ_H are the phase planes normal to the diffraction vector $\mathbf{H}$. These planes for $\Phi_H = 0$ are designated as P_H; see Fig. 1. They make up a set of equiphase planes, which are known to be fixed with respect to the structure. The corresponding interplane spacing is given by $d_H = |\mathbf{H}|^{-1}$. It follows from (1) that

$$\Phi_H = 2\pi\delta_H/d_H, \tag{2}$$

where δ_H is the distance from the origin to the P_H plane. Similarly, the phase planes for Φ_{-H} of the structure factor $F_{-H} = 0$ are designated as P_{-H}.

Consider three-wave $(0, H, K)$ diffraction where H is the primary reflection, K is the secondary reflection and L is the coupling reflection, with diffraction vectors $\mathbf{H}$, $\mathbf{K}$ and $\mathbf{L} = \mathbf{H} - \mathbf{K}$, respectively. It is known that the product of the structure factors, $\prod_m F_{H_m}$, is independent of the choice of the origin if $\sum_m \mathbf{H}_m = 0$. This is indeed true for the three-wave case. For the crystallographic planes in question, the value of the phase sum

$$\Phi_3 = \Phi_{-H} + \Phi_K + \Phi_L \tag{3}$$

is also independent of the coordinate system, *i.e.* Φ_3 is the triplet phase invariant. In numerical terms, the triplet phase invariant is given by

$$\Phi_3 = 2\pi(-\delta_{-H}/d_H + \delta_K/d_K + \delta_L/d_L), \tag{4}$$

where δ_{-H} is the distance from the origin to the P_{-H} plane. The values associated with the reflections K and L are determined in a similar way. Similarly,

$$\Phi_3^* = \Phi_H + \Phi_{-K} + \Phi_{-L} \tag{5}$$

is also a triplet phase invariant. For a nonabsorbing crystal, $\Phi_3^* = -\Phi_3$, whereas for an absorbing crystal in the case of diffraction rather far from the absorption edges, this equality is accurate to within several degrees of arc. In this paper, we deal only with this conventional multiple-wave X-ray diffraction situation when the anomalous-scattering effects are negligibly small.

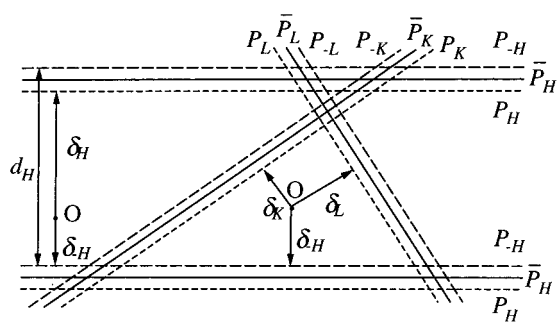

Fig. 1. Representation of the phase planes in the straight space.

For numerical studies of multiple-wave diffraction in an absorbing crystal, it is convenient to take advantage of the modified-phase concept proposed earlier by the present authors (see Stetsko & Chang, 1999). When the anomalous-scattering effects are negligibly small, there exists a coordinate system in which $F_H \simeq F_{-H} \equiv \bar{F}_H$. The structure factor in an arbitrary coordinate system can be represented as $F_H = \bar{F}_H \exp(i\bar{\Phi}_H)$, where $\bar{\Phi}_H$ is the modified phase. In Fig. 1, the planes for which $\bar{\Phi}_H = 0$ are designated as $\bar{P}_H$. In terms of (2), $\bar{\Phi}_H$ is proportional to the distance from the origin to the $\bar{P}_H$ plane. For a non-absorbing crystal, $\bar{\Phi}_H = \Phi_H$, $\bar{F}_H$ is a real value and the phase planes P_H, P_{-H} and $\bar{P}_H$ coincide with one another, while, for an absorbing crystal, $\bar{\Phi}_H$ differs from Φ_H by several degrees of arc. $\bar{F}_H$ is a complex quantity, the imaginary part of which is responsible for X-ray absorption, and the planes P_H and P_{-H} are at equal distances from the plane $\bar{P}_H$. This situation is shown in Fig. 1. Under such a definition of a phase, $\bar{\Phi}_{-H} = -\bar{\Phi}_H$, and, for modified triplet phase invariants $\bar{\Phi}_3 = \bar{\Phi}_{-H} + \bar{\Phi}_K + \bar{\Phi}_L$ and $\bar{\Phi}_3^* = \bar{\Phi}_H + \bar{\Phi}_{-K} + \bar{\Phi}_{-L}$, the condition $\bar{\Phi}_3^* = -\bar{\Phi}_3$ is fulfilled regardless of the absorption. For consistency, in what follows we shall use the triplet phase invariant $\bar{\Phi}_3$.

In the present paper, the numerical study of the phase sensitivity of three-wave diffraction was carried out by varying the value of $\bar{\Phi}_3$ for a crystal of known structure, while leaving the values of $\bar{F}_H$, $\bar{F}_K$ and $\bar{F}_L$ unchanged. Such a variation of $\bar{\Phi}_3$ results in a change in the relative position of one of the sets of equiphase planes (for example, $\bar{P}_H$) with respect to the other two sets ($\bar{P}_K$ and $\bar{P}_L$). This, in turn, results in a hypothetical modification in the crystal structure.

The magnitude and the imaginary part of the modified structure factor $\bar{F}_H$ can, in principle, be determined from the intensity of two-wave X-ray reflection by using the width and the asymmetry of the reflection curve. Certainly, these values can be determined with high accuracy for 'rather perfect' crystals (for real crystals, the determination of the real and the imaginary parts of $\bar{F}_H$ from the intensity of two-wave X-ray reflection is difficult). Thus, the respective positions of phase planes P_H, P_{-H} and $\bar{P}_H$ for nearly perfect crystals can be determined. By the same token, the value of the triplet phase invariant $\bar{\Phi}_3$, and thus the respective positions of phase planes $\bar{P}_H$, $\bar{P}_K$ and $\bar{P}_L$, can be determined from the intensity of a three-wave X-ray reflection. Note that no structure-factor modulus is assumed to be equal or close enough to zero; otherwise, the value of the triplet phase invariant is indeterminate.

3. The analysis scheme of the phase sensitivity

The phase sensitivity of using three-wave diffraction for determining the triplet phase invariant is analysed for the three-wave configuration Ge[0(000), H(111), K(220)] and linearly σ-polarized Cu

$K\alpha_1$ radiation. The polarization vectors for the primary reflection $H(111)$ are introduced as a convention: $\boldsymbol{\sigma} \equiv \boldsymbol{\sigma}_0 \equiv \boldsymbol{\sigma}_H = [\mathbf{s}_0 \times \mathbf{s}_H]/|[\mathbf{s}_0 \times \mathbf{s}_H]|$, $\boldsymbol{\pi}_0 = [\boldsymbol{\sigma} \times \mathbf{s}_0]$, $\boldsymbol{\pi}_H = [\boldsymbol{\sigma} \times \mathbf{s}_H]$, where $\mathbf{s}_0$ and $\mathbf{s}_H$ are the unit vectors of the incident and the diffracted waves, respectively. In the present case, $H(111)$ is a symmetrical Bragg primary reflection and $K(220)$ is a Bragg-type secondary reflection. When considering the distribution of reflection coefficients of the diffracted waves, the incident wave is assumed to deviate from the exact three-wave diffraction position in the Bragg and azimuthal directions by angles $\Delta\theta_H$ and $\Delta\varphi_H$, respectively. The directions of the $O_{\Delta\theta_H}$ and $O_{\Delta\varphi_H}$ axes are chosen so that the positive deviations correspond to a situation where the primary H and the secondary K reciprocal-lattice points move towards the Ewald sphere.

The aforementioned outline of the analysis of phase sensitivity for conventional three-wave diffraction is in many respects similar to that proposed by the present authors (Stetsko & Chang, 1999) for grazing-beam diffraction. However, in view of some specific features, the three-wave diffraction process needs to be discussed in detail. The essence of the proposed three-wave reflection model is that the intensity of a diffracted wave is represented as a result of the interference of the waves, of which one is due to the direct two-wave reflection, while the other is due to an *Umweganregung* of the same primary reflection. These two waves can be considered separately by assuming either that both the secondary reflection K and the coupling reflection L are forbidden reflections or that the primary reflection H is a forbidden reflection. As a first approximation, the amplitude E_H^s of a diffracted wave H can be treated as the addition of the amplitudes $E_{\rm dir}^s$ and $E_{\rm um}^s$ of a directly excited and an *Umweg*-excited wave:

$$E_H^s = E_{\rm dir}^s + E_{\rm um}^s, \tag{6}$$

where the superscripts $s = \sigma,\ \pi$ refer to the two components of polarization with respect to the H reflection.

For a common case of three-wave diffraction, it is impossible to separate the orthogonally polarized components involved in the interference. However, when considering the interference of the directly excited and the *Umweg*-excited waves, only the same polarized components have to be taken into account. For σ polarization, the reflection coefficient can be represented as

$$\begin{aligned} R_H^\sigma &= |E_{\rm dir}^\sigma \sigma + E_{\rm um}^\sigma \sigma + E_{\rm um}^\pi \pi_H|^2/|E^\sigma|^2 \\ &= (|E_{\rm dir}^\sigma + E_{\rm um}^\sigma|^2 + |E_{um}^\pi|^2)/|E^\sigma|^2, \end{aligned} \tag{7}$$

where E^σ is the amplitude of the incident wave. It can be seen that the π component of the *Umweg*-excited wave does not participate in the interference, giving only an additive contribution to the reflection coefficient.

3.1. *Two-wave diffraction*

Consider a case where the secondary and the coupling reflections are forbidden, *i.e.* only a two-wave diffraction $(0, H)$ takes place. The amplitude of a diffracted wave in the two-wave case is known to be proportional to the structure factor F_H and the polarization factor P_H^s ($P_H^\sigma = 1$ and $P_H^\pi = \cos 2\theta_H$, where θ_H is the diffraction angle). Moreover, the amplitude is appreciably dependent on the angle $\Delta\theta_H$ and independent of or weakly dependent on the azimuthal angle $\Delta\varphi_H$. The strong dependence of the amplitude on the azimuthal angle only happens for grazing-beam diffraction geometry. The amplitude of a diffracted wave for the present case can be represented as

$$E_{\rm dir}^s(\Delta\varphi_H, \Delta\theta_H) = E^s P_H^s A_H^s(\Delta\theta_H) F_H, \tag{8a}$$

where E^s is the amplitude of the incident wave in vacuum and $A_H^s(\Delta\theta_H)$ is the fraction of the amplitude of the diffracted wave, depending on the Bragg angle θ_H, the structure-factor product $F_H F_{-H}$, the square of the polarization factor and the deviated angle $\Delta\theta_H$. In particular, the amplitude of a diffracted wave for the symmetrical Bragg case for a semi-infinite crystal is represented as

$$\begin{aligned} &E_{\rm dir}^s(\Delta\varphi_H, \Delta\theta_H) \\ &\quad = -E^s P_H^s \chi_H/[\Delta\theta_H \sin(2\theta_H) + {\rm Im}(\chi_0) + g], \end{aligned} \tag{8b}$$

where

$$g = \pm\{[\Delta\theta_H \sin(2\theta_H) + {\rm Im}(\chi_0)]^2 - (P_H^s)^2 \chi_H \chi_{-H}\}^{1/2}$$

with ${\rm Im}(g) < 0$. The quantities $\chi_i = -r_e \lambda^2 F_i/(\pi V)$ are the Fourier components of the crystal polarizability, r_e is the classical radius of the electron, λ is the incident X-ray wavelength and V is the unit-cell volume. The phase of this wave is given by

$$\Psi_{\rm dir}^s = \Psi_0^s + \Delta_{\rm dir}^s + \Phi_H, \tag{9}$$

where Ψ_0^s is the phase of the incident wave and $\Delta_{\rm dir}^s$ is the phase of the diffracted wave, depending on the incident angle and the polarization. The term $\Delta_{\rm dir}^s$ stands for the 'diffraction' phase shift and Φ_H for the 'structural' phase shift. The $\Delta_{\rm dir}^s$ value can be represented as

$$\Delta_{\rm dir}^s(\Delta\varphi_H, \Delta\theta_H) = Y^s(\Delta\theta_H) + \Lambda_H^s, \tag{10}$$

where

$$\Lambda_H^s = \begin{cases} 0 & \text{if} \quad P_H^s > 0 \\ -\pi & \text{if} \quad P_H^s < 0 \end{cases} \tag{11}$$

and $Y^s(\Delta\theta_H)$ describes the phase shift of the diffracted wave when the reciprocal-lattice point H moves across the surface of the Ewald sphere. Such a motion, or a transition from a positive to a negative $\Delta\theta_H$ angle, is accompanied by an increase of π in the phase of the diffracted wave. It is known that, for a nonabsorbing crystal, the angle width $\delta^s\theta_H$ of the total reflection region is

$$\delta^s\theta_H = 2|\chi_H P_H^s|/\sin(2\theta_H). \quad (12)$$

Changing the incident angle by crossing this reflection region causes a phase increase of π of the diffracted wave. As can be seen from (11), Λ_H^σ is always zero for σ polarization because P_H^σ is always positive.

Fig. 2 shows the angular distributions of the reflection coefficient and the phase $\Delta_{\rm dir}^\sigma$ of the diffracted wave. They are given here solely to preserve the completeness of exposition of the phase sensitivity mechanism for later comparison. The line T_H in Fig. 2 corresponds to the case when the lattice point H is on the surface of the Ewald sphere, the area designated as IN_H corresponds to the case when H is inside the Ewald sphere, and OUT_H is for the H lattice point outside the Ewald sphere. For convenience, the Ewald sphere for waves propagating inside a crystal is considered, *i.e.* the sphere with radius equal to $(|1+\chi_0|)^{1/2}/\lambda$. The line T_H is then the loci of the Lorentz points for the H reflection. It is worth noting that, along the T_H ($\Delta\theta_H = 0$) line, $\Delta_{\rm dir}^\sigma = Y^\sigma(\Delta\theta_H) = Y^\pi(\Delta\theta_H) = \pi/2$.

3.2. *Umweganregung three-wave diffraction*

We now assume that the primary reflection H is forbidden and the secondary reflection K and the coupling reflection L are allowed. The approximation that the *Umweg*-excited wave is considered as resulting from the sequential two-wave reflections of the incident wave from two crystallographic planes K and L (see also, for example, Post, 1977; Weckert & Hümmer, 1997; Chang, 1998) is adopted. That is, the K diffracted wave is then considered as the incident wave for the L plane that is scattered back to the H direction. In this case, the amplitude of the *Umweg*-excited wave can be represented as

$$E_{\rm um}^s(\Delta\varphi_H, \Delta\theta_H) = E^s p_{\rm um}^s A_K^s(\Delta\theta_K) F_K A_L^s(\Delta\theta_L) F_L, \quad (13)$$

where $p_{\rm um}^s$ is the polarization factor of the *Umweg*-excited wave, and $A_K^s(\Delta\theta_K)$ and $A_L^s(\Delta\theta_L)$ are the amplitude components dependent on the Bragg angles θ_K and θ_L, the structure-factor products $F_K F_{-K}$ and $F_L F_{-L}$, the squares of the polarization factors and the angles $\Delta\theta_K$ and $\Delta\theta_L$ deviated from the Bragg angles of the reflections K and L, respectively. The details of the angular distribution of $E_{\rm um}^s$ (more exactly, the reflection coefficient $|E_{\rm um}^s|^2$) and the comparison with that calculated within the framework of the dynamical theory will be discussed later.

Since the resultant polarization factor of the *Umweg*-excited wave exhibits rather complex dependence on the polarization factors of the individual reflections involved, it has been included in (13) as a whole. The magnitude of the polarization factor and its sign (the latter being even more important) are the determining factors in the analysis of phase sensitivity of three-wave diffraction. Without trying to derive the exact expression for the polarization factor, which is complicated to obtain within the framework of the dynamical theory, we estimate it using the kinematical approximation, *i.e.* in geometrical terms. Suppose that the polarization vector $\mathbf{p}_0$ of the incident wave is arbitrary, such that the electric wavefield $\mathbf{E}$ of the incident wave equals $E\mathbf{p}_0$; $\mathbf{p}_0 = \alpha\boldsymbol{\sigma} + \beta\boldsymbol{\pi}_0$, where α and β ($\alpha^2 + \beta^2 = 1$) are the polarization components in the coordinate system $(\boldsymbol{\sigma}, \boldsymbol{\pi}_0)$. For the σ and π components of the amplitude for the kinematical reflection H, the connection $E_H^\pi = E_H^\sigma \cos 2\theta_H$ can be used when $E^\sigma = E^\pi \equiv E$ (see, for example, Zachariasen, 1965; Caticha-Ellis, 1969; Unangst & Melle, 1975). For the electric wavefield $\mathbf{E}_H$ of the diffracted wave,

$$\begin{aligned}\mathbf{E}_H &= \alpha E_H^\sigma \boldsymbol{\sigma} + \beta E_H^\pi \boldsymbol{\pi}_H \\ &= E_H^\sigma[\alpha\boldsymbol{\sigma} + \beta\cos(2\theta_H)\boldsymbol{\pi}_H] \\ &\equiv E_H^\sigma \mathbf{p}_H, \end{aligned} \quad (14)$$

which implies that the polarization vector $\mathbf{p}_H$ of the diffracted wave is a transverse component of the vector $\mathbf{p}_0$ with respect to the diffracted wave vector $\mathbf{s}_H$:

$$\mathbf{p}_H = \mathbf{p}_0 - (\mathbf{p}_0 \cdot \mathbf{s}_H)\mathbf{s}_H. \quad (15)$$

In the general two-wave case, *i.e.* when the vector $\mathbf{p}_0$ is arbitrary, it is necessary to consider two polarization factors that are the projections of the vector $\mathbf{p}_H$ on the unit polarization vectors $\boldsymbol{\sigma}$ and $\boldsymbol{\pi}_H$ of the diffracted wave:

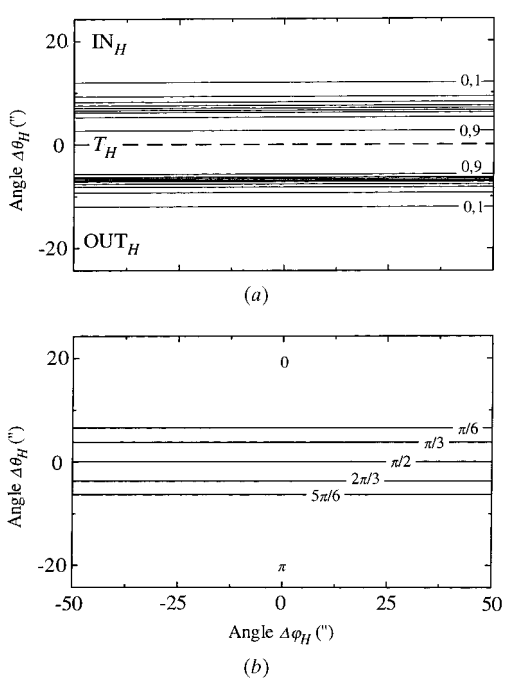

Fig. 2. Two-wave diffraction: (*a*) reflection coefficient $R_H(\Delta\varphi_H, \Delta\theta_H)$ and (*b*) the phase $\Delta_{\rm dir}^\sigma$. Contour levels in (*a*) are from 0.1 to 0.9 with the step 0.1.

$$p_H^{\sigma} = (\mathbf{p}_H \cdot \boldsymbol{\sigma}) = (\mathbf{p}_0 \cdot \boldsymbol{\sigma}) = \alpha P_H^{\sigma}, \tag{16a}$$

$$p_H^{\pi} = (\mathbf{p}_H \cdot \boldsymbol{\pi}_H) = (\mathbf{p}_0 \cdot \boldsymbol{\pi}_H) = \beta P_H^{\pi}. \tag{16b}$$

These general expressions of the polarization factors are in good agreement with those for the conventional cases: for the σ-polarized incident wave ($\mathbf{p}_0 = \boldsymbol{\sigma}$, $\alpha = 1$; $\beta = 0$), $p_H^{\sigma}(\sigma) = P_H^{\sigma} = 1$ and $p_H^{\pi}(\sigma) = 0$; for the π-polarized incident wave ($\mathbf{p}_0 = \boldsymbol{\pi}_0$, $\alpha = 0$; $\beta = 1$), $p_H^{\sigma}(\pi) = 0$ and $p_H^{\pi}(\pi) = P_H^{\pi} = \cos 2\theta_H$.

For the case involving a forbidden primary reflection, the *Umweg*-excited wave is considered, as before, as resulting from the sequential reflections K and L. Applying expression (15) first to the reflection K and then to the reflection L, we obtain

$$\begin{aligned} \mathbf{p}_K &= \mathbf{p}_0 - (\mathbf{p}_0 \cdot \mathbf{s}_K)\mathbf{s}_K \\ \mathbf{p}_{\mathrm{um}} &= \mathbf{p}_K - (\mathbf{p}_K \cdot \mathbf{s}_H)\mathbf{s}_H \\ &= \mathbf{p}_0 - (\mathbf{p}_0 \cdot \mathbf{s}_K)\mathbf{s}_K - (\mathbf{p}_0 \cdot \mathbf{s}_H)\mathbf{s}_H \\ &\quad + (\mathbf{p}_0 \cdot \mathbf{s}_K)(\mathbf{s}_H \cdot \mathbf{s}_K)\mathbf{s}_H, \end{aligned} \tag{17}$$

where $\mathbf{s}_K$ is the unit vector of the diffracted wave K. By analogy with the two-wave case, the polarization factors of the *Umweg*-excited wave are

$$p_{\mathrm{um}}^{\sigma} = (\mathbf{p}_{\mathrm{um}} \cdot \boldsymbol{\sigma}) = (\mathbf{p}_0 \cdot \boldsymbol{\sigma}) - (\mathbf{p}_0 \cdot \mathbf{s}_K)(\mathbf{s}_K \cdot \boldsymbol{\sigma}), \tag{18a}$$

$$p_{\mathrm{um}}^{\pi} = (\mathbf{p}_{\mathrm{um}} \cdot \boldsymbol{\pi}_H) = (\mathbf{p}_0 \cdot \boldsymbol{\pi}_H) - (\mathbf{p}_0 \cdot \mathbf{s}_K)(\mathbf{s}_K \cdot \boldsymbol{\pi}_H). \tag{18b}$$

In particular, these polarization factors are

$$p_{\mathrm{um}}^{\sigma}(\sigma) = 1 - (\boldsymbol{\sigma} \cdot \mathbf{s}_K)^2, \tag{19a}$$

$$p_{\mathrm{um}}^{\pi}(\sigma) = -(\boldsymbol{\sigma} \cdot \mathbf{s}_K)(\boldsymbol{\pi}_H \cdot \mathbf{s}_K), \tag{19b}$$

for a σ-polarized incident wave when $\mathbf{p}_0 = \boldsymbol{\sigma}$, and

$$p_{\mathrm{um}}^{\sigma}(\pi) = -(\boldsymbol{\sigma} \cdot \mathbf{s}_K)(\boldsymbol{\pi}_0 \cdot \mathbf{s}_K), \tag{19c}$$

$$p_{\mathrm{um}}^{\pi}(\pi) = (\boldsymbol{\pi}_0 \cdot \boldsymbol{\pi}_H) - (\boldsymbol{\pi}_0 \cdot \mathbf{s}_K)(\boldsymbol{\pi}_H \cdot \mathbf{s}_K), \tag{19d}$$

for a π-polarized incident wave when $\mathbf{p}_0 = \boldsymbol{\pi}_0$. The analysis of the expressions (19a)–(19d) will be given later. For the case in question, $p_{\mathrm{um}}^{\sigma}(\sigma) = 0.83$, $p_{\mathrm{um}}^{\pi}(\sigma) = -0.08$, $p_{\mathrm{um}}^{\sigma}(\pi) = -0.24$ and $p_{\mathrm{um}}^{\pi}(\pi) = 0.78$.

For obtaining (19a)–(19d), we adopted the expression of the polarization factor from the kinematical theory, which actually differs from that of the dynamical theory. However, this kinematical approach gives us the approximately correct expressions for polarization factors of the *Umweg*-excited wave. Moreover, as will be seen latter, these expressions can be effectively used for qualitative analysis of the phase sensitivity of three-wave diffraction.

In considering the interference of the directly excited and the *Umweg*-excited waves, only the waves of the same polarization must be taken into account. Therefore, we consider the phase only for the σ component of the *Umweg*-excited wave coincident with that of the incident wave. The phase takes the form

$$\Psi_{\mathrm{um}}^{ss} = \Psi_0^s + \Delta_{\mathrm{um}}^{ss} + \Phi_K + \Phi_L, \tag{20}$$

where $\Delta_{\mathrm{um}}^{ss}$ depends only on the incident wavelength and the angles of incidence. Similar to (10), $\Delta_{\mathrm{um}}^{ss}$ is given as

$$\Delta_{\mathrm{um}}^{ss}(\Delta\varphi_H, \Delta\theta_H) = Y^s(\Delta\theta_K) + Y^s(\Delta\theta_L) + \Lambda_{\mathrm{um}}^{ss}, \tag{21}$$

where

$$\Lambda_{\mathrm{um}}^{ss} = \begin{cases} 0 & \text{if} \quad p_{\mathrm{um}}^s(s) > 0 \\ -\pi & \text{if} \quad p_{\mathrm{um}}^s(s) < 0 \end{cases} \tag{22}$$

and $Y^s(\Delta\theta_K)$ and $Y^s(\Delta\theta_L)$, as will be evident from the following discussion, describe the phase shifts of the diffracted wave when the reciprocal-lattice points move across the surface of the Ewald sphere. It can be seen from (19a) and (22) that $\Lambda_{\mathrm{um}}^{\sigma\sigma}$ is always zero for σ polarization.

As we have already mentioned, an analytical expression for the amplitude of the diffracted wave is difficult to obtain for a three-wave case. Alternatively, a numerical analysis of the angular distributions of the reflection coefficient and the phase of the *Umweg*-excited wave may carried out. Fig. 3 shows the angular distributions of the reflection coefficient and the phase $\Delta_{um}^{\sigma\sigma}$ of the σ component of the *Umweg*-excited wave. The value of $p_{\mathrm{um}}^{\sigma}(\sigma)$ is much greater than that of $p_{\mathrm{um}}^{\pi}(\sigma)$ for the case in question. Therefore, the main contribution to the reflection coefficient of the *Umweg*-excited

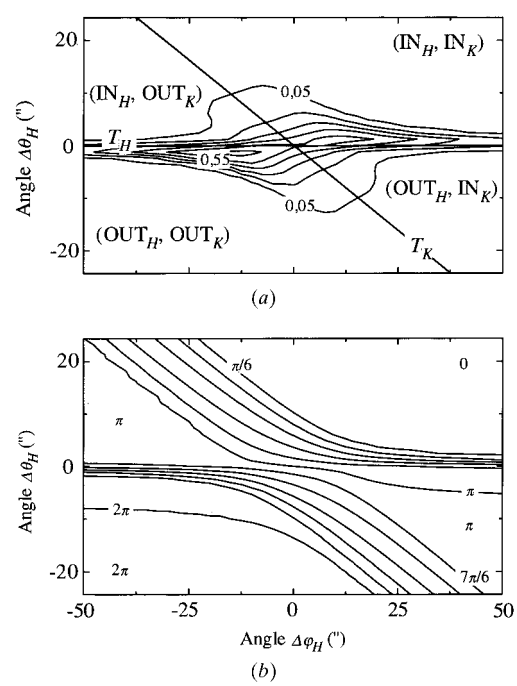

Fig. 3. Three-wave *Umweganregung* diffraction: (*a*) the reflection coefficient $R_H(\Delta\varphi_H, \Delta\theta_H)$ and (*b*) the phase $\Delta_{\mathrm{um}}^{\sigma\sigma}$. Contour levels are from 0.05 to 0.55 with step 0,1 in (*a*) and from $\pi/6$ to 2π with step $\pi/6$ in (*b*).

wave is given by the σ component. The reflection region exhibits three intersecting bands extended along the lines T_H and T_K, which is typical for *Umweganregung*. For the secondary Bragg reflection K, the line T_K in Fig. 3 corresponds to the situation in which the lattice point K is on the surface of the Ewald sphere. The area designated by IN_K corresponds to the case when K is inside the Ewald sphere, and OUT_K is for the K lattice point outside the Ewald sphere. The line T_K is the loci of the Lorentz points for the Bragg reflection K. The intersection of lines T_H and T_K is the three-wave Lorentz point. A characteristic feature of the 'diffraction' component $\Delta^{\sigma\sigma}_{\mathrm{um}}$ of the phase is that crossing the lines T_H or T_K results in a phase change of π, *i.e.* the lines of equal values of the functions $Y^s(\Delta\theta_K)$ and $Y^s(\Delta\theta_L)$ from (21) are oriented in the $(\Delta\varphi_H, \Delta\theta_H)$ plane along one of the lines T_K and T_H. Such features are characteristic for *Umweg*-excited waves. This is explained as follows.

The electric wavefields, $\mathbf{E}$, inside the crystal in the three-wave case are known to satisfy the set of equations (see, for example, Chang, 1984):

$$\begin{aligned} 2\varepsilon_0\mathbf{E}_0 &= \chi_0\mathbf{E}_0 + \chi_{-H}\mathbf{E}_H + \chi_{-K}\mathbf{E}_K,\\ 2\varepsilon_H\mathbf{E}_H &= \chi_H\mathbf{E}_0 + \chi_0\mathbf{E}_H + \chi_L\mathbf{E}_K,\\ 2\varepsilon_K\mathbf{E}_K &= \chi_K\mathbf{E}_0 + \chi_{-L}\mathbf{E}_H + \chi_0\mathbf{E}_K, \end{aligned} \tag{23}$$

where $\varepsilon = (K_j^2 - k^2)/k^2$ $(j \equiv 0; H; K)$, k is the magnitude of the incident wave vector in vacuum and K_j are the magnitudes of the diffracted waves in the crystal. Here, the unknown quantities are the ε_j and the vectors $\mathbf{E}_j$. In the vicinity of the Lorentz point, ε_j values are of the order of χ_i $(i \equiv 0; \pm H; \pm K; \pm L)$. To analyse the angular distributions of the reflection coefficient and the phase of the *Umweg*-excited wave, the two-wave approximation for three-wave diffraction (see, for example, Chang, 1984) is employed. Consider a situation where Bragg's condition is almost satisfied for the H reflection, but not for the K reflection; that is, in the $(\Delta\varphi_H, \Delta\theta_H)$ plane, the situation (*i.e.* the tie point) is close to the T_H line and far from the T_K line. In this case, ε_K is much greater than ε_0 and ε_H in absolute values. The wavefields $\mathbf{E}_0$ and $\mathbf{E}_H$ can be approximated using the two-wave approach. By substituting the wavefield $\mathbf{E}_K$ of the third equation of (23) into the first two equations, we obtain

$$\begin{aligned} 2\varepsilon_0\mathbf{E}_0 &= \chi_0\mathbf{E}_0 + (\chi_{-L}\chi_{-K}/2\varepsilon_K)\mathbf{E}_H,\\ 2\varepsilon_H\mathbf{E}_H &= (\chi_L\chi_K/2\varepsilon_K)\mathbf{E}_0 + \chi_0\mathbf{E}_H. \end{aligned} \tag{24}$$

Here, the following assumptions have been made:

$$2\varepsilon_K - \chi_0 \approx 2\varepsilon_K$$

and

$$\chi_0 + \chi_K\chi_{-K}/2\varepsilon_K \approx \chi_0 + \chi_L\chi_{-L}/2\varepsilon_K \approx \chi_0.$$

It was also assumed that $\chi_H = \chi_{-H} = 0$ for the forbidden primary reflection case considered in this section. Equation (24) is similar to that for the two-wave case, the difference being that it involves $\chi_L\chi_K/2\varepsilon_K$ and $\chi_{-L}\chi_{-K}/2\varepsilon_K$ instead of χ_H and χ_{-H}. Therefore, the solutions of (24) exhibit also the characteristics of two-wave diffraction, *i.e.*, for a fixed ε_K value, the maximum of the reflection coefficient is observed along the line T_H, and the crossing of this line results in a phase change of π. Besides, the reflection coefficient decreases as we move away from the T_K line because of the increase of $|\varepsilon_K|$. On the other hand, ε_K has opposite signs on either side of the T_K line. $\varepsilon_K < 0$ when the lattice point K is inside the Ewald sphere and $\varepsilon_K > 0$ when it is outside the Ewald sphere. According to (24), this means that crossing the T_K line also results in a phase change of π. Thus, for the *Umweg*-excited wave, the motion of the lattice points H and K leaving the Ewald sphere causes a phase change of π.

We have so far considered the Bragg–Bragg case where a primary reflection H and a secondary reflection are of a Bragg type. For a Bragg–Laue case with a Bragg-type primary reflection and a Laue-type (transmission) secondary reflection, it has been shown (Chang, 1978, 1984; Pinsker, 1977) that according to the reciprocity theorem (Born & Wolf, 1970) the corresponding Bragg–Bragg and Bragg–Laue cases [for example, the $0(000), H(111), K(220)$ case and the $0(000), H(111), K(\bar{1}\bar{1}1)$ case, respectively] should have the same reflection coefficient of the primary reflection H. Moreover, the direction of the secondary reflection in the Bragg–Bragg case coincides with the direction of the coupling reflection of the Bragg–Laue case. In the present calculation, the same results are also obtained. Namely, the calculated results of Fig. 3 are repeatedly obtained for the Bragg–Laue case $0(000), H(111), K(\bar{1}\bar{1}1)$, except that the T_K line of the Bragg–Bragg case is now the T_L line of the Bragg–Laue case, and the T_L line now corresponds to the locus of the point K crossing the surface of the Ewald sphere centred at the point H.

In accordance with the above arguments, (21) can be rewritten as

$$\Delta^{ss}_{\mathrm{um}}(\Delta\varphi_H, \Delta\theta_H) = Y^s(\Delta\theta_K) + \bar{Y}^s(\Delta\theta_H) + \Lambda^{ss}_{\mathrm{um}}, \tag{25}$$

where $Y^s(\Delta\theta_K)$ and $\bar{Y}^s(\Delta\theta_H)$ describe the increase of the phase of π when the lattice points K and H move outside the Ewald sphere. The function $\bar{Y}^s(\Delta\theta_H)$ is not identical to $Y^s(\Delta\theta_H)$, because the expression of the angular width $\bar{\delta}^s\theta_H$ of the total reflection region derived from (24),

$$\bar{\delta}^s\theta_H = |\chi_L\chi_K P^s_H| / \sin(2\theta_H)|\varepsilon_K|, \tag{26}$$

is not the same as (12). As the situation (*i.e.* the tie point) moves from the three-wave Lorentz point along the T_H line, $\bar{\delta}^s\theta_H \to 0$ because of the increase of $|\varepsilon_K|$.

However, $\bar{Y}^s(\Delta\theta_H)$, as before, approaches $\pi/2$ along the T_H line.

3.3. *Interference of waves*

The interference of waves relies on the difference in the phase of the waves involved. In view of (9) and (20), the difference in phases between an *Umweg*-excited and a directly excited wave is given as

$$\begin{aligned}\Psi^s &= \Psi^{ss}_{\rm um} - \Psi^s_{\rm dir} \\ &= \Delta^{ss}_{\rm um} - \Delta^s_{\rm dir} + \Phi_K + \Phi_L - \Phi_H \\ &= \Delta^{ss}_{\rm um} - \Delta^s_{\rm dir} + \bar{\Phi}_3. \end{aligned} \tag{27}$$

The last equality holds exactly for nonabsorbing crystals. $\Delta^{ss}_{\rm um} - \Delta^{ss}_{\rm dir}$ represents a 'diffraction' phase difference and $\bar{\Phi}_3$ a 'structural' phase difference between an *Umweg*-excited and a directly excited wave. The difference in the phase is therefore directly related to the triplet phase invariant.

The 'diffraction' phase difference, according to (10) and (25), is given as

$$\begin{aligned}\Delta^s &= \Delta^{ss}_{\rm um} - \Delta^s_{\rm dir} \\ &= Y^s(\Delta\theta_K) + \bar{Y}^s(\Delta\theta_H) - Y^s(\Delta\theta_H) + \Lambda^s_3, \end{aligned} \tag{28}$$

where

$$\Lambda^s_3 = \Lambda^{ss}_{\rm um} - \Lambda^s_H. \tag{29}$$

As follows from (11), (19*a*) and (22), for σ polarization, $\Lambda^s_3 = 0$. The behaviour of Δ^s is qualitatively rather well described by the expression

$$\Delta^s = \Delta^{ss}_{\rm um} - \Delta^s_{\rm dir} = Y^s(\Delta\theta_K) + \Lambda^s_3 \tag{30}$$

in the vicinity of the T_H line as well as far from it because $\bar{Y}^s(\Delta\theta_H) \cong Y^s(\Delta\theta_H)$. Fig. 4 gives the angular distributions of Δ^σ, which are in good agreement with this statement.

The Δ^σ distribution thus obtained, in principle, gives a qualitative account of the phase dependence of the distribution of the reflection coefficients of the diffracted wave. This can be proved by analysing the interference of the directly excited and the *Umweg*-excited waves, taking into account the Δ^σ distribution and the magnitude of the triplet phase invariant.

We now compare the qualitative results with those obtained from the calculations for the reflection coefficients $R_H(\Delta\varphi_H, \Delta\theta_H)$ and the semi-integral curves $R_H(\Delta\varphi_H) = \int R_H(\Delta\varphi_H, \Delta\theta_H)\,\mathrm{d}\Delta\theta_H$ of a diffracted wave with the triplet phase invariant values $\bar{\Phi}_3 = -\pi/2;\ 0;\ \pi/2;\ \pi$ (Figs. 5 and 6). In Fig. 6, the semi-

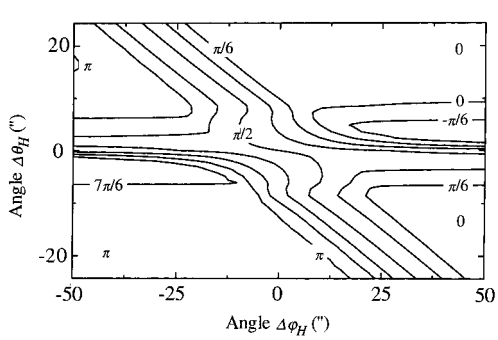

Fig. 4. Angular distributions of Δ^σ. Contour levels are from $-\pi/6$ to $7\pi/6$ with step $\pi/6$.

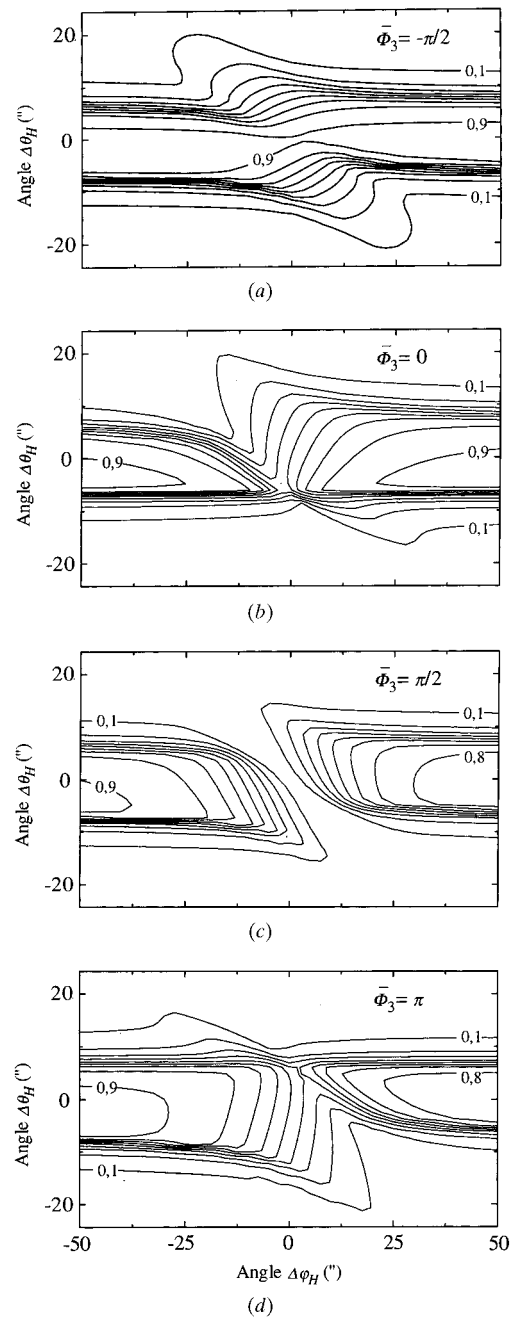

Fig. 5. Three-wave diffraction. Reflection coefficient $R_H(\Delta\varphi_H, \Delta\theta_H)$ for $\bar{\Phi}_3 = -\pi/2;\ 0;\ \pi/2;\ \pi$. Contour levels are from 0.1 to 0.9 with step 0.1.

integral curves are normalized to the two-wave value of the corresponding reflection.

For the phase invariant $\bar{\Phi}_3 = 0$, the interference-induced amplification and attenuation of waves occurs on the opposite sides [IN_K and OUT_K in Fig. 3(*a*)] of the T_K line in the vicinity of the T_H line. The amplification and attenuation is observed as the intensity variation of the directly excited wave, since this intensity is higher than that of an *Umweg*-excited wave (see Figs. 2*a* and 3*a*). For $\Delta\varphi_H < 0$, according to (27) and (30), the phase difference Ψ^σ of the waves is close to π and the attenuation in intensity occurs [see Fig. 5(*b*) and curve 2 of Fig. 6]. For $\Delta\varphi_H > 0$, Ψ^σ is close to zero and the amplification in intensity takes place. A change of π in the value of the triplet phase invariant reverses the order of appearance of the regions of amplification and attenuation [see Fig. 5(*d*) and curve 4 of Fig. 6].

Since, for the phase invariant equal to $-\pi/2$, Ψ^σ is close to zero in the vicinity of the line T_K, the amplification in intensity occurs [see Fig. 5(*a*) and curve 1 of Fig. 6]. For a triplet phase invariant $\pi/2$, the situation is reversed, *i.e.* Ψ^σ is close to π and the attenuation in intensity takes place [see Fig. 5(*c*) and curve 3 of Fig. 6]. The distributions of the reflection coefficients of a diffracted wave for intermediate values of the triplet phase invariant can be interpreted in a similar way.

Fig. 7 shows the semi-integrated reflection coefficient $R_H(\Delta\varphi_H, \bar{\Phi}_3) = \int R_H(\Delta\varphi_H, \bar{\Phi}_3, \Delta\theta_H)\,\mathrm{d}\Delta\theta_H$ obtained with a continuously varying triplet phase invariant $\bar{\Phi}_3$. It can be seen that the profile of the three-wave peak of a diffracted wave is a single-valued and continuous function of the triplet phase invariant.

We note that, in the vicinity of the three-wave Lorentz point, some quantitative disagreement between the calculated reflection coefficients and those obtained using the above model exists. This is because the present model does not take into account the actual energy transfer from the wave H to the wave K, resulting in a general decrease in the reflection coefficients in the vicinity of the Lorentz point. Apparently, instead of using directly excited two-wave diffraction, a more fruitful and exact approach to the analysis of phase sensitivity would be to utilize directly excited three-wave diffraction with either K or L as a forbidden reflection. Under these circumstances, the directly excited waves will then be designated as wave I with the forbidden K diffraction and wave II with the forbidden L diffraction. The energy outflow from the wave H into the wave K is through the *Umweg* process for the former case and the direct excitation for the latter case. This causes the decrease of the reflection coefficient of the directly excited wave H near the Lorentz point. The above features are easily observed from the semi-integral curves. For example, Fig. 8 shows two three-wave semi-integral curves, 1 and 2, for the intensity distributions of waves I and II, respectively. For comparison, a straight line, 3, calculated for the two-wave diffraction H is also given. It can be easily seen that, in comparison with the proposed scheme, the distribution $R_H(\Delta\varphi_H)$ calculated for $\bar{\Phi}_3 = \pi/2$ (curve 4) is more exactly associated with the interference attenuation of the *Umweg*-excited wave (curve 6) and of one of the waves I or II. For $\bar{\Phi}_3 = -\pi/2$, the distribution $R_H(\Delta\varphi_H)$ (curve 5) is associated with the interference amplification of these waves. For a more detailed description of phase

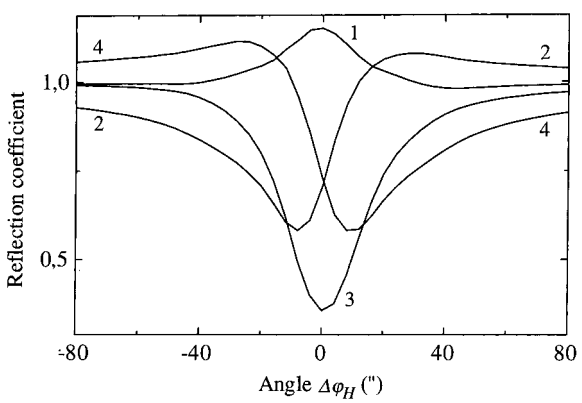

Fig. 6. Semi-integral curves 1–4 for $R_H(\Delta\varphi_H) = -\pi/2; 0; \pi/2; \pi$, respectively.

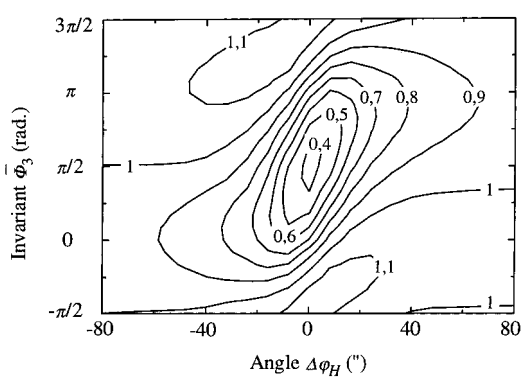

Fig. 7. Semi-integral reflection coefficient $R_H(\Delta\varphi_H, \bar{\Phi}_3)$.

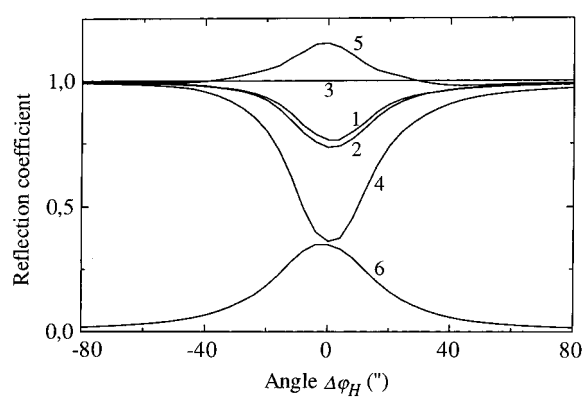

Fig. 8. Semi-integral curves $R_H(\Delta\varphi_H)$.

sensitivity, it is difficult to give preference to either of the waves I or II. Probably, in this case it is necessary to consider a more complex scheme for the interaction of the waves involved.

The purpose of making the aforementioned remarks is to indicate possibilities for further more detailed studies of the interference of the waves in three-wave diffraction. We believe, however, that the simple scheme proposed here accounts rather well for the phase sensitivity of three-wave diffraction and can be used to develop an experimental technique for determining the magnitude of the triplet phase invariant.

4. A technique for direct determination of the triplet phase invariant

The technique for the determination of a triplet phase invariant is reduced to the measurement of the three-wave peak profile $I_{\rm exp}(\Delta\varphi_H)$ and its comparison with those $I_{\rm calc}(\bar{\Phi}_3, \Delta\varphi_H)$ calculated for various phase invariant values. A proper check for the correctness of the resulting triplet phase invariant could be a minimum value of the parameter

$$P(\bar{\Phi}_3, \Delta\varphi) = \int [I_{\rm exp}(\Delta\varphi_H) - I_{\rm calc}(\bar{\Phi}_3, \Delta\varphi_H + \Delta\varphi)]^2 \, {\rm d}\Delta\varphi_H. \quad (31)$$

The calculations are made by assuming that the structure factors of the reflections $\bar{F}_H$, $\bar{F}_K$ and $\bar{F}_L$ are known from the measured two-wave reflection intensities. Evidently, to determine the $\bar{\Phi}_3$ value to a high degree of accuracy, one must take into account the actual spectral and angular characteristics of the incident X-ray beam. The above-described approach has been realized by Kshevetskiy *et al.* (1987). Certainly, this technique can be used with high accuracy for 'rather perfect' crystals.

For a centrosymmetric structure, the value of the triplet phase invariant can be determined in a simpler way. One of the two possible values, $\bar{\Phi}_3 = 0$ or π, is determined from the asymmetry of the three-wave peak, *i.e.* from the order of appearance of the local minimum and maximum (Weckert & Hümmer, 1997; Chang, 1998, and references therein). Note that the results obtained here refer to the case in which the increase of an azimuthal angle corresponds to the exit of a secondary lattice point K from the Ewald sphere. As follows from (27)–(29), for a fixed value of the triplet phase invariant, the order of appearance of the interference-induced amplification and attenuation regions for σ-polarized incident radiation is dependent on the position of the K lattice point with respect to the Ewald sphere, rather than on the three-wave diffraction geometry, *i.e.* it is independent of the diffraction vectors **H** and **K** of a particular configuration. In particular, when the lattice point K moves outside the Ewald sphere for σ polarization and $\bar{\Phi}_3 = 0$, the attenuation region will follow the amplification region.

For a correct comparison of the measured three-wave peak profile and the calculated profiles, it is necessary to establish whether the lattice point K enters or leaves the Ewald sphere for the selected direction of azimuthal scanning. On the one hand, the choice of a direction of azimuthal scanning is rather arbitrary. On the other hand, it is well known that a multiple-wave diffractogram exhibits two peaks associated with a particular multiple-wave configuration which have mutually inversed profile asymmetry. It is useful to view Fig. 9 (see also Chang, 1984) in which the multiple-wave diffraction geometry in the reciprocal space is illustrated. The plane of the figure is normal to the diffraction vector **H**, *i.e.* the reciprocal-lattice points 0 and H coincide with each other. The Ewald sphere S in Fig. 9 is fixed, while the secondary lattice points K_i describe circles p_i as a result of the crystal rotation about the diffraction vector **H**. The circles of intersection of the Ewald sphere with the planes of circles p_i are designated as s_i, and the intersections of the circles s_i and p_i are designated as $K_i^{(1)}$ and $K_i^{(2)}$. The arcs of the circles p_i with the ends $K_i^{(1)}$ and $K_i^{(2)}$, for the lattice point K_i being inside and outside the Ewald sphere, are designated as IN_i and OUT_i, respectively. Fig. 9 illustrates two different cases: the case $i = 1$, when the length of the arc IN_1 is shorter than that of the arc OUT_1, and the corresponding azimuthal angle $\varphi_1 < \pi$, and the case $i = 2$, when the length of the arc OUT_2 is shorter than that of the arc IN_2, and the angle $\varphi_1 > \pi$. It can be easily seen that, for the case $i = 1$, the angle between the vectors $\mathbf{L}_i$ and $\mathbf{K}_i$ is acute and the condition

$$C_i = \mathbf{H} \cdot \mathbf{K}_i - \mathbf{K}_i^2 > 0 \quad (32)$$

is satisfied, while, for the case $i = 2$, this angle is obtuse and $C_i < 0$.

It is then possible to determine experimentally the direction of movement of the lattice point K_i traversing

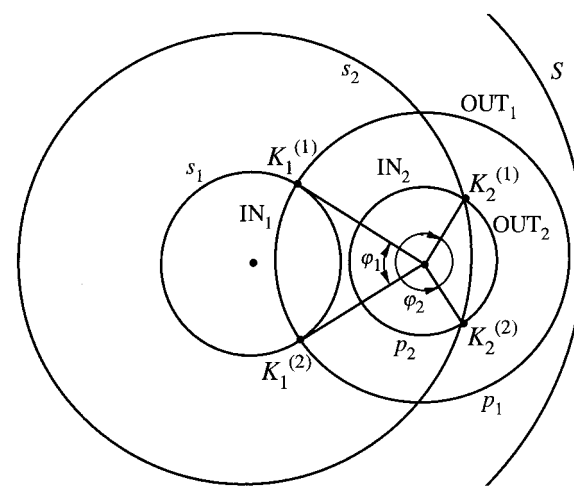

Fig. 9. Multiple-wave diffraction geometry in reciprocal space.

the Ewald sphere. For this, we first determine from the multiple-wave diffractogram the two angular positions, $K_i^{(1)}$ and $K_i^{(2)}$, of the peaks associated with the three-wave configuration under consideration. If a section of the diffractogram located between these peaks corresponds to the azimuthal angle $\varphi_i < \pi$ and the condition $C_i > 0$ is satisfied, this section is in the IN_i region; otherwise, when $C_i < 0$, it is in the OUT_i region. The direction of further movement of the lattice point K_i with respect to the Ewald sphere for each of the peaks under consideration can be determined from the diffractogram without difficulty.

5. Polarization and phase sensitivity

We now analyse the polarization factors given in (19*a*)–(19*d*) for the *Umweg*-excited wave. This will enable us to reveal the phase sensitivity of three-wave diffraction for different incident-wave polarizations.

As was noted in §3.3, for σ polarization, $\Lambda_3^\sigma = 0$. For π polarization, Λ_3^π can assume values 0 or $\pi \pmod{2\pi}$, depending on whether the $p_{\mathrm{um}}^\pi(\pi)$ and P_H^π have the same signs. It follows from (29) that, for σ and π polarizations, the angular distributions of Δ^σ and Δ^π qualitatively coincide with each other for $\Lambda_3^\pi = 0$ and differ by π for $\Lambda_3^\pi = \pi$. Within the model under consideration, this means that, for the two polarizations in the former case, the regions of amplification and attenuation appear in the same order, while, in the latter case, these regions appear in the reverse order (Juretschke, 1986; Weckert & Hümmer, 1997; Chang, 1998, and references therein). This observation is supported by the numerical calculations. In particular, Fig. 10 gives the calculated profiles of semi-integral curves for the three-wave configuration Ge(000, 331, $\bar{3}11$) and Cu $K\alpha_1$ radiation, where $\Lambda_3^\pi = \pi$. The peak profiles calculated for the two polarizations have mutually inversed asymmetry (curve 3 compared with curve 1 for $\bar{\Phi}_3 = 0$ and curve 4 compared with curve 2 for $\bar{\Phi}_3 = \pi$).

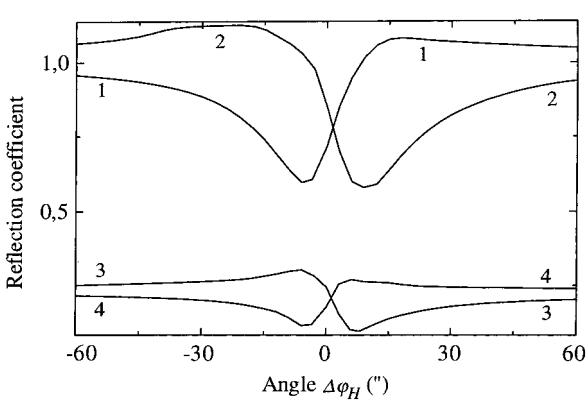

Fig. 10. Three-wave diffraction (000, 331, $\bar{3}11$). Semi-integral curves $R_H(\Delta\varphi_H)$: 1 ($\bar{\Phi}_3 = 0$), 2 ($\bar{\Phi}_3 = \pi$) for σ-polarized incident radiation, and 3 ($\bar{\Phi}_3 = 0$), 4 ($\bar{\Phi}_3 = \pi$) for π-polarized incident radiation. Values are given in units of $R_H(\Delta\varphi_H)$ for the two-wave case for σ-polarized incident radiation.

Using expression (19*b*), we have identified the regions of the Ewald sphere for which $\Lambda_3^\pi = 0$ and $\Lambda_3^\pi = \pi$. Fig. 11 shows the projection of these regions onto the primary two-wave diffraction plane. The regions corresponding to $\Lambda_3^\pi = \pi$ are shaded. The boundaries of these regions are the branches of the hyperbola with the asymptotes coincident with the lines of the vectors $\mathbf{s}_0$ and $\mathbf{s}_H$. As can be seen, the area of the shaded regions is smaller than that of the non-shaded regions. It is then concluded that the mutually inversed asymmetry of peak profiles for the two polarizations is encountered less often than the identical asymmetry. As the diffraction angle of the primary reflection approaches $\pi/4$, the area of the shaded regions increases to up to half of the Ewald sphere.

The conditions of mutually inversed asymmetry of peak profiles for the two polarizations proposed in the present paper based on the signs of the polarization factors of the directly excited and the *Umweg*-excited waves are the same as the conditions proposed by Juretschke (1986), derived from the two-wave approximation. Weckert & Hümmer (1997) also indicated the above conditions, which are necessary but not sufficient for the appearance of this inversed asymmetry. In particular, for the three-wave configuration

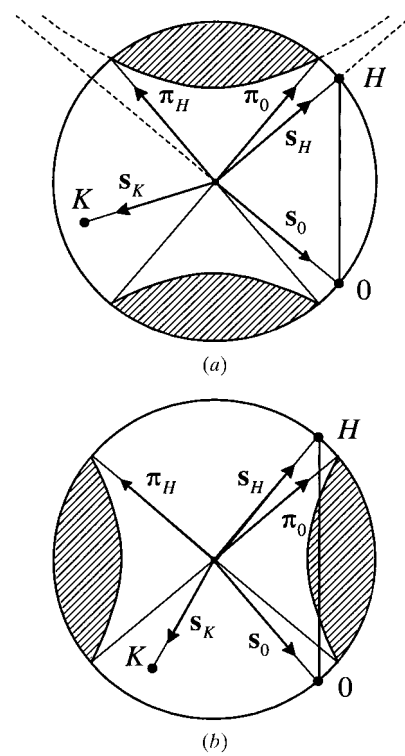

Fig. 11. Projection of the Ewald sphere onto the primary two-wave diffraction plane. $\theta_H < \pi/4$ for (*a*) and $\theta_H > \pi/4$ for (*b*).

Ge(000, 311, $\bar{2}4\bar{2}$) and Cu $K\alpha_1$ radiation, the mutually inversed asymmetry of peak profiles for the two polarizations does not occur in reality. This is in agreement with our conditions as well as the conditions of Juretschke (1986) and with the dynamical calculations. However, because of the conditions indicated by Weckert & Hümmer (1997), the occurrence of the mentioned change of asymmetry is possible. Besides, our conditions depend on the wave vectors involved and the polarization vectors of the incident and the primary reflected waves. That is, the conditions are independent of the polarization unit vectors $\boldsymbol{\sigma}_K$ and $\boldsymbol{\pi}_K$ of the secondary reflection K, and thus are independent of the choice of these vectors. In contrast, the conditions given by Weckert & Hümmer (1997) are dependent on this choice. From this point of view, their conditions are not convenient for practical use.

It seems that σ polarization should be used in the determination of the value of the triplet phase invariant, in view of the fact that, for π polarization, an additional feature is observed. However, when determining the value of the triplet phase invariant, other facts must be considered. From (19*a*) and (19*b*), when the wavevector of a secondary wave and the vector $\boldsymbol{\sigma}$ are collinear, $p^{\sigma}_{\rm um}(\sigma)$, $p^{\pi}_{\rm um}(\sigma) = 0$, whereas $p^{\sigma}_{\rm um}(\pi)$, $p^{\pi}_{\rm um}(\pi) \neq 0$. Thus, the *Umweg*-excited wave amplitude is zero only for the σ polarization and thus the primary wave is insensitive to the change of the value of the triplet phase invariant. Numerical calculations support this observation. For a Ge crystal and Cu $K\alpha_1$ radiation, there exist several configurations for which $p^{\sigma}_{\rm um}(\sigma)$, $p^{\pi}_{\rm um}(\sigma) = 0$; in particular, this condition is fulfilled with the (000, 220, 115) configuration. It should be noted that in this case the wave vector of the secondary wave is parallel to the crystal surface; therefore, the conventional solution of the fundamental equations of the dynamical theory of X-ray diffraction is inapplicable. To calculate the reflection coefficients of a diffracted wave, a generalized approach proposed by Stetsko & Chang (1997) should apply. Fig. 12 shows the semi-integral curves for the two polarizations and the triplet phase invariant values $\bar{\Phi}_3 = 0$ and π. Indeed, only the peak profiles for the π polarization are sensitive to the change of the value of the triplet phase invariant. For the diffraction geometry in question, the three-wave peak profile (line 1) for the σ polarization coincides with the two-wave profile irrespective of the value of $\bar{\Phi}_3$.

Therefore, the key factors in determining the value of the triplet phase invariant are the phase sensitivity of the peak profiles and the peak contrast against the background of the two-wave intensity. High phase sensitivity can be achieved when the absolute value of at least one of the polarization factors, $p^{\sigma}_{\rm um}(\sigma)$ or $p^{\pi}_{\rm um}(\pi)$, is significantly larger than zero. For a selected primary reflection, the change of the polarization factor is only possible by changing the incident wavelength. Therefore, to obtain high phase sensitivity, it is necessary to select the wavelengths for which the polarization factors can reach large values. However, unfavourable situations could possibly occur when the absolute values of the structure factors of the secondary and the coupling reflections turn out to be significantly smaller than that of the primary reflection even though the aforementioned conditions have been met. Thereby, the intensity of the *Umweg*-excited wave is significantly lower than that of the directly excited wave, irrespective of the value of the polarization factor. Under this circumstance, it is necessary to use π-polarized radiation and to select a wavelength so that the diffraction angle of the primary reflection is close to $\pi/4$. Then a good contrast of the three-wave peak can be achieved against the two-wave intensity background.

In conclusion, we have proposed a model for analysing the phase sensitivity of the reflection coefficients of diffracted waves in the case of three-wave X-ray diffraction which is based on the interference of the directly excited and *Umweg*-excited diffracted waves. The present model properly accounts for the phase sensitivity of this type of diffraction, as well as the behaviour of a diffracted wave as a function of the triplet phase invariant, the polarization state of the incident wave and the diffraction geometry. This model provides the diffraction conditions for achieving high phase sensitivity that are necessary for determining the values of triplet phase invariants to a high degree of accuracy. Good agreement between the results obtained by this model and the numerical calculations carried out within the framework of the dynamical theory is shown. A method of determining the value of the triplet phase invariant has been developed, based on the comparison of the experimentally measured three-wave peak profiles with the profiles calculated for different values of the triplet phase invariant.

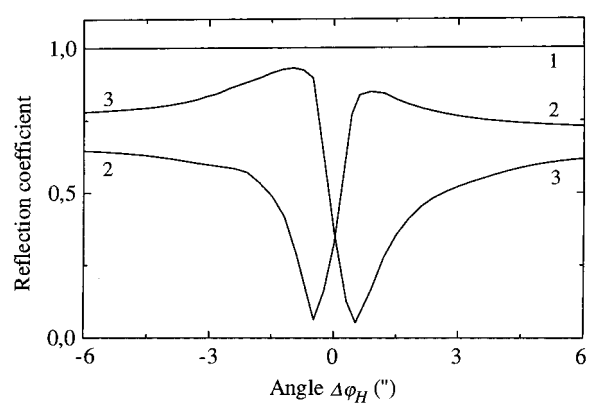

Fig. 12. Three-wave diffraction (000, 220, 115). Semi-integral curves $R_H(\Delta\varphi_H)$: 1 (for any values of $\bar{\Phi}_3$) for σ-polarized incident radiation, and 2 ($\bar{\Phi}_3 = 0$), 3 ($\bar{\Phi}_3 = \pi$) for π-polarized incident radiation. Curves are normalized to a corresponding value for two-wave diffraction for σ-polarized incident radiation.

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References

Born, M. & Wolf, E. (1970). *Principles of Optics.* Oxford: Pergamon.
Caticha-Ellis, S. (1969). *Acta Cryst.* A**25**, 666–673.
Chang, S. L. (1978). *Acta Cryst.* A**34**, S232.
Chang, S. L. (1982). *Phys. Rev. Lett.* **48**, 163–166.
Chang, S. L. (1984). *Multiple Diffraction of X-rays in Crystals.* Berlin: Springer-Verlag.
Chang, S. L. (1998). *Acta Cryst.* A**54**, 886–894.
Chang, S. L., Huang, Y. S., Chao, C. H., Tang, M. T. & Stetsko, Y. P. (1998). *Phys. Rev. Lett.* **80**, 301–304.
Chang, S. L. & Tang, M. T. (1988). *Acta Cryst.* A**44**, 1065–1072.
Chang, S. L. & Valladares, J. A. P. (1985). *Appl. Phys.* A**37**, 57–64.
Chapman, L. D., Yoder, D. R. & Colella, R. (1981). *Phys. Rev. Lett.* **46**, 1578–1581.
Collella, R. (1974). *Acta Cryst.* A**30**, 413–423.
Hart, M. & Lang, A. R. (1961). *Phys. Rev. Lett.* **7**, 120–121.
Hoier, R. & Aanestad, A. (1981). *Acta Cryst.* A**37**, 787–794.
Hümmer, K. & Billy, H. W. (1982). *Acta Cryst.* A**38**, 841–848.
Hümmer, K. & Billy, H. W. (1986). *Acta Cryst.* A**42**, 127–133.
Hümmer, K., Weckert, E. & Bondza, H. (1989). *Acta Cryst.* A**45**, 182–187.
Juretschke, H. J. (1982*a*). *Phys. Rev. Lett.* **48**, 1487–1489.
Juretschke, H. J. (1982*b*). *Phys. Lett.* A**92**, 183–185.
Juretschke, H. J. (1986). *Phys. Status Solidi B*, **135**, 455–466.
Kambe, K. (1957). *J. Phys. Soc. Jpn*, **12**, 13–25.
Kambe, K. & Miyake, S. (1954). *Acta Cryst.* **7**, 218–219.
Kohn, V. G. (1979). *Phys. Status Solidi A*, **54**, 375–384.
Kshevetskiy, S. A., Stetsko, Y. P. & Sheludko, S. A. (1987). *Kristallografiya*, **32**, 308–310. (In Russian.)
Lipscomb, W. N. (1949). *Acta Cryst.* **2**, 193–194.
Miyake, S. & Kambe, K. (1954). *Acta Cryst.* **7**, 216–217.
Mo, F., Haubach, B. C. & Thorkildsen, G. (1988). *Acta Chem. Scand. Ser. A*, **42**, 130–138.
Pinsker, Z. G. (1977). *Dynamical Scattering of X-rays in Crystals.* Berlin: Springer-Verlag.
Post, B. (1977). *Phys. Rev. Lett.* **39**, 760–763.
Sheludko, S. A. (1987). Doctoral thesis, Chernovtsy University, Ukraine. (In Russian.)
Shen, Q. (1998). *Phys. Rev. Lett.* **80**, 3268–3271.
Shen, Q. & Colella, R. (1988). *Acta Cryst.* A**44**, 17–21.
Stetsko, Y. P. (1990). Doctoral thesis, Chernovtsy University, Ukraine. (In Russian.)
Stetsko, Y. P. & Chang, S. L. (1997). *Acta Cryst.* A**53**, 28–34.
Stetsko, Y. P. & Chang, S. L. (1999). *Acta Cryst.* A**55**, 457–465.
Tseng, T. P. & Chang, S. L. (1990). *Acta Cryst.* A**46**, 567–576.
Unangst, D. & Melle, W. (1975). *Acta Cryst.* A**31**, 234–235.
Weckert, E. & Hümmer, K. (1997). *Acta Cryst.* A**53**, 108–143.
Zachariasen, W. H. (1965). *Acta Cryst.* **18**, 705–710.