Acta Cryst. (1980). A**36**, 1044–1050

On the Polarization of X-rays Diffracted in Mosaic Crystals

By V. E. Dmitrienko and V. A. Belyakov

All Union Scientific Research Institute of Physical-Technical and Radiotechnical Measurements, 141570 *Moscow, USSR*

(*Received* 8 *December* 1978; *accepted* 27 *May* 1980)

Abstract

The theory of polarized X-ray diffraction in mosaic crystals, which takes into account multiple Bragg scattering, is developed in the framework of transfer equations for the polarization tensors of X-ray beams. Both the depolarization and differences in the phase velocities of polarized X-rays due to Bragg scattering in mosaic crystals are determined. Exact solutions of the equations are obtained for a plane-parallel plate and expressions for the polarization characteristics of reflected and transmitted beams are given for Bragg and Laue geometries. The approach developed may also be applied to neutron or Mössbauer γ-ray diffraction in magnetically ordered mosaic crystals.

Introduction

Recent progress in the development of an experimental technique and, particularly, intense sources of highly polarized X-rays such as synchrotron radiation have attracted fresh attention to polarization measurements in X-ray diffraction (Skalicky & Malgrange, 1972; Jennings, 1968; Olekhnovich, Rubtsov & Shmidt, 1975; Mikhajljuk, Kshevetskij, Ostapovich & Shafranjuk, 1977; Olekhnovich & Markovich, 1978; Vaillant, 1977; Cohen & Kuriyama, 1978; Hart, 1978). The earlier works were reviewed by Chandrasekhar (1960). The usefulness of such measurements is now doubtless and is connected with the possibility of obtaining new and more detailed information about structural properties of crystals. This is related to the diffraction both in perfect and in imperfect crystals, but in the latter case the potential advantage of the polarization measurements is restricted by the absence of a complete theory of polarization phenomena.

The theory of X-ray polarization properties is well developed for the case of perfect crystals (Skalicky & Malgrange, 1972; Mikhajljuk *et al.*, 1977; Cohen & Kuriyama, 1978; Hart, 1978) and is based on the dynamical theory of diffraction. It is clear that in the case of imperfect crystals the properties of X-ray beams are also determined by diffraction, but it is very difficult to use the dynamical equations directly. A simpler description of definite types of imperfect crystals (mosaic crystals) was originally proposed by Darwin (1922) (see also Zachariasen, 1967; Becker, 1977). Darwin's approach is based on transfer equations for intensities of linearly (π and σ) polarized beams (the plane of π polarization coincides with the plane formed by $\mathbf{k}_0$ and $\mathbf{k}_\mathrm{H}$, the wave vectors of the direct and diffracted waves respectively; σ polarization is perpendicular to π polarization). Note that the incoherence of scattering by individual blocks of a mosaic crystal is used in the derivation of these simplified equations.

The present paper deals with the theory of arbitrarily polarized X-ray diffraction in mosaic crystals. It is well known (Chandrasekhar, 1950; Rozenberg, 1977) that for arbitrarily polarized radiation the transfer equations for intensities should be replaced by the transfer equations for polarization tensors $\hat{J}$. The diagonal elements of a polarization tensor $\hat{J}_{\sigma\sigma}$ and $\hat{J}_{\pi\pi}$ are the intensities of σ- and π-polarized components of the X-ray beam and the off-diagonal elements $J_{\sigma\pi} = J^*_{\pi\sigma}$ contain the product of the amplitudes of σ- and π-polarized components. The physical meaning of $J_{\sigma\pi}$ is determined by the following relations: Im $J_{\sigma\pi}$ is equal to the intensity of the circularly polarized component and Re $J_{\sigma\pi}$ is equal to the intensity of the linearly polarized component with the electric vector inclined at 45° to σ or π. The polarization tensor $\hat{J}$ determines the beam intensity and all polarization properties (the degree of polarization, the orientation and axial ratio of polarization ellipse); the well known Stokes's parameters are also determined by the tensor $\hat{J}$ (Born & Wolf, 1964). The solution of the transfer equations for polarization tensors therefore connects the intensity and polarization properties of the diffracted beam with those of the incident one.

The transfer equations for polarization tensors are the straightforward generalization of transfer equations for intensities and are reduced to the latter if the incident beam is σ or π polarized (or unpolarized). If the incident beam polarization is neither σ nor π, one needs the transfer equations for polarization tensors to describe the polarization properties of diffracted beams.

There are various approaches to X-ray transfer equations in mosaic crystals (Darwin, 1922;

0567-7394/80/061044-07$01.00

Zachariasen, 1967; Kato, 1976; Becker, 1977). The present paper deals with the simplest Darwin model of mosaic crystals. The sizes of mosaic blocks are supposed to be small enough that X-ray diffraction in the individual block may be described by kinematical theory. Under the mentioned assumptions, the transfer equations for polarization tensors may be derived in the same way as the transfer equations for intensities. The detailed derivation of the transfer equations for polarization tensors was discussed earlier both for the general case (Chandrasekhar, 1950) and for the case of Bragg diffraction (Dmitrienko & Belyakov, 1977).

In the present paper it is found in the framework of the transfer equations of the polarization tensors that the qualitative difference in X-ray diffraction in perfect and mosaic crystals reveals itself in the depolarization of diffracted beams in mosaic crystals. A quantitative description of X-ray birefringence and other polarization phenomena in X-ray diffraction in mosaic crystals is given.

Basic equations

Let us examine the diffraction of polarized X-rays in a mosaic crystal. The mosaic crystal is assumed to be formed by a large number of small perfect blocks which are slightly misoriented one to the other. The typical angle of misorientation is supposed to be much larger than the angular width of diffraction in the individual block (type I mosaic crystal). As was mentioned, this model of an imperfect crystal permits the use of transfer equations for the description of X-ray diffraction. The straightforward generalization of the Darwin (1922) transfer equations for the case of arbitrarily polarized X-rays gives the following equations for the polarization tensors of direct $\hat{J}^0$ and diffracted $\hat{J}^{\rm H}$ beams in a mosaic crystal.

$$\begin{aligned}\frac{\partial \hat{J}^0}{\partial s_0} &= -\mu \hat{J}^0 + i(\sigma_0 \hat{R}^2 \hat{J}^0 - \sigma_0^* \hat{J}^0 \hat{R}^2)/2 + \sigma_{0H} \hat{R} \hat{J}^{\rm H} \hat{R} \\ \frac{\partial \hat{J}^{\rm H}}{\partial s_{\rm H}} &= -\mu \hat{J}^{\rm H} + i(\sigma_{\rm H} \hat{R}^2 \hat{J}^{\rm H} - \sigma_{\rm H} \hat{J}^{\rm H} \hat{R}^2)/2 + \sigma_{\rm H0} \hat{R} \hat{J}^0 \hat{R}\end{aligned} \tag{1}$$

where s_0 and $s_{\rm H}$ are the coordinates along $\mathbf{k}_0$ and $\mathbf{k}_{\rm H} = \mathbf{k}_0 + \mathbf{H}$, the directions of the direct and the diffracted beams respectively, $\mathbf{H}$ is the reciprocal-lattice vector and μ is the absorption coefficient. The tensor $\hat{R}$ describes the polarization properties of diffraction in an individual block and is determined by

$$\hat{R} = \begin{pmatrix} 1 & 0 \\ 0 & C \end{pmatrix} \tag{2}$$

where C is the polarization factor, $C = \cos 2\theta_B$, θ_B is the Bragg angle. Now we shall describe the coefficients σ_0, $\sigma_{\rm H}$, $\sigma_{0\rm H}$, $\sigma_{\rm H0}$ in (1) and discuss the physical meaning of these equations. The coefficients $\sigma_{\rm H0}$ and $\sigma_{0\rm H}$ are determined, respectively, by the cross sections of the Bragg scattering from the direct to the diffracted beam and *vice versa*. As in the Darwin equations, these coefficients are given by

$$\begin{aligned}\sigma_{\rm H0}(\varepsilon) &= \frac{\lambda^3}{\sin 2\theta_B}\left(\frac{e^2}{vmc^2}\right)^2 |F_{\rm H}|^2\, W(\varepsilon), \\ \sigma_{0\rm H}(\varepsilon) &= \frac{\lambda^3}{\sin 2\theta_B}\left(\frac{e^2}{vmc^2}\right)^2 |F_{-\rm H}|^2\, W(\varepsilon),\end{aligned} \tag{3}$$

where $\varepsilon = \theta - \theta_B$, the departure angle from Bragg's law, λ is the wavelength, v is the volume of the unit cell, $F_{\rm H}$ and $F_{-\rm H}$ are the structure amplitudes, $W(\varepsilon)$ is the orientational distribution function of blocks in the crystal, e, m and c are the physical constants in the conventional usage. Note that $\sigma_{\rm H0}$ and $\sigma_{0\rm H}$ may be regarded as the averaged diffraction power of an individual block.

The imaginary and real parts of the complex coefficients σ_0 and $\sigma_{\rm H}$ are determined, respectively, by diffractional attenuation and birefringence in a mosaic crystal. These coefficients may be obtained in the same manner as $\sigma_{0\rm H}$ and $\sigma_{\rm H0}$. They may be regarded as the averaged attenuation and birefringence of an individual block and are given by

$$\sigma_0(\varepsilon) = \frac{\lambda^3}{\sin 2\theta_B}\left(\frac{e^2}{vmc^2}\right)^2 F_{\rm H} F_{-\rm H} [\tilde{W}(\varepsilon) + iW(\varepsilon)] \tag{4a}$$

$$\sigma_{\rm H}(\varepsilon) = \frac{\lambda^3}{\sin 2\theta_B}\left(\frac{e^2}{vmc^2}\right)^2 F_{\rm H} F_{-\rm H} [-\tilde{W}(\varepsilon) + iW(\varepsilon)] \tag{4b}$$

where $\tilde{W}(\varepsilon)$ is connected with the distribution function $W(\varepsilon)$ by the following relation

$$\tilde{W}(\varepsilon) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{W(\varepsilon')\,{\rm d}\varepsilon'}{\varepsilon' - \varepsilon}. \tag{5}$$

Omitting the straightforward derivation of (4), we shall only show how (5) may be found from the well known Kramers–Kronig relations (dispersion relations). Taking into account that σ_0 determines the diffractional part of the complex refractive index of X-rays in a mosaic crystal and making use of the Kramers–Kronig relations for the dielectric constant, one finds that Re σ_0 and Im σ_0 are connected by the following dispersion relation (Landau & Lifshitz, 1958):

$$\mathrm{Re}\,\sigma_0(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\mathrm{Im}\,\sigma_0(\omega')\,{\rm d}\omega'}{\omega' - \omega} \tag{6}$$

where ω is the frequency. In (6), frequency variables may be changed by angular ones because the diffractional part of the refractive index is significant only if Bragg diffraction occurs. Taking into account that in the Bragg condition a frequency deviation $\Delta\omega$ is directly proportional to the angular deviation $\Delta\varepsilon$, $\Delta\varepsilon = (\Delta\omega/\omega)\tan\theta_B$, one obtains the following relation from (6) to a good approximation:

$$\operatorname{Re}\sigma_0(\varepsilon) = \frac{1}{\pi} \fint_{-\infty}^{\infty} \frac{\operatorname{Im}\sigma_0(\varepsilon')\,d\varepsilon'}{\varepsilon' - \varepsilon}. \quad (7)$$

Inserting (4) into (7) one can obtain (5). (For the sake of simplicity it may be assumed that $F_{-H} = F_H^*$.) Note that the minus sign at $\tilde{W}(\varepsilon)$ in (4*b*) arises because in type I mosaic crystals the sign of angular departures from Bragg's law is opposite for direct and diffracted beams (originally pointed out by Darwin, 1922). Note also that for $F_H = F_H^*$ equations (4) give the well known expressions for the coefficients in (1)

$$\operatorname{Im}\sigma_0 = \operatorname{Im}\sigma_H = \sigma_{0H} = \sigma_{H0} = QW(\varepsilon), \quad (8)$$

where

$$Q = \frac{\lambda^3}{\sin 2\theta_B}\left(\frac{e^2}{vmc^2}\right)^2 |F_H|^2.$$

The function $\tilde{W}(\varepsilon)$ contains the same information about block orientations as $W(\varepsilon)$ does. In the cases of Lorentzian and Gaussian mosaic distributions one obtains:

$$W_L(\varepsilon) = (\varepsilon_m/\pi)/(\varepsilon^2 + \varepsilon_m^2),$$
$$\tilde{W}_L(\varepsilon) = -(\varepsilon/\pi)/(\varepsilon^2 + \varepsilon_m^2), \quad (8a)$$

$$W_G(\varepsilon) = (\varepsilon_m\sqrt{\pi})^{-1}\exp -(\varepsilon/\varepsilon_m)^2,$$
$$\tilde{W}_G(\varepsilon) = \frac{-\varepsilon}{\pi\varepsilon_m^2}\sum_{n=0}^{\infty}\frac{(-2)^n(\varepsilon/\varepsilon_m)^{2n}}{(2n+1)!!}, \quad (8b)$$

where ε_m is the width of mosaic distribution. Note that $\tilde{W}(\varepsilon)$ is an odd function if $W(\varepsilon)$ is an even function as is usually supposed.

Let us discuss now the tensor properties of the coefficients in equations (1). Naturally, these properties are determined by the polarization properties of diffraction in individual mosaic blocks. Therefore, let us examine the diffraction of the arbitrarily polarized wave with the amplitude $\mathbf{E} = E_\sigma\boldsymbol{\sigma} + E_\pi\boldsymbol{\pi}$ in the block. For the amplitude of the diffracted wave in the kinematical approximation one easily gets

$$\mathbf{E}^d \simeq (E_\sigma\boldsymbol{\sigma} + \cos 2\theta_B E_\pi\boldsymbol{\pi}) \equiv \hat{K}\mathbf{E} \quad (9)$$

where $\hat{K}$ is given by (2). If one takes into account that the polarization tensor of a plane wave is defined by the following relation

$$\hat{J} = \begin{pmatrix} |E_\sigma|^2 & E_\sigma E_\pi^* \\ E_\pi E_\sigma^* & |E_\pi|^2 \end{pmatrix}, \quad (10)$$

the expression for the polarization tensor of the diffracted wave may be written in the form

$$\hat{J}^d \simeq \begin{pmatrix} |E_\sigma|^2 & E_\sigma E_\pi^*\cos 2\theta_B \\ E_\pi E_\sigma^*\cos 2\theta_B & |E_\pi|^2\cos^2 2\theta_B \end{pmatrix} \equiv \hat{K}\hat{J}\hat{K}. \quad (11)$$

Thus, we obtain the tensor structure of the terms with the coefficients σ_{0H} and σ_{H0} in equations (1). In the same way (Dmitrienko & Belyakov, 1977) one can get the tensor structure of the other terms in equations (1).

Now tensor equations (1) can be rewritten as the following equations for the elements of the polarization tensors $\hat{J}^0$ and $\hat{J}^H$:

$$\frac{\partial J^0_{\sigma\sigma}}{\partial s_0} = -(\mu + QW)J^0_{\sigma\sigma} + QWJ^H_{\sigma\sigma} \quad (12a)$$

$$\frac{\partial J^H_{\sigma\sigma}}{\partial s_H} = -(\mu + QW)J^H_{\sigma\sigma} + QWJ^0_{\sigma\sigma} \quad (12b)$$

$$\frac{\partial J^0_{\pi\pi}}{\partial s_0} = -(\mu + C^2QW)J^0_{\pi\pi} + C^2QWJ^H_{\pi\pi} \quad (13a)$$

$$\frac{\partial J^H_{\pi\pi}}{\partial s_H} = -(\mu + C^2QW)J^H_{\pi\pi} + C^2QWJ^0_{\pi\pi} \quad (13b)$$

$$\frac{\partial J^0_{\sigma\pi}}{\partial s_0} = -[\mu + (1 + C^2)QW/2 + i(1 - C^2)Q\tilde{W}/2]J^0_{\sigma\pi} + CQWJ^H_{\sigma\pi} \quad (14a)$$

$$\frac{\partial J^H_{\sigma\pi}}{\partial s_H} = -[\mu + (1 + C^2)QW/2 - i(1 - C^2)Q\tilde{W}/2]J^H_{\sigma\pi} + CQWJ^0_{\sigma\pi}. \quad (14b)$$

The equations for $J_{\pi\sigma}$ are omitted here because $J_{\pi\sigma} = J^*_{\sigma\pi}$.

It follows from (12)–(14) that the equations for diagonal and off-diagonal elements are unconnected. Equations (12) and (13) for diagonal elements are the well known Darwin transfer equations. The new equations in the developed approach are only equations (14) for off-diagonal elements of polarization tensors. The solutions of (14) may be found in the same way as those of (12) and (13). The boundary conditions for off-diagonal elements are the same as for intensities: $J_{\sigma\pi}$ are continuous at the crystal boundaries.

Note that some qualitative features of the diffraction of polarized X-rays in mosaic crystals can be found without solving (12)–(14). For example, it follows from (12)–(14) that the polarization properties of X-ray beams vary during their propagation in a mosaic crystal. This variation is an immediate consequence of the different coordinate dependences of the diagonal and off-diagonal elements of the polarization tensors, the relation between which determines the polarization properties of the beams. The less-evident consequence of (12)–(14) is the depolarization of X-rays in mosaic crystals. A more detailed discussion of these polarization properties will be presented below after the solution of (12)–(14) for some cases.

Diffraction in a mosaic plate

Let us examine the diffraction of an arbitrarily polarized plane wave with the polarization tensor $\hat{J}^i$ in the plane-parallel mosaic plate. In this case $\hat{J}^0$ and $\hat{J}^H$ are dependent on the z coordinate only (z axis is normal to the plate surface). After obvious substitutions $(\partial\hat{J}^0/\partial s_0) = \gamma_0(\mathrm{d}\hat{J}^0/\mathrm{d}s)$ and $(\partial\hat{J}^H/\partial s_H) = \gamma_H(\mathrm{d}\hat{J}^H/\mathrm{d}z)$, one gets from (12)–(14) the ordinary linear differential equations (γ_0 and γ_H are the magnitudes of the direction cosines of the direct and diffracted beams relative to the normal to the crystal surface). Omitting here the simple solution of (12)–(14), let us give and analyze the final results only.

For the off-diagonal elements of the polarization tensors $\hat{J}^r$ and $\hat{J}^t$ of the reflected and transmitted beams respectively, one can obtain from (14) the following expressions:
in the Bragg case

$$J^r_{\sigma\pi} = J^i_{\sigma\pi}\frac{CQW(\exp\mu_1 L - \exp\mu_2 L)}{a_2\exp\mu_1 L - a_1\exp\mu_2 L},$$

$$J^t_{\sigma\pi} = J^i_{\sigma\pi}\frac{(a_2 - a_1)\exp(\mu_1+\mu_2)L}{a_2\exp\mu_1 L - a_1\exp\mu_2 L}; \qquad (15)$$

and in the Laue case

$$J^r_{\sigma\pi} = J^i_{\sigma\pi}\frac{CQW(\exp\mu_2 L - \exp\mu_1 L)}{a_2 - a_1},$$

$$J^t_{\sigma\pi} = J^i_{\sigma\pi}\frac{a_2\exp\mu_2 L - a_1\exp\mu_1 L}{a_2 - a_1}; \qquad (16)$$

where L is the plate thickness, $J^i_{\sigma\pi}$ is the off-diagonal element of the polarization tensor of the incident beam,

$$a_j = \gamma_H\mu_j + \mu + (1 + C^2)QW/2 + i(1 - C^2)Q\tilde{W}/2, \quad j = 1, 2,$$

μ_j are the roots of the characteristic equation of (14):

$$\gamma_0\gamma_H\mu_j^2 + \{(\gamma_0+\gamma_H)[\mu + (1+C^2)QW/2] + i(\gamma_0-\gamma_H)(1-C^2)Q\tilde{W}/2\}\mu_j + [\mu + (1+C^2)QW/2]^2 - C^2Q^2W^2 + (1-C^2)^2Q^2\tilde{W}^2/4 = 0. \qquad (17)$$

Expressions (15) and (16), with the well known expressions for the diagonal elements, completely determine the intensity and polarization of reflected and transmitted beams in the case of a mosaic crystal.

It should be remembered that the intensity and polarization characteristics of a beam are connected with the elements of its polarization tensor in the following ways:
the intensity I

$$I = J_{\sigma\sigma} + J_{\pi\pi}; \qquad (18)$$

the degree of polarization P

$$P = [(J_{\sigma\sigma} - J_{\pi\pi})^2 + 4|J_{\sigma\pi}|^2]^{0\cdot5}/(J_{\sigma\sigma} + J_{\pi\pi}); \quad (19)$$

the axial ratio b of the polarization ellipse

$$b = \tan\eta, \qquad (20)$$

where $\sin 2\eta = 2\,\mathrm{Im}\,J_{\sigma\pi}/(PI)$;
the angle φ between the long axis of the polarization ellipse and σ direction

$$\tan 2\varphi = 2\,\mathrm{Re}\,J_{\sigma\pi}/(J_{\sigma\sigma} - J_{\pi\pi}) \qquad (21)$$

(Born & Wolf, 1964).

Expressions (15)–(21) describe the dependence of polarization characteristics on the plate thickness, the angular departure from the Bragg law, the type of block distribution, *etc.* The most interesting result is the depolarization of reflected and transmitted beams: in the general case the degree of polarization of these beams is less than unity, even if the incident beam is completely polarized. This depolarization is caused by the combined action of the transformation of beam polarizations inside the crystal and the incoherence of diffraction in different blocks (it is well known that the summation of incoherent beams with different polarizations leads to a partially depolarized beam). Note that for σ- or π-polarized beams the transformation of polarization is absent; thus, σ- and π-polarized beams are not depolarized in mosaic crystals.

The above expressions describe the differential (over the angle) characteristics of the beams. To obtain the integrated characteristics in (18)–(21) one has to use instead of J_{ik} the corresponding elements $\bar{J}_{ik}$ averaged over the angle of incidence, *i.e.* $\bar{J}_{ik} = \int_{-\infty}^{\infty} J_{ik}\,\mathrm{d}\varepsilon$.

The Bragg case

In the general case, (15)–(16) are rather formidable after substitution of the expressions for the roots of (17). Therefore, it will be assumed below that the usual absorption exceeds the extinction, *i.e.* $\mu \gg QW$ and $\mu \gg Q\tilde{W}$. We shall also assume that the mosaic plate is rather thick (so that $\mu L \gg 1$). With these assumptions the expressions for the elements of the polarization tensor of the reflected beam in the Bragg case are

$$J^r_{\sigma\sigma} = QW\gamma_0 J^i_{\sigma\sigma}/(\gamma_0 - \gamma_H)(\mu + QW),$$

$$J^r_{\pi\pi} = C^2QW\gamma_0 J^i_{\pi\pi}/(\gamma_0 - \gamma_H)(\mu + C^2QW), \qquad (22)$$

$$J^r_{\sigma\pi} = CQW\gamma_0 J^i_{\sigma\pi}/\{(\gamma_0 - \gamma_H)[\mu + (1+C^2)QW/2] + i(\gamma_0+\gamma_H)(1-C^2)Q\tilde{W}/2\},$$

where $J^i_{\sigma\sigma}$, $J^i_{\pi\pi}$, $J^i_{\sigma\pi}$ are the elements of the polarization tensor of the incident beam.

Note that for the asymmetric Bragg case ($\gamma_H \neq \gamma_0$) the reflected beam is slightly elliptically polarized even for a linearly polarized incident beam; the ellipticity is of order $Q\tilde{W}/\mu$ and is due to the imaginary part of the coefficient at $J^i_{\sigma\pi}$. The polarized incident beam (with the polarization different from σ or π) gives a slightly depolarized reflected beam $[1 - P$ is of order $(QW/\mu)^2$ or $(Q\tilde{W}/\mu)^2]$.

For the transmitted beam, within the accuracy of the terms $(QW/\mu)^2$ and $(Q\tilde{W}/\mu)^2$ one can obtain

$$\begin{aligned} J^t_{\sigma\sigma} &= J^i_{\sigma\sigma} \exp[-(\mu + QW)L/\gamma_0], \\ J^t_{\pi\pi} &= J^i_{\pi\pi} \exp[-(\mu + C^2 QW)L/\gamma_0], \\ J^t_{\sigma\pi} &= J^i_{\sigma\pi} \exp\{-[\mu + (1 + C^2)QW/2 \\ &\quad - i(1 - C^2)Q\tilde{W}/2]L/\gamma_0\} \end{aligned} \tag{23}$$

(there is no depolarization in this approximation). It follows from (23) that the ellipticity of the transmitted beam, unlike that of the reflected beam, may be large even for the linearly polarized incident beam if $(1 - C^2)Q\tilde{W}L/\gamma_0 \simeq 1$.

The Laue case

In the asymmetrical Laue case $(|\gamma_0 - \gamma_H|\mu \gg Q\tilde{W})$ the results are similar to the Bragg case. For example, the expressions for the diffracted beam are

$$\begin{aligned} J^r_{\sigma\sigma} &= J^i_{\sigma\sigma} QW\gamma_0\{\exp[-(\mu + QW)L/\gamma_0] \\ &\quad - \exp[-(\mu + QW)L/\gamma_H]\} \\ &\quad \times [(\gamma_0 - \gamma_H)(\mu + QW)]^{-1}, \\ J^r_{\pi\pi} &= J^i_{\pi\pi} C^2 QW\gamma_0\{\exp[-(\mu + C^2 QW)L/\gamma_0] \\ &\quad - \exp[-(\mu + C^2 QWL/\gamma_H]\} \\ &\quad \times [(\gamma_0 - \gamma_H)(\mu + C^2 QW)]^{-1}, \\ J^r_{\sigma\pi} &= J^i_{\sigma\pi} CQW\gamma_0\{\exp[-\mu_{\sigma\pi} L/\gamma_0] \\ &\quad - \exp[-\mu^*_{\sigma\pi} L/\gamma_H]\}[\gamma_0\mu^*_{\sigma\pi} - \gamma_H\mu_{\sigma\pi}]^{-1}, \end{aligned} \tag{24}$$

where $\mu_{\sigma\pi} = \mu + (1 + C^2)QW/2 - i(1 - C^2)Q\tilde{W}/2$. From (24) it follows that depolarization is small as in the Bragg case, but the variation of the polarization may be large and oscillates with the plate thickness. The angular dependences of polarization parameters, described by (24), are given in Fig. 1(*a*).

The above analysis of polarization properties was carried out with the assumption of strong absorption $(\mu \gg QW,\ \mu \gg Q\tilde{W})$. In the symmetrical Laue case $(\gamma_0 = \gamma_H)$ the polarization properties do not depend on absorption. For example, the expressions for the diffracted beam are given by

$$\begin{aligned} J^r_{\sigma\sigma} &= J^i_{\sigma\sigma} \sinh(QWL/\gamma_0)\exp[-(\mu + QW)L/\gamma_0], \\ J^r_{\pi\pi} &= J^i_{\pi\pi} \sinh(C^2 QWL/\gamma_0) \\ &\quad \times \exp[-(\mu + C^2 QW)L/\gamma_0], \\ J^r_{\sigma\pi} &= J^i_{\sigma\pi}(CW/\alpha)\sinh(Q\alpha L/\gamma_0) \\ &\quad \times \exp\{-[\mu + (1 + C^2)QW/2]L/\gamma_0\}, \end{aligned} \tag{25}$$

where $\alpha = [C^2 W^2 - (1 - C^2)^2 \tilde{W}^2/4]^{0.5}$. From (25) it follows that the diffracted beam may be strongly and even completely depolarized. The polarization dependences obtained from (25) are given in Fig. 1(*b*). From (25) it follows also that all polarization characteristics depend on the plate thickness in an oscillatory way if the departure angle from the Bragg law is large [so that $(1 - C^2)\tilde{W} > 2CW$]. Note that for a linearly polarized incident beam $(\mathrm{Im}\, J^i_{\sigma\pi} = 0)$ the diffracted beam remains linearly polarized, but only partially.

For the transmitted beam the results are similar to those for a diffracted one:

$$\begin{aligned} J^t_{\sigma\sigma} &= J^i_{\sigma\sigma} \cosh(QWL/\gamma_0)\exp[-(\mu + QW)L/\gamma_0], \\ J^t_{\pi\pi} &= J^i_{\pi\pi} \cosh(C^2QWL/\gamma_0)\exp[-(\mu + C^2QW)L/\gamma_0], \\ J^t_{\sigma\pi} &= J^i_{\sigma\pi}[\cosh(Q\alpha L/\gamma_0) \\ &\quad + i(1 - C^2)\tilde{W}\sinh(Q\alpha L/\gamma_0)/2\alpha] \\ &\quad \times \exp\{-[\mu + (1 + C^2)QW/2]L/\gamma_0\}. \end{aligned} \tag{26}$$

Unlike the diffracted beam, transformation of linear polarization into elliptic and *vice versa* is possible for the transmitted beam (owing to the imaginary part of the coefficient in the equation for $J^t_{\sigma\pi}$).

Integral properties

The above expressions for the polarization tensors of diffracted and transmitted beams describe the

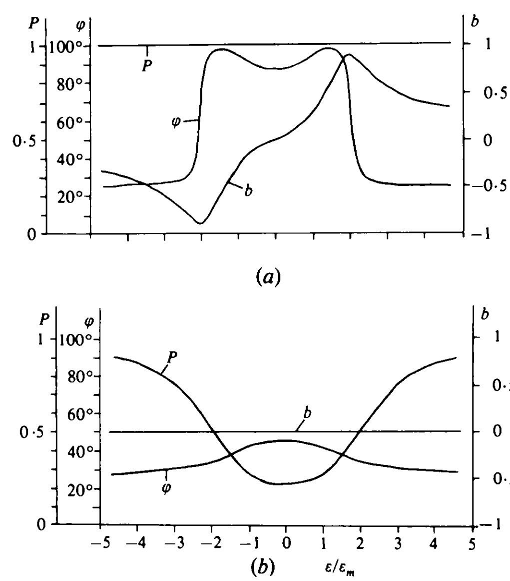

Fig. 1. The angular dependence of the polarization characteristics of the diffracted beam. P the degree of polarization; b the axial ratio of the polarization ellipse; φ the angle between the long axis of the polarization ellipse and the σ direction; ε the angular departure from the Bragg law. The incident beam is linearly polarized at 45° to the σ direction. $W(\varepsilon) = W_L(\varepsilon)$ [see equation (8*a*)]; $L = 2{\cdot}5L_e = 5\pi\varepsilon_m/Q$. (*a*) Asymmetrical Laue case [from equations (24)]; $\gamma_0 = 1$, $\gamma_H = \cos 2\theta_B = 0{\cdot}5$. (*b*) Symmetrical Laue case [from equations (25)]; $\gamma_0 = \gamma_H \cos\theta_B = \sqrt{3}/2$.

differential (over the angle) polarization properties. These expressions are applicable in the case of a narrow incident beam with angular width much less than the width of mosaic distribution. To obtain the polarization characteristics in the case of a divergent beam, these expressions should be averaged over the angles of incidence. In the general case, this averaging can be performed using numerical integration, but in special cases analytical expressions can be obtained which are also useful for the general case analysis. For example, in the asymmetrical Laue case one gets from (24) (assuming that the block distribution is Lorentzian and $\mu \gg QW$, $\mu \gg Q\tilde{W}$) the following equations for the elements of the integral polarization tensor of the diffracted beam:

$$\bar{J}^r_{ik} = \int_{-\infty}^{\infty} J^r_{ik}\,\mathrm{d}\varepsilon = \frac{J^i_{ik}\,Q\gamma_0\,C_{ik}}{(\gamma_0 - \gamma_{\mathrm{H}})} \times \{I_0(C_{ik}L/\gamma_0 L_e)\exp[-(\mu + C'_{ik}/L_e)L/\gamma_0] - I_0(C_{ik}L/\gamma_{\mathrm{H}} L_e)\exp[-(\mu + C'_{ik}/L_e)L/\gamma_{\mathrm{H}}]\}, \quad (27)$$

where $I_0(x)$ is the modified Bessel function of zeroth order, $C_{\sigma\sigma} = C'_{\sigma\sigma} = 1$, $C_{\pi\pi} = C'_{\pi\pi} = C^2$, $C_{\sigma\pi} = C$, $C'_{\sigma\pi} = (1 + C^2)/2$, $L_e = 2\pi\varepsilon_m/Q$, L_e is the secondary extinction length. For example, in the silicon crystal with $\varepsilon_m = 1'$, $L_e \simeq 200\,\mu$m for the Cu $K\alpha$ 220 reflection [the primary extinction length is $\sim 15\,\mu$m for this case (Pinsker, 1978)]. It follows from (27) that the diffracted beam is partially depolarized. In the case of a linearly polarized incident beam the diffracted one is partially polarized linearly. The variations of the polarization characteristic with plate thickness, which follow from (27), are shown in Fig. 2.

It can be shown that the variations of the integral characteristics with plate thickness are rather strongly dependent on the distribution function $W(\varepsilon)$ and diffraction geometry, but the qualitative conclusions obtained from (27) are quite general. For example, the depolarization of divergent beams is larger than that of narrow beams. This additional depolarization arises owing to the dependence of the beam polarization upon small angular departures from Bragg's law. Note that analogous depolarization of narrow beams may occur if the characteristics of a mosaic crystal (for example, the mean direction of blocks orientation) vary from point to point.

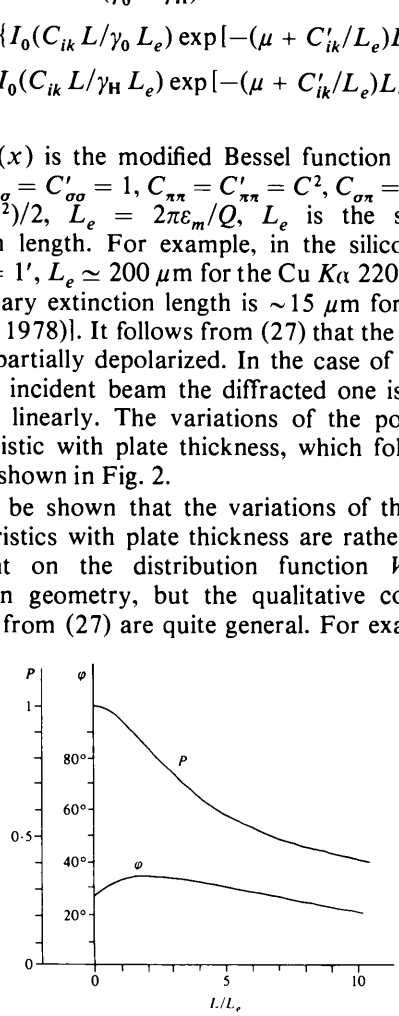

Fig. 2. The integral (over the angle of incidence) polarization characteristics of the diffracted beam *versus* the crystal thickness. Asymmetrical Laue case: $\gamma_0 = 1$, $\gamma_{\mathrm{H}} = \cos 2\theta_B = 0{\cdot}5$; $W(\varepsilon) = W_L(\varepsilon)$. $L_e = 2\pi\varepsilon_m/Q$. The incident beam is linearly polarized at 45° to the σ direction.

Conclusion

The results presented here reveal qualitative differences of X-ray polarization properties in mosaic crystals as compared with perfect ones. The most natural and pronounced difference is the depolarization of X-ray beams in mosaic crystals. (This depolarization occurs only if the polarization of the incident beam differs from σ or π.)

The mosaic crystals, as are the perfect ones, are birefringent. The birefringence and the secondary extinction lead to the transformation of X-ray polarization. Being determined by the function $\tilde{W}(\varepsilon)$, the birefringence decreases rather slowly (as $1/\varepsilon$) for large deviations ε of the incident beam from the Bragg condition. Therefore, the birefringence for the direct beam is significant even far from the Bragg angle where the intensity of the diffracted beam is practically negligible.

Thus, there are rather complicated and informative dependences of the X-ray polarization properties on the parameters of mosaic crystals. In particular, the measurements of polarization characteristics as a function of departure from Bragg's law give us a way to determine simultaneously both the distribution function $W(\varepsilon)$ and the related function $\tilde{W}(\varepsilon)$. The latter gives a way to check on the self-consistency of the measurements by means of the dispersion relation (5).

Polarization dependences discussed above have been experimentally examined for perfect crystals (Mikhajljuk *et al.*, 1977; Cohen & Kuriyama, 1978; Hart, 1978). The results of corresponding measurements in mosaic crystals are not available. The measurements in mosaic crystals could be performed in the ways similar to those realized by Mikhajljuk *et al.*, Cohen & Kuriyama and Hart. The other promising way is the application of synchrotron radiation which is naturally polarized (Codling, 1973; Yakimenko, 1974).

In the present treatment it is assumed that $F_{\mathrm{H}}F_{-\mathrm{H}}$ is real. In general, $F_{\mathrm{H}}F_{-\mathrm{H}}$ is a complex quantity and its imaginary part accounts for Borrmann absorption. The Borrmann effect in mosaic crystals will be discussed elsewhere.

In conclusion it should be noted that equations for polarization tensors may be useful for the description of diffraction of other types of radiation in mosaic crystals, for example neutrons and Mössbauer radiation in magnetically ordered crystals and light in cholesteric liquid crystals (Dmitrienko & Belyakov, 1977).

References

BECKER, P. (1977). *Acta Cryst.* A**33**, 243–249.
BORN, M. & WOLF, E. (1964). *Principles of Optics*. Oxford: Pergamon Press.
CHANDRASEKHAR, S. (1950). *Radiative Transfer*. Oxford: Clarendon Press.
CHANDRASEKHAR, S. (1960). *Adv. Phys.* **9**, 363–386.
CODLING, K. (1973). *Rep. Prog. Phys.* **36**, 541–624.
COHEN, G. G. & KURIYAMA, M. (1978). *Phys. Rev. Lett.* **40**, 957–960.
DARWIN, C. G. (1922). *Philos. Mag.* **43**, 800–829.
DMITRIENKO, V. E. & BELYAKOV, V. A. (1977). *Zh. Eksp. Teor. Fiz.* **73**, 681–691. (*Sov. Phys. – JETP*, **46**, 356–362.)
HART, M. (1978). *Philos. Mag.* B**38**, 41–56.
JENNINGS, L. D. (1968). *Acta Cryst.* A**24**, 472–474.
KATO, N. (1976). *Acta Cryst.* A**32**, 458–466.
LANDAU, L. D. & LIFSHITZ, E. M. (1958). *Quantum Mechanics*. Reading, Mass.: Addison-Wesley.
MIKHAJLJUK, I. P., KSHEVETSKIJ, S. A., OSTAPOVICH, M. V. & SHAFRANJUK, V. P. (1977). *Ukr. Fiz. Zh.* (*Ukr. Ed.*), **22**, 61–64.
OLEKHNOVICH, N. M. & MARKOVICH, V. L. (1978). *Kristallografiya*, **23**, 658–661.
OLEKHNOVICH, N. M., RUBTSOV, V. A. & SHMIDT, M. P. (1975). *Kristallografiya*, **20**, 796–802.
PINSKER, Z. G. (1978). *Dynamical Scattering of X-rays in Crystals*. Berlin: Springer Verlag.
ROZENBERG, G. V. (1977). *Usp. Fiz. Nauk*, **121**, 97–138.
SKALICKY, P. & MALGRANGE, C. (1972). *Acta Cryst.* A**28**, 501–507.
VAILLANT, F. (1977). *Acta Cryst.* A**33**, 967–970.
YAKIMENKO, M. N. (1974). *Usp. Fiz. Nauk*, **114**, 55–66.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1980). A**36**, 1050–1057

Direct Analysis of Nuclear Distributional Moments in Zinc*

BY AINO VAHVASELKÄ

Department of Physics, University of Helsinki, Siltavuorenpenger 20 *D, SF*-00170 *Helsinki* 17, *Finland*

(*Received* 4 *February* 1980; *accepted* 14 *July* 1980)

Abstract

The direct-analysis formalism of Kurki-Suonio [*e.g. Isr. J. Chem.* (1977), **16**, Nos. 2–3, 115–123, 132–136] is modified to apply to the calculation of nuclear distributional moments $\langle x^\lambda y^\mu z^\nu \rangle$, which are linear combinations of the multipole moments $\langle r^k y_{lmp} \rangle$. They are integrated from the radial coefficients of the corresponding multipole terms through Gaussian and difference series procedures. An application to the thermal neutron diffraction structure factors of Merisalo & Larsen [*Acta Cryst.* (1977), A**33**, 351–354] on zinc indicates that the moment $\langle x^2 \rangle$ agrees with the anharmonic result of Merisalo & Larsen. $\langle z^2 \rangle$ does not show discrepancy with the value based on harmonic assumption. The existence of the third-order component in the nuclear smearing function and, due to this, anharmonicity of thermal motion is well established, but the magnitude of $\langle x^3 \rangle$ is not accurately defined on the basis of the present data. The ratios of the fourth and second moments do not reveal deviation from harmonic thermal smearing.

* Part of the doctoral thesis of Aino Vahvaselkä (1978). Report Series in Physics, HU-P-D10, University of Helsinki, Department of Physics, Helsinki, Finland.

0567-7394/80/061050-08$01.00

1. Introduction

The study of nuclear distributional moments by direct analysis in this work is intended to deal with deformation of harmonic nuclear smearing in hexagonal close-packed zinc. The non-centrosymmetric positions of the Zn atoms offer a possibility to study anharmonicity beyond merely centrosymmetric contributions. The direct-analysis formalism applied has been developed from the principles in studies concerning electronic charge and nuclear density distributions presented by Kurki-Suonio and his collaborators (*e.g.* Kurki-Suonio & Meisalo, 1967; Kurki-Suonio & Ruuskanen, 1971; Kurki-Suonio, Merisalo, Vahvaselkä & Larsen, 1976).

Merisalo & Larsen (1977) (hereafter M & L) have recently performed elastic neutron scattering measurements of the structure factors of Zn in order to study anharmonicity of lattice vibrations by a parameter-fitting procedure. The insufficiency of a harmonic formalism to explain thermal vibrations in crystals has caused vivid interest to focus on anharmonicity. This phenomenon seems to be amenable to study by several different methods as summarized by Willis & Pryor (1975), and indicated by the studies of Whiteley, Moss & Barnea (1978); Merisalo, Järvinen & Kurittu (1978);