Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 15 May 2005
Accepted 24 June 2005

Polarization factors in the general case of three-wave diffraction

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The polarization properties of diffracted radiation depending on the geometry of three-wave configurations and spectral and polarization states of the incident radiation are considered on the basis of the representation of multiple diffraction geometry in the natural crystallographic coordinates. The analytical expressions, obtained earlier for the symmetric cases [Sheludko (2004). *Acta Cryst.* A**60**, 281–282], are extended for the general case of three-wave diffraction of radiation on single crystals. The problem of the description of conditions of inverse asymmetry of three-wave diffraction profiles is reduced to a classical analysis of quadratic and cubic equations.

1. Introduction

It has been shown recently by the author (Sheludko, 2004) that use of a new geometrical model simplifies the problem of the analytical description of polarization factors. It appears that, in the case of symmetric three-wave diffraction, polarization interrelations can be expressed by functions of only two variables, one of which is naturally defined in crystallographic terms. In the present work, this approach is extended to a general case of three-wave diffraction.

2. Definition of variables and geometrical conditions of multiple diffraction

The adopted definitions of variables is based on three-dimensional curvilinear orthogonal coordinates (σ, τ, ϕ), previously proposed by the author [Sheludko (2003); see also Korn & Korn (1968) for general references]. This approach is perfectly applicable to the description of geometrical conditions of multiple diffraction in the Renninger experiment scheme [Renninger (1937); see also Chang (2004) and references therein], *i.e.* where the effects of multiple diffraction are observed as intensity perturbations of one (*principal reflection*) of the two-wave reflections as a crystal rotates around the diffraction vector **H** corresponding to this reflection. The suggested treatment is an alternative with respect to the widely used vector approach given by Cole *et al.* (1962). In the present communication, only a compact account of the approach is presented.

In reciprocal space, coordinates Σ_i, T_i and Φ_i are assigned to each reciprocal-lattice point H_i whose corresponding diffraction vector $\mathbf{H}_i$ is not collinear with vector **H**. In addition to various definitions of coordinate Σ_i given earlier by Sheludko (2004), we can also determine it as an angle, with which from the point H_i one can see the O and H end-points of the vector **H**. The diffraction vectors **H**, $\mathbf{H}_i$ and $\mathbf{H}_i^* = \mathbf{H} - \mathbf{H}_i$, corresponding to principal, additional and coupling reflections, respectively, compose a three-wave configuration, designated as $\mathbf{H} - \mathbf{H}_i/\mathbf{H}_i^*$. The spatial position of the circumscribing circle (*circle of configuration*) of the triangle OHH_1 is defined by the relative azimuthal coordinate Φ_i of its center L_i (see Fig. 1). The value of this coordinate is also referred to each point of the circumference with the exception of the singularity points O and H. The position indeterminacy of the point H_i on the circle of configuration is eliminated by the following definition of the third (bi-)polar coordinate: $\mathrm{T}_i = \ln(|\mathbf{H}_i|/|\mathbf{H}_i^*|) = \ln(\sin\Theta_i/\sin\Theta_i^*)$, where Θ_i and Θ_i^* are the Bragg angles for additional and coupling reflections, respectively.

The coordinates of the center L_i of the circle of configuration are defined as $L_i = L_i(2\Sigma_i^*, 0, \Phi_i)$, where Σ_i^* means the acute angle defined by the condition $\cos\Sigma_i^* = |\cos\Sigma_i|$. To each ith three-wave configuration $\mathbf{H} - \mathbf{H}_i/\mathbf{H}_i^*$, there exists a conjugate configuration $\mathbf{H} - \mathbf{H}_i^*/\mathbf{H}_i$ with center of circumference L_i^* and corresponding reciprocal-lattice point $H_i^* = H_i^*(\Sigma_i, -\mathrm{T}_i, \Phi_i \pm \pi)$ conjugate to point H_i. In particular cases of multiple-wave configurations with $\Sigma_i = \pi/2$, *i.e.* when intrinsic multiple diffraction takes place, the two circumferences coincide and their common center L_{int} is located at the point that divides the segment OH in two. Such configurations can only be of an even multiplicity as has been found earlier (Sheludko, 2004; see also Burbank, 1965; Zachariasen, 1965).

Let a crystal be in the position of principal reflection with the possibility of rotating around the vector **H**. The angle between wavevectors $\mathbf{K}_0$ of incident and **K** of diffracted waves, respectively, in

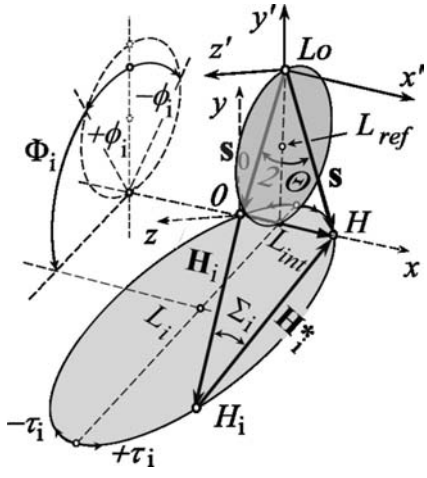

Figure 1
Geometrical relations between diffraction vectors, wavevectors, the circle of configuration and the circle of reflections. The coordinate plane $z = z' = 0$ coincides with the diffraction plane $OHLo$ of the principal reflection.

the crystal is 2Θ, where Θ is the Bragg angle for the principal reflection. For simplicity, we shall scale all vectors by replacing $\mathbf{v}_x$ with $\mathbf{v}_x/|\mathbf{K}_0|$ so that all wavevectors normalized in such a way are designated by $\mathbf{s}_x$, with $|\mathbf{s}_x| = 1$ (here $\mathbf{v}_x$ and $\mathbf{s}_x$ are the placeholders for an arbitrary vector and a unit wavevector, respectively). The normalized Ewald sphere of unit radius can be circumscribed from the Lorentz point $Lo = Lo(2\Theta, 0, 0)$. The bipolar coordinate system introduced here can be imagined as two sets of σ and τ circumferences on the surface of the Ewald sphere, which are mutually perpendicular at each point of this surface (see Fig. 2).

Let us construct a circumference (*circle of reflections*) in the coordinate plane $\tau = 0$ with segment $LoL_{\rm int} = \cos\Theta$ as its diameter (see Fig. 1) and the point $L_{\rm ref} = L_{\rm ref}[2\arctan(2\tan\Theta), 0, 0]$ as its center. Completing the auxiliary constructions, we formulate the following statement, whose rigorous proof is omitted for shortness. Non-intrinsic multiple diffraction in a Renninger experiment scheme takes place when, with the crystal rotating about the diffraction vector of the principal reflection, the center L_i of a circle of configuration moves onto the circle of reflections. The conditions of intrinsic multiple diffraction, *i.e.* when the center of the circle of configuration is permanently placed on the circle of the reflections, consists in the mutual orthogonality of the configuration plane and the diameter $LoL_{\rm int}$ of the circle of reflections.

The problem of determination of multiple diffraction conditions is reduced now to an elementary plane problem. Taking into consideration that $L_iL_{\rm int} = \sin\Theta/\tan\Sigma_i$, one obtains immediately the expression for angular positions of multiple diffraction peaks on an azimuthal scan plot:

$$\varphi_i = \pm\arccos(\tan\Theta/\tan\Sigma_i^*) - \Phi_i \pm n\pi, \qquad (1)$$

where n is even for the ith configuration and n is odd for the conjugate one, say i^*th, configuration.

We obtain as simply and clearly all the other geometrical relations of multiple diffraction. In particular, the spectral condition of coincidental multiple diffraction, *i.e.* when diffraction conditions are accomplished simultaneously for two (say ith and jth) or more systematic multiple-wave configurations, can be easily obtained in the following analytical form:

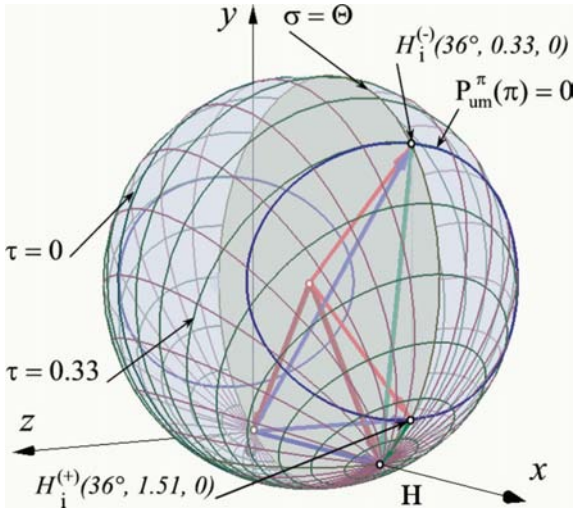

Figure 2
The two sets of mutually perpendicular coordinate circumferences on the surface of the Ewald sphere constructed for Bragg angle $\Theta = 36^\circ$. Two of the four possible solutions of equation (17) are pointed out as the reciprocal-lattice points $H_i^{(-)}$ and $H_i^{(+)}$ on the surface. See explanations in the text.

$$\cot\Theta = (\cot^2\Sigma_i + \cot^2\Sigma_j - 2\cot\Sigma_i^*\cot\Sigma_j^*\cos\Phi_{ij})^{1/2}/\sin\Phi_{ij}, \qquad (2)$$

where $\Phi_{ij} = \Phi_j - \Phi_i$.

3. Analytical form of polarization factors and their application

Now we can use the outcomes gained in the previous section for the analysis of geometrical relations of a special kind – *polarization relations* – between diffracted waves in the general case of three-wave diffraction. We introduce an auxiliary Cartesian coordinate system $x'y'z'$ with its origin at Lorentz point Lo and the axis x' parallel to the vector $\mathbf{H}$ (see Fig. 1) and write down the unit wavevectors $\mathbf{s}_0$ and $\mathbf{s}$ of the incident and diffracted waves, respectively, as:

$$\mathbf{s}_0(x', y', z') = \mathbf{s}_0(-\sin\Theta, -\cos\Theta, 0) \qquad (3)$$

and

$$\mathbf{s}(x', y', z') = \mathbf{s}(\sin\Theta, -\cos\Theta, 0). \qquad (4)$$

The unit wavevector $\mathbf{s}_i$ of the additional reflection is then determined as follows:

$$\mathbf{s}_i(x', y', y') = \mathbf{s}_i\left[\frac{\sin\Theta\sinh T_i}{\cosh T_i - \cos\Sigma_i}, \frac{\cos\Sigma_i - \cos^2\Theta\cosh T_i}{\cos\Theta(\cosh T_i - \cos\Sigma_i)}, \pm\frac{\sin\Theta(\cos^2\Theta - \cos^2\Sigma_i)^{1/2}}{\cos\Theta(\cosh T_i - \cos\Sigma_i)}\right]. \qquad (5)$$

The unit polarization vectors for the two-wave case can be represented in one of the conventional forms (see, for example, Shen, 1986):

$$\boldsymbol{\pi}_0(x', y', z') = \boldsymbol{\pi}_0(-\cos\Theta, \sin\Theta, 0), \qquad (6)$$

$$\boldsymbol{\pi}(x', y', z') = \boldsymbol{\pi}(\cos\Theta, \sin\Theta, 0), \qquad (7)$$

$$\boldsymbol{\sigma}_0(x', y', z') = \boldsymbol{\sigma}_0(0, 0, 1), \qquad (8)$$

$$\boldsymbol{\sigma}(x', y', z') = \boldsymbol{\sigma}(0, 0, -1). \qquad (9)$$

For additional reflections, the unit polarization vectors can be chosen arbitrarily as long as they satisfy the mutual orthogonality conditions. Taking into account the inconsistency of conventional two-wave definitions of σ and π polarization with respect to the additional reflections in the non-coplanar case, we introduce ρ- and τ-polarization terms by the following definition of the corresponding unit polarization vectors:

$$\boldsymbol{\tau}_i(x', y', z') = \boldsymbol{\tau}_i\left[\frac{1 - \cos\Sigma_i\cosh T_i}{\cosh T_i - \cos\Sigma_i}, -\frac{\tan\Theta\cos\Sigma_i\sinh T_i}{\cosh T_i - \cos\Sigma_i}, -\frac{\sinh T_i(\cos^2\Theta - \cos^2\Sigma_i)^{1/2}}{\cos\Theta(\cosh T_i - \cos\Sigma_i)}\right] \qquad (10)$$

$$\boldsymbol{\rho}_i(x', y', z') = \boldsymbol{\rho}_i\left[-\frac{\sinh T_i(\cos^2\Theta - \cos^2\Sigma_i)^{1/2}}{\cosh T_i - \cos\Sigma_i}, -\frac{\tan\Theta(\cos^2\Theta - \cos^2\Sigma_i)^{1/2}}{\cosh T_i - \cos\Sigma_i}, \frac{\cos\Sigma_i\cosh T_i - \cos^2\Theta}{\cos\Theta(\cosh T_i - \cos\Sigma_i)}\right]. \qquad (11)$$

Now, according to the accepted system of symbols (see Weckert & Hümmer, 1997; Stetsko *et al.*, 2004; Sheludko, 2004), we can write down the expressions of polarization factors for '*Umweg*' reflections and σ- and π- polarization states of incident (see the symbols in round brackets) and diffracted (upper index) radiation:

$$P^{\sigma}_{um}(\sigma) = (\boldsymbol{\sigma}_0 \cdot \boldsymbol{\rho}_i)(\boldsymbol{\rho}_i \cdot \boldsymbol{\sigma}) + (\boldsymbol{\sigma}_0 \cdot \boldsymbol{\tau}_i)(\boldsymbol{\tau}_i \cdot \boldsymbol{\sigma}) = \frac{\tan^2\Theta(\cos^2\Theta - \cos^2\Sigma_i)}{(\cosh \mathrm{T}_i - \cos\Sigma_i)^2} - 1, \quad (12)$$

$$P^{\pi}_{um}(\sigma) = (\boldsymbol{\sigma}_0 \cdot \boldsymbol{\rho}_i)(\boldsymbol{\rho}_i \cdot \boldsymbol{\pi}) + (\boldsymbol{\sigma}_0 \cdot \boldsymbol{\tau}_i)(\boldsymbol{\tau}_i \cdot \boldsymbol{\pi}) = -\tan^2\Theta(\cos^2\Theta - \cos^2\Sigma_i)^{1/2} \times \frac{\cos\Sigma_i + \cos^2\Theta(\sinh \mathrm{T}_i - \cosh \mathrm{T}_i)}{(\cosh \mathrm{T}_i - \cos\Sigma_i)^2}, \quad (13)$$

$$P^{\sigma}_{um}(\pi) = (\boldsymbol{\pi}_0 \cdot \boldsymbol{\rho}_i)(\boldsymbol{\rho}_i \cdot \boldsymbol{\sigma}) + (\boldsymbol{\pi}_0 \cdot \boldsymbol{\tau}_i)(\boldsymbol{\tau}_i \cdot \boldsymbol{\sigma}) = \tan^2\Theta(\cos^2\Theta - \cos^2\Sigma_i)^{1/2} \times \frac{\cos\Sigma_i - \cos^2\Theta(\sinh \mathrm{T}_i + \cosh \mathrm{T}_i)}{(\cosh \mathrm{T}_i - \cos\Sigma_i)^2}, \quad (14)$$

$$P^{\pi}_{um}(\pi) = (\boldsymbol{\pi}_0 \cdot \boldsymbol{\rho}_i)(\boldsymbol{\rho}_i \cdot \boldsymbol{\pi}) + (\boldsymbol{\pi}_0 \cdot \boldsymbol{\tau}_i)(\boldsymbol{\tau}_i \cdot \boldsymbol{\pi}) = -\cos 2\Theta - \frac{\tan^2\Theta(\cos^4\Theta - 2\cos^2\Theta\cos\Sigma_i\cosh \mathrm{T}_i + \cos^2\Sigma_i)}{(\cosh \mathrm{T}_i - \cos\Sigma_i)^2}. \quad (15)$$

The above approach can have a wide spectrum of applications to explain various behaviors of multiple diffraction events. In particular, by combining the products of individual unit polarization vectors (6)–(11) in pairs, we obtain analytical expressions of polarization coefficients, which are involved in the system of fundamental equations of the dynamical theory of three-wave diffraction (see, for example, Authier, 2003, equation 9.7).

Further, one can deduce from comparison of expressions (13) and (14) that polarization states and intensity of mutually conjugate three-wave reflections in the case of linearly polarized incident radiation are, generally speaking, different because of the inequality of the two polarization factors under consideration. At the same time, it is easy to recognize from the parity properties of hyperbolic functions that the intensities of such reflections in the case of unpolarized incident radiation will be indistinguishable. This explains the well known behavior of experimentally observed peaks.

Most interesting is the analysis of equation (15) for solving the problem of the conditions of inverse asymmetry of three-wave peaks in the case of π-polarized incident radiation (Juretschke, 1986; Weckert & Hümmer, 1997; Stetsko & Chang, 1999; Sheludko, 2004). In fact, by analogy to the treatment presented by Sheludko (2004) for the symmetrical case, one obtains criteria for the sign change of the P^{π}_{um} factor in the general case of three-wave diffraction:

$$P^{\pi}_{um}(\pi) = \cos^2\Sigma_i(1 + \tan^4\Theta) + \cosh^2 \mathrm{T}_i(1 - \tan^2\Theta) - 2\cos\Sigma_i\cosh \mathrm{T}_i + \sin^2\Theta = 0. \quad (16)$$

By substitution of $T_i = 0$ in (16), which corresponds to the symmetrical case of three-wave diffraction, one easily obtains the equation, given by Sheludko (2004). Again, the substitution of $\Sigma^*_i = \Theta$ in (16) leads us to the conditions for the sign change of $P^{\pi}_{um}(\pi)$ in the case of coplanar three-wave diffraction:

$$\mathrm{T}^{(\pm)}_{i,\mathrm{copl}} = \pm\,\mathrm{arccosh}\left(\frac{\cos^3\Sigma_i \pm \sin^3\Theta}{\cos 2\Theta}\right). \quad (17)$$

If the wavelength of radiation is fixed and the value of the Bragg angle Θ is measured directly, from solving (16) which is a quadratic in $\cos\Sigma_i$ or $\cosh \mathrm{T}_i$ [like equation (5) in Sheludko (2004)], one gets the analytical form of various criteria similar to those discussed by Juretschke (1986). The geometrical meaning of such criteria is illustrated in Fig. 2. Equation (16) describes two closed curves on the surface of the Ewald sphere, as is shown in Fig. 2 for the particular case $\Theta = 36^\circ$. If the equation is solvable for some value of Σ_i (or T_i), one obtains the unknown values of the second coordinate of the intersection points. For example, for $\Sigma_i = 36^\circ$, corresponding to the coplanar three-wave diffraction, one obtains from (17) a set of solutions: $\mathrm{T}^{(-)}_i \approx \pm 0.33$ and $\mathrm{T}^{(+)}_i \approx \pm 1.51$. The two (positive) solutions are represented in Fig. 2 by the fictive reciprocal-lattice points $H^{(-)}_i$ and $H^{(+)}_i$, lying on the surface of the Ewald sphere. The behavior of the possible solutions of equation (16) is thus evident.

However, since the values of Σ_i and T_i for a given three-wave configuration are fixed by the crystal structure and cannot be changed during the experiment, the spectral criteria of inverse asymmetry are of more practical interest. One obtains such criteria by transforming equation (16):

$$\cos^6\Theta - (3 + \cos 2\Sigma_i - 2\cos\Sigma_i\cosh \mathrm{T}_i + \cosh 2\mathrm{T}_i)\cos^4\Theta + (2\cos^2\Sigma_i + \cosh^2 \mathrm{T}_i)\cos^2\Theta - \cos^2\Sigma_i = 0, \quad (18)$$

from which it is easy to realize that the problem is reduced to the elementary analytical problem of the determination of positive roots of a cubic equation in $\cos^2\Theta$ with well known coefficients.

In conclusion, we propose a model for analyzing the geometrical conditions of multiple diffraction in the Renninger scanning experiment. The same model is applied to the analytical description of the polarization factors in the case of multiple diffraction. The analytical expressions for some standard polarization states of incident and diffracted radiation in the case of three-wave diffraction are considered.

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