POLARIZATION PHENOMENA IN X-RAY DIFFRACTION

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INTRODUCTION

The dielectric properties of most materials in the X-ray fre-
quency region are such that the polarization phenomena which are ob-
served for visible light (such as birefringence and optical activity)
are not found. This is due to the fact that K or L electrons which
are important in X-ray scattering are shielded from crystalline fields.
The problem was already considered theoretically as early as 1939 by
Moliere (1,2) who concluded that polarization phenomena are expected
to be very small exept very close to an absorption edge. Hojo, Oht-
suki & Yanagawa (3) showed that what they call "polarization mixing"
is expected to be theoretically exactly zero as long as hydrogen –
like eigenfunctions are used to describe the scattering of X-rays.

The situation is different for a diffracting crystal. The
Thomson electron scattering depends on the relationship between the
polarization vector and the wave vectors. We can therefore expect
that polarization phenomena would be marked when elastic (Bragg)-
scattering is important.

THEORY

The influence of the dielectric properties of crystals on the
polarization of the crystal waves was explored in detail in two pa-
pers by Moliere (1,2). The results shall be briefly discussed here.
The fundamental equations of the dynamical theory which is discussed
by Authier (4) have the following form

$$(1) \qquad (1 - \frac{k^2}{K_m^2}) \vec{D}_m = \sum_q \left[C_{mq} \vec{D}_q \right]_\perp \vec{K}_m$$

The C_{mq} have generally tensor character (in x,y,z, not in m,q!).
They consist of the Fourier coefficients of the scalar dielectric
susceptibility χ_{m-q} and a complex term A_{mq} which can be split into
a scattering and an absorption term:

(2)
$$C_{mq} = \chi_{m-q} + A_{mq}^{scat} + A_{mq}^{abs}$$

These A_{mq} terms become important only near an absorption edge. They have tensor character and thus determine the tensor properties of C_{mq}. For X-ray frequencies far from an absorption edge A_{mq} is neglegibly small and C_{mq} is equal to the Fourier coefficient of the dielectric susceptibility χ.

Following Moliere (1,2), we introduce N different coordinate systems (one for each beam) for a "mixed representation" of the tensor C_{mq}. The mth coordinate system has its z-axis parallel to the wave vector $\vec{K}_m$. The amplitudes $\vec{D}_m$ are perpendicular to the corresponding $\vec{K}_m$. Taking the index $\vec{K}_m$ on the right hand side of equation (1) into account, we obtain a two-dimensional reduced tensor C'_{mq} which contains no z-components. With the introduction of the excitation errors ε_m as usual (4):

(3)
$$2\,\varepsilon_m = (1 - \frac{k^2}{K_m^2})$$

a system of two dimensional matrix equations is obtained

(4)
$$\sum_{q}^{N} \left\{ C_{mq} - 2\,\varepsilon_m\,\delta_{mq} \right\} \vec{D}_q = 0$$

where δ_{mq} is Kronecker's delta. This can alternatively be written as a 2N dimensional matrix equation

(5)
$$([C] - 2[\varepsilon])\,\vec{D} = 0$$

where $[\varepsilon]$ contains the excitation errors and the two-dimensional unitary matrices E_2:

(6)
$$[\varepsilon] = \begin{bmatrix} \varepsilon_0 E_2 & 0 & 0 & \cdot \\ 0 & \varepsilon_m E_2 & 0 & \cdot \\ 0 & 0 & \varepsilon_q E_2 & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

Equation (5) can be regarded as an eigenvalue problem. The 2N-dimensional eigenvectors $\vec{D}$ contain the components of the electric vectors of the crystal waves. Their polarization depends on the properties of the matrix $[C]$. In the most general case, this is a non-hermitean matrix and the system of crystal waves is elliptically polarized with no definite relationship between the axes and the eccentricities

of the ellipses. When the crystal has a center of symmetry and no absorption the matrix $[C]$ is real and symmetric and the system of crystal waves is linearly polarized with mutually perpendicular planes of polarization. This is the case which is generally assumed in the dynamical theory of diffraction. The following Table 1 summarizes the polarization of the crystal waves as a function of the properties of the matrix $[C]$.

Table 1

center of symmetry	no center
$A_{oo}^{abs} = 0$	
$[C]$ real, symmetric $$\vec{D}_{o1} = \begin{pmatrix} a \\ 0 \end{pmatrix} \qquad \vec{D}_{o2} = \begin{pmatrix} 0 \\ a \end{pmatrix}$$ linearly polarized	$[C]$ complex, hermitean $$\vec{D}_{o1} = \begin{pmatrix} a \\ ib \end{pmatrix} \qquad \vec{D}_{o2} = \begin{pmatrix} ib \\ a \end{pmatrix}$$ elliptically polarized
$A_{oo}^{abs} \neq 0$	
$[C]$ $\quad A_{oo}^{scat} + A_{oo}^{abs}$ $\qquad\quad\downarrow \qquad\qquad \downarrow$ $\qquad\quad$ real $\qquad$ imaginary $\qquad\quad$ symm. $\qquad$ symm. $$\vec{D}_{o1} = \begin{pmatrix} a \\ ib \end{pmatrix} \qquad \vec{D}_{o2} = \begin{pmatrix} -ib \\ a \end{pmatrix}$$	$[C]$ complex, non-hermitean $\vec{\vec{D}}$ $\quad$ elliptically polarized $\qquad$ no relation between a,b

For simple transmission (no Bragg reflection excited) the optical properties of the crystal are determined by the quantity $\chi_o + A_{oo}$.

Following Moliere (1,2) we can better understand the nature of the terms making up the $[C]$ matrix when we consider the electric polarization $\vec{P}(\vec{r},t)$ in the crystal which is induced by the X-ray field $\vec{E}(\vec{r},t)$. It has the following form:

$$(7) \qquad \vec{P}(\vec{r},t) = \int_{crystal} \left[\chi(\vec{r}') \cdot \delta(\vec{r}-\vec{r}') + \underline{A}(\vec{r},\vec{r}') \right] \vec{E}(\vec{r}',t) \, dV$$

The quantity $\underline{A}(\vec{r},\vec{r}')$ has tensor character and its Fourier coefficients are the A_{mq} in equation (2). From this equation we see that the polarization $\vec{P}(\vec{r},t)$ depends not only on the electric field at the

same position but depends on the electric field throughout the crystal. These non-local terms cause non-diagonal elements in the matrix [C] and consequently complex eigenvectors which describe polarization phenomena. The quantity $\underline{A}(\vec{r},\vec{r}')$ has the following form:

$$(8) \quad \underline{A}(\vec{r},\vec{r}') = \frac{1}{\varepsilon_0} \frac{e^2}{hmc^2} \frac{\lambda^2}{4\pi^2} \sum_n \left[\frac{\{\vec{J}_{on}(\vec{r}) \cdot \vec{J}_{on}^+(\vec{r}')\}}{\gamma - \gamma_{no}} + \frac{\{\vec{J}_{on}^+(\vec{r}) \cdot \vec{J}_{on}(\vec{r}')\}}{\gamma + \gamma_{no}} \right]$$

where the $\vec{J}_{on}$ are the current matrix elements between the unperturbed $|0\rangle$ state and the various other states $|n\rangle$ of the many electron solid. The $\{\}$ brackets denote tensor products. The γ_{no} are the resonance frequencies. There are some important points to the behaviour of $\underline{A}(\vec{r},\vec{r}')$. With increasing frequency $\underline{A}$ falls off as γ^{-3} whereas χ falls off as γ^{-2}. From a certain γ_{no} we can therefore neglect A_{mq} in equn.(2). Also, $\underline{A}$ falls off very rapidly with increasing difference between $\vec{r}$ and $\vec{r}'$, having nearly the character of a delta function such as the first term in equn.(7). This would cause $\underline{A}$ to loose its tensor character and to become essentially a scalar correction term for χ_{m-q}. The reason for this behaviour is that the current (indicated by $\vec{J}_{on}$) which flows in atom Nr. i when an electron in its K-shell is excited flows to a good approximation only in that one atom, causing the non-local character of the second term in eqn.(7) to be small. The argument is similar to the one that justifies the use of the random phase approximation in the treatment of many electron systems which neglects, in the electron field and electron electron interactions, the coupling between interactions of different momentum transfers (5,6). Since K or L electrons (which are important at X-ray frequencies) are rather well shielded from crystalline fields we can expect this to be the case in X-ray scattering.

It is therefore not surprising that up to now no polarization effects have been found for X-rays in simple transmission. Careful measurements by Hart (7) performed for $\lambda = 1,54$ Å were able to detect neither significant optical rotatory power, nor circular dichroism in quartz, nor linear dichroism in sheet polaroid.

BRAGG REFLECTING CRYSTALS

Even if the matrix $[C]$ is real and symmetric (Table 1) a wide variety of polarization phenomena exists in the case where a strong Bragg reflection is excited. We restrict the discussion to the well-known two-beam case (4). Figure 1 shows the four-branch dispersion surface for this case which lies in real k-space when absorption is neglected. The excitation points (tie-points) for waves with their electric vectors perpendicular and parallel to the plane of incidence (the plane of the drawing) lie on the σ and π -branches, respectivel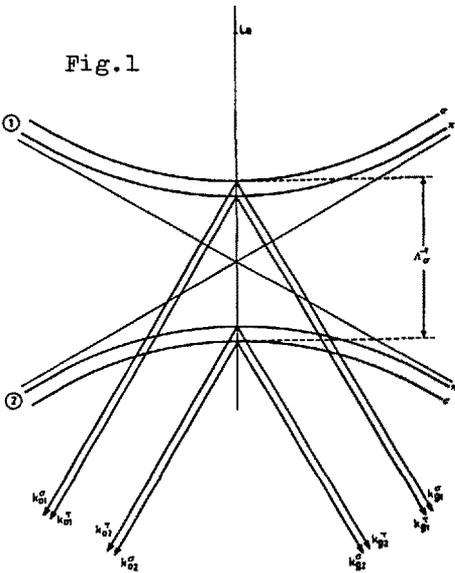y. The important points are that the wave field propagation (wave fields (1) and (2)) is perpendicular to the dispersion surface at the tie-point of the wave vectors and that the absorption is different for both wave fields (1) and (2) and for both states of polarization. A diffracting crystal will therefore exhibit linear dichroisms (8,9). It is also birefringent as was shown in ray tracing experiments. At the exit surface of the crystal we expect a fringe system (the "Pendellösung-fringes") for each state of polarization due to the wave vector difference $\Delta\vec{k}_{1,2}$. When natural light (i.e. light where all states of polarization are equally present) is diffracted this will result in the superposition of two fringe systems with different spacings Λ_σ and Λ_π for the two polarization states, respectively. This causes a "beat-pattern" or a periodic fading of the fringes which was first explained by Hart and Lang (11) and by Hattori et.al.(12) for spherical waves. The amplitude of the fringes is modulated by the beat of the two patterns with the factor

Fig.1

(9)
$$\cos\left\{\pi\left(\frac{1}{\Lambda_\sigma} - \frac{1}{\Lambda_\pi}\right)\cdot t\right\}$$

where t is the crystal thickness. For the exact Bragg condition and the symmetrical Laue-case, the wave vector difference is given by

(10) $$(\vec{k}_{g1} - \vec{k}_{g2})_{\sigma,\pi} = \frac{k}{\cos\theta} C |\chi_g| = \frac{1}{\Lambda_{\sigma,\pi}}$$

with the polarization factor C which is 1 for σ-polarization and $C = \cos 2\theta$ for the π-polarization. The quantity χ_g is again the Fourier coefficient of the susceptibility χ. Both the transmitted and the diffracted waves at the exit surface remain unpolarized.

When the incident wave is already linearly polarized we must consider a possible interference between all crystal waves which are now coherent. As was shown by Skalicky and Malgrange (9) the crystal will produce elliptically polarized crystal waves and turn the plane of polarization of the incident wave. Let us assume that the electrical vector is inclined at 45° with respect to the plane of incidence. If we consider the diffracted waves only we have four component plane waves with the wave vectors $\vec{k}_{g1}^{\sigma}$, $\vec{k}_{g1}^{\pi}$, $\vec{k}_{g2}^{\sigma}$, $\vec{k}_{g2}^{\pi}$. Unlike in the case of natural light these waves with different states of polarization are not independent. The phase difference between the waves of index (1) is given by

(11) $$2\pi(\vec{k}_{g1}^{\sigma} - \vec{k}_{g1}^{\pi})\cdot\vec{r} = \pi(\frac{1}{\Lambda_{\sigma}} - \frac{1}{\Lambda_{\pi}})\cdot t$$

This means that the wave fields belonging to branch (1) of the dispersion surface will generally be elliptically polarized. The amplitude ratio is

(12) $$\frac{\vec{D}_{g1}^{\sigma}}{\vec{D}_{g1}^{\pi}} = \frac{a_1^{\sigma}}{a_1^{\pi}} \cdot \exp(-\frac{1}{2}[\mu_1^{\sigma} - \mu_1^{\pi}]t) \cdot \exp(2\pi i[k_{g1}^{\sigma} - k_{g1}^{\pi}]\cdot t)$$

where μ_1^{σ} and μ_1^{π} are the absorption coefficients for the two states of polarization. The ratio of the amplitudes of the plane wave components is $a_1^{\sigma}/a_1^{\pi} = a_2^{\sigma}/a_2^{\pi} = \cos 2\theta$. The wave fields belonging to branch (1) of the dispersion surface are of right hand polarization while the branch (2) waves are of opposite hand. The state of polarization of the crystal waves and the result of their interference are schematically summarized in Fig.2. We can introduce a polarization periodicity Ω. It is given by:

(13) $$\frac{1}{\Omega} = \frac{1}{2}(1 - |\cos 2\theta|)\frac{1}{\Lambda_{\sigma}}$$

Fig.2
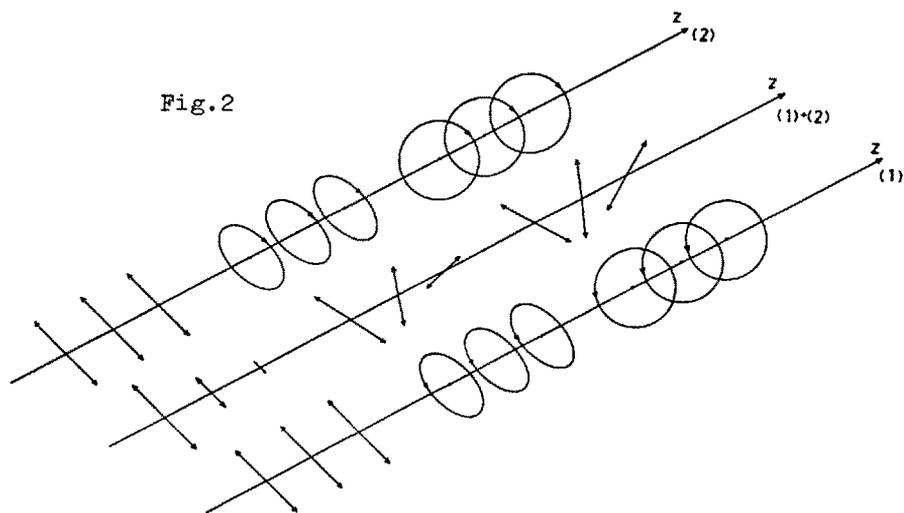
The phase difference between the σ and the π components can thus be expressed as $\exp(2\pi i t/\Omega)$. This means that the same state of polarization is repeated with a depth periodicity of Ω . Circular polarization occurs for a thickness of $\Omega/4 + n\Omega/2$. A crystal with such a thickness is therefore a quarter wave plate for both wave fields (1) and (2). The thickness of a silicon quarter wave plate for copper K_α radiation using the 220 Bragg reflection is 24,2 μm.

If the two wave fields (1) and (2) overlap, they will interfere and give fringes at the exit surface. The interference between two elliptically polarized waves with the same amplitude and eccentricity but opposite sense of turning gives a linearly polarized wave. The amplitude and orientation of this linearly polarized resultant wave depends on the phase difference between the two elliptically polarized waves. The contrast of the fringes depends therefore on the state of polarization. It is strongest where both wave fields have linear polarization and fading is expected where both wave fields have circular polarization. The results are summarized in Table 2 and Fig.2.

An elegant way of doing experiments with polarized X-rays is the use of synchrotron radiation which has been used to verify the above results (13). The advantage is a high intensity for any given orientation of the plane of polarization with respect to the plane of incidence which is always a problem in many crystal settings (7,9). The two photographs in Fig.3 were both recorded with the same exposure time of 2 min at the D.C.I. storage ring at L.U.R.E. (Orsay, France).

Table 2 Crystal thickness and polarization			
thickness	$\delta = \left|k^{\pi} - k^{\sigma}\right|$	polarization	fading
0	0	linear	fringes
$\Omega/4$	$\pi/2$	circular	fading
$\Omega/2$	π	linear	fringes
$3\Omega/4$	$3\pi/2$	circular	fading

(a)   Fig.3   (b)
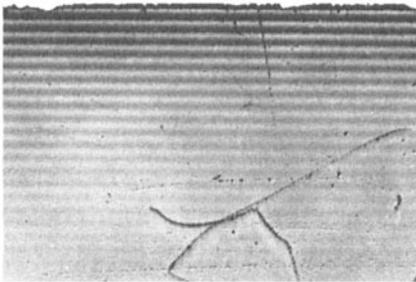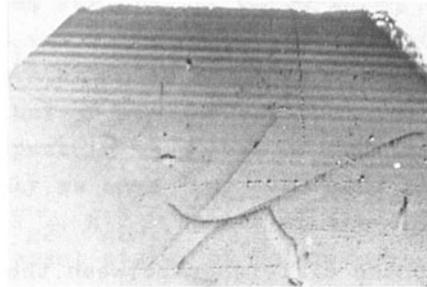
A silicon wedge shaped crystal was oriented for a 220 reflection of $\lambda = 0,9$ Å with the plane of polarization normal to the plane of incidence (Fig.3a) and inclined at 45° with respect to the plane of incidence at nearly the same wavelength $\lambda = 1,1$ Å (Fig.3b). According to the theory a periodic fading of the fringes separated by 5,2 fringes is observed thus indicating the excitation of component waves on all four branches of the dispersion surface.

When a beam of circularly polarized X-rays is desired, the diffracting crystal must either be very thick and set away from the exact Bragg condition so that the wave fields (1) and (2) will propagate in different directions which are given by the normals to the dispersion surface or the Borrmann effect may be employed to damp wave field (2) which has the higher absorption, out. Such a setting was used by Hart (7) with a three quarter wave plate which is superior to the quarter wave plate because it is thicker.

In principle thus all polarization experiments which are possible with visible light can be performed with X-rays with the help of diffracting crystals.

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