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Forbidden Reflections due to Anisotropic X-ray Susceptibility of Crystals

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Abstract

Methods have been developed for predicting the properties of the new type of structurally forbidden reflections arising from anisotropic X-ray susceptibility of crystals. The general symmetry properties of the spatially dependent tensor of X-ray susceptibility are described. From this tensor the structure amplitudes and new extinction rules for the screw-axis and glide-plane 'forbidden' reflections are derived. All these forbidden reflections may be excited except the $00l$ ($l = 2n + 1$) reflections for a 6_3 screw axis and the $00l$ ($l = 6n + 3$) reflections for 6_1 and 6_5 screw axes. The polarization properties of these forbidden reflections are very unusual. For example, a σ-polarized incident beam can give a π-polarized diffracted one and *vice versa*; in some cases only a circularly polarized beam is diffracted, *etc.* Some estimations show that near the X-ray absorption edges the structure amplitudes of these reflections can be of the order of a few electrons atom^{-1}. The general methods are illustrated by their application to the rutile structure.

Introduction

It is well known that the conditions limiting possible X-ray reflections are only applied when the equivalent positions in a crystal are assumed to be occupied by atoms with the same scattering amplitude. In fact, the interatomic interaction leads to small asphericity of atoms and, in general, the scattering amplitudes of the crystallographically equivalent atoms are not the same. Hence, 'forbidden' reflections can occur.

There are several physical reasons for the scattering amplitudes of the crystallographically equivalent atoms to be nonequivalent. The asphericity of atomic electron density and anisotropic and anharmonic thermal motion in crystals are the best known causes of forbidden reflections (Renninger, 1937; Dawson, 1967*a*, 1967*b*). The well known example is the 222 reflection in crystals with the diamond structure. Then, the scattering amplitude is spin-dependent and the magnetic X-ray reflections are observed in the magnetically ordered crystals (de Bergevin & Brunel, 1981; Brunel & de Bergevin, 1981; Faleyev, Lomov & Labushkin, 1981). The least known cause of forbidden reflections is the anisotropy of X-ray susceptibility of atoms in crystals (Templeton & Templeton, 1980). This anisotropy is very small in the X-ray region and in conventional X-ray diffraction theories the tensor of susceptibility is supposed to be isotropic (Vainshtein, 1979; Iveronova & Revkevich, 1972; Pinsker, 1978). But near X-ray absorption edges the absorption of X-ray beams depends on their polarization and in this case the anisotropy of susceptibility is essential (Azároff & Pease, 1974; Heald & Stern, 1977; Templeton & Templeton, 1980; Cox & Beaumont, 1980, and references therein). Thus, near the absorption edges the anisotropy of X-ray susceptibility should be taken into account in X-ray diffraction and the intensities of the forbidden reflections mentioned above may have measurable values (for convenience, hereafter these reflections will be called ATS reflections, where ATS denotes the anisotropy of the tensor of susceptibility). It is our purpose here to show how the general properties of ATS reflections can be obtained from the symmetry considerations. The optimum conditions for the experimental observation of ATS reflections and possible applications of these reflections are also discussed.

Symmetry properties of the tensor of susceptibility

To describe the diffraction of X-rays in crystals one needs the tensor of susceptibility $\hat{\chi}(\mathbf{r})$ for the X-ray frequency range. For the optical range all crystals may be regarded as a homogeneous media and only the uniform part of the susceptibility should be taken into account. The symmetry properties of this part are completely determined by the point group of the crystal and are well known from optics. For X-ray diffraction the spatially-dependent periodic part of $\hat{\chi}(\mathbf{r})$ is essential. The symmetry of this part of $\hat{\chi}(\mathbf{r})$ is different in the different points of a unit cell and is determined by the space group of the crystal. The general properties of

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X-ray susceptibility have been discussed by Kolpakov, Bushuyev & Kuz'min (1978). In the present paper it will be assumed for simplicity that the susceptibility $\hat{\chi}(\mathbf{r})$ gives at every point $\mathbf{r}$ the local relationship between the X-ray electric field $\mathbf{E}(\mathbf{r})$ and the polarization of the crystal $\mathbf{P}(\mathbf{r})$,

$$4\pi\mathbf{P}(\mathbf{r}) = \hat{\chi}(\mathbf{r})\,\mathbf{E}(\mathbf{r}). \qquad (1)$$

Owing to the anisotropy of susceptibility the vector $\mathbf{P}(\mathbf{r})$ is not parallel to $\mathbf{E}(\mathbf{r})$. Equation (1), usually used in X-ray diffraction theories, implies that spatial dispersion is absent. The frequency dispersion is not omitted and $\hat{\chi}(\mathbf{r})$ is supposed to be a function of X-ray frequency. The tensor $\hat{\chi}(\mathbf{r})$ is symmetrical: $\chi_{ik}(\mathbf{r}) = \chi_{ki}(\mathbf{r})$; $i, k = 1, 2, 3$.

Thus, we should obtain the most general tensor $\hat{\chi}(\mathbf{r})$ which is invariant under the space group of the crystal. This may be done in the following way. All atoms occupy the definite set of equivalent positions in a unit cell. Therefore, first we can obtain the tensor $\hat{\chi}_b(\mathbf{r})$ for some basic atom of the set taking into account the point symmetry of its position. Then, the tensor $\hat{\chi}_j(\mathbf{r})$ for the jth atom of the set can be obtained from $\hat{\chi}_b(\mathbf{r})$ by the symmetry transformation which connects the jth atom with the basic one. Finally, the complete tensor $\hat{\chi}(\mathbf{r})$ is the sum taken over all j and over all sets of equivalent positions occupied by atoms.

To do all these calculations we should know the transformations of $\hat{\chi}(\mathbf{r})$ under symmetry operations. Let us consider a symmetry operation g which includes a point operation (rotation and/or mirror reflection) and some translation. Under this operation an arbitrary tensor $\hat{\chi}(\mathbf{r})$ is transformed into another tensor $\hat{\chi}_g(\mathbf{r})$ in the following way (Korn & Korn, 1968; Shubnikov & Koptsik, 1972):

$$\hat{\chi}_g(\mathbf{r}) = \hat{R}_g\,\hat{\chi}(\mathbf{r}')\,\hat{R}_g^{-1}, \qquad (2)$$

where $\mathbf{r}' = R_g^{-1}(\mathbf{r} - \mathbf{a}_g)$, $\hat{R}_g$ is the matrix of the point operation, $\mathbf{a}_g$ is the vector of translation. If $\hat{\chi}(\mathbf{r})$ is invariant under the operation g, then $\hat{\chi}_g(\mathbf{r}) = \hat{\chi}(\mathbf{r})$ and, hence,

$$\hat{\chi}(\mathbf{r}) = \hat{R}_g\,\hat{\chi}(\mathbf{r}')\,\hat{R}_g^{-1}. \qquad (3)$$

The tensor $\hat{\chi}_b(\mathbf{r})$ of the basic atom should be invariant under all $g \in G$, where G is the point group of the basic atom position. The most general tensor with such properties may be constructed from an arbitrary symmetric tensor $\hat{\alpha}(\mathbf{r})$ by the following averaging over the group G

$$\hat{\chi}_b(\mathbf{r}) = \langle\hat{\alpha}(\mathbf{r})\rangle_G \equiv \sum_{g \in G} \hat{R}_g\,\hat{\alpha}(\hat{R}_g^{-1}\,\mathbf{r})\,\hat{R}_g^{-1} \qquad (4)$$

[in (4) we put $\mathbf{a}_g = 0$ because G is the point group]. Then, from (2) we can obtain the tensor $\hat{\chi}_j(\mathbf{r})$ of the jth atom using the symmetry operation g_j which connects the position of the jth atom with the basic one. Finally, the summation over all j and over all sets of occupied positions gives us the most general tensor $\hat{\chi}(\mathbf{r})$ which is invariant under the space group of the crystal. Notice that in these calculations the asphericity of the atomic electron density is taken into account automatically {being scalar the electron density is proportional to $Sp[\hat{\chi}(\mathbf{r})]$}. Now, using the symmetry properties of $\hat{\chi}(\mathbf{r})$ we can study the properties of ATS reflections.

Forbidden reflections

It is well known that the conditions limiting possible reflections may be different for general and special sets of positions (*International Tables for X-ray Crystallography*, 1952). If the asphericity of the atomic electron density or thermal motion is taken into account, then the special conditions are violated but the general ones are not. However, the latter conditions can also be violated if the anisotropy of the tensor of susceptibility is taken into account. It is clear that those general conditions which arise for centred lattices remain valid, because for pure translations the transformations are the same both for tensors and for scalars. But the glide-plane and screw-axis conditions are no longer valid (Templeton & Templeton, 1980) and now we shall prove this rigorously.

It is convenient to introduce the tensor structure amplitude $\hat{F}^H$, which is proportional to the Fourier component $\hat{\chi}^H$ of the tensor $\hat{\chi}(\mathbf{r})$:

$$\hat{F}^H = -\frac{v}{r_0\lambda^2}\,\hat{\chi}^H \equiv -\frac{v}{r_0\lambda^2}\int \hat{\chi}(\mathbf{r})\exp(2\pi i\mathbf{H}\mathbf{r})\,\mathrm{d}\mathbf{r}, \qquad (5)$$

where v is the volume of the unit cell; r_0 is the classical electron radius, $r_0 = e^2/(mc^2)$; λ is the X-ray wavelength; $\mathbf{H}$ is the reciprocal-lattice vector; the integration is over the volume of the unit cell.

Consider first the glide-plane forbidden reflections. Let the glide plane c be normal to the axis x and, hence, any point x,y,z is transformed into $\bar{x}, y, z + \frac{1}{2}$. For $0kl$ reflections the tensor structure amplitude is given by

$$F^{0kl} = -\frac{v}{r_0\lambda^2}\int \hat{\chi}(x,y,z)\exp[2\pi i(ky + lz)]\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z. \qquad (6)$$

The susceptibility $\hat{\chi}(x,y,z)$ should be invariant under the glide-plane transformation and from (3) it follows that

$$\hat{\chi}(x,y,z) = \hat{R}_m\,\hat{\chi}(\bar{x}, y, z - \tfrac{1}{2})\,\hat{R}_m^{-1}, \qquad (7)$$

where the transformation matrices $\hat{R}_m$ and $\hat{R}_m^{-1}$ are given by

$$\hat{R}_m = \hat{R}_m^{-1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (8)$$

Substituting (7) into (6) and changing the integration variables we have

$$\hat{F}^{0kl} = e^{-i\pi l}\,\hat{R}_m \hat{F}^{0kl}\,\hat{R}_m^{-1}. \qquad (9)$$

If the anisotropy of susceptibility is absent then the structure amplitude is scalar and from (9) we obtain

$$F_{0kl} = e^{-i\pi l}\,F_{0kl}. \qquad (10)$$

In this case $F_{0kl} \neq 0$ if $l = 2n$ ($n = 1, 2, 3, \ldots$) and we have the well known glide-plane condition for possible reflections (*International Tables for X-ray Crystallography*, 1952). But if the anisotropy of susceptibility is taken into account then the matrices $\hat{R}_m$ and $\hat{R}_m^{-1}$ change the sign of the xy and xz components of the tensor structure amplitude $\hat{F}^{0kl}$ on the right side of (9). For forbidden reflections we have $e^{-i\pi l} = -1$ and tensor $\hat{F}^{0kl}$ can contain the xy and xz components only:

$$\hat{F}^{0kl} = \begin{pmatrix} 0 & F_1 & F_2 \\ F_1 & 0 & 0 \\ F_2 & 0 & 0 \end{pmatrix}, \qquad (11)$$

where F_1 and F_2 are independent parameters, $l = 2n + 1$. From (11) it is clear that reflections with $l = 2n + 1$ arise due to the anisotropy of susceptibility and cannot arise due to the asphericity of atomic electron density because the Fourier transformation of the density is proportional to $Sp(\hat{F}^{0kl})$ and is equal to zero. For nonforbidden reflections the tensor structure amplitude is determined by four independent parameters

$$\hat{F}^{0kl} = \begin{pmatrix} F_1 & 0 & 0 \\ 0 & F_2 & F_4 \\ 0 & F_4 & F_3 \end{pmatrix}; \quad l = 2n. \qquad (12)$$

Now let us consider the screw-axis forbidden reflections. The screw axis n_j is assumed to be along z and contains the rotation at angle $\psi = 2\pi/n$ around z and the translation j/n along z ($j < n$). For the 00l reflections the structure amplitude (5) is given by

$$\hat{F}^{00l} = -\frac{v}{r_0 \lambda^2} \int \hat{\chi}(x,y,z) \exp\,(2\pi i l z)\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z. \qquad (13)$$

The susceptibility $\hat{\chi}(x,y,z)$ should be invariant under the screw-axis transformations and from (3) we find that

$$\hat{\chi}(x,y,z) = \hat{R}_\psi\, \hat{\chi}(x', y', z - j/n)\, \hat{R}_\psi^{-1}, \qquad (14)$$

where $\psi = 2\pi/n$, $\hat{R}_\psi^{-1} = \hat{R}_{-\psi}$,

$$\hat{R}_\psi = \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix};$$

$$\begin{cases} x' = x\cos\psi + y\sin\psi \\ y' = -x\sin\psi + y\cos\psi. \end{cases} \qquad (15)$$

Then, substituting (14) into (13) and changing the integration variables we have

$$\hat{F}^{00l} = \exp\,(2\pi i l j/n)\, \hat{R}_\psi \hat{F}^{00l}\, \hat{R}_\psi^{-1}. \qquad (16)$$

This tensor equation may be regarded as a set of linear homogeneous equations for the components of the tensor $\hat{F}^{00l}$. For some l the determinant of this set of equations is equal to zero and, hence, nonzero solutions of these equations are possible, $\hat{F}^{00l} \neq 0$ and corresponding reflections are allowed. Some of these reflections are those given in *International Tables for X-ray Crystallography* (1952), but the others arise due to the anisotropy of susceptibility (ATS reflections). Omitting here the details of tedious calculations, let us give and analyse the final results for ATS reflections only (see Table 1). From Table 1 it follows that for each ATS reflection all components of the tensor structure amplitude $\hat{F}^H$ are determined by at most two independent parameters F_1 and F_2 (F_1 and F_2 may be complex). To avoid confusion it should be emphasized that these parameters are different for different reflections and their numerical values may be obtained from the microscopic theory of X-ray susceptibility. From the developed phenomenological theory it follows only that these parameters may be non-zero if only a screw axis (or glide plane) is taken into account [in the above calculations of $\hat{F}^H$ we used only the screw-axis and glide-plane transformation properties of $\hat{\chi}(\mathbf{r})$]. Other symmetry operations can lead to additional relationships between F_1 and F_2 or even make them vanish. For example, there are 2_1 screw axes in the crystals with space group $I2_13$ but the 00l ($l = 2n + 1$) reflections remain forbidden because the group is body centred. Note that in the case of the 6_3 screw axis the

Table 1. *The components of the tensorial structure amplitudes $\hat{F}^H$ and indices l for ATS reflections* ($n = 0, \pm1, \pm2, \ldots$; *other components of $\hat{F}^H$: $\hat{F}^H_{yy} = -\hat{F}^H_{xx}$; $\hat{F}^H_{zz} = 0$; $\hat{F}^H_{yx} = \hat{F}^H_{xy}$; $\hat{F}^H_{zx} = \hat{F}^H_{xz}$; $\hat{F}^H_{zy} = \hat{F}^H_{yz}$*)

Screw axis or glide plane	F^H_{xx}	F^H_{xy}	F^H_{xz}	F^H_{yz}	l	Type
2_1	0	0	F_1	F_2	$2n + 1$	I
3_1	F_1	$\mp iF_1$	F_2	$\pm iF_2$	$3n \pm 1$	II
3_2	F_1	$\pm iF_1$	F_2	$\mp iF_2$	$3n \pm 1$	II
4_1	0	0	F_1	$\pm iF_1$	$4n \pm 1$	I
4_1	F_1	F_2	0	0	$4n + 2$	II
4_2	F_1	F_2	0	0	$2n + 1$	II
4_3	0	0	F_1	$\mp iF_1$	$4n \pm 1$	I
4_3	F_1	F_2	0	0	$4n + 2$	II
6_1	0	0	F_1	$\pm iF_1$	$6n \pm 1$	I
6_1	F_1	$\pm iF_1$	0	0	$6n \pm 2$	II
6_1	0	0	0	0	$6n + 3$	
6_2	F_1	$\pm iF_1$	0	0	$3n \pm 1$	II
6_3	0	0	0	0	$2n + 1$	
6_4	F_1	$\mp iF_1$	0	0	$3n \pm 1$	II
6_5	0	0	F_1	$\mp iF_1$	$6n \pm 1$	I
6_5	F_1	$\mp iF_1$	0	0	$6n \pm 2$	II
6_5	0	0	0	0	$6n + 3$	
c	0	F_1	F_2	0	$2n + 1$	II

$00l$ ($l = 2n + 1$) reflections remain forbidden (see Table 1) because in the xy plane the anisotropy of susceptibility is absent due to the inevitable threefold rotation axis. For 6_1 and 6_5 axes the reflections with $l = 6n + 3$ remain forbidden because only the dipole interaction of X-rays is taken into account in the developing theory. It may be shown that, for example, the quadrupole interaction makes these reflections possible.

Intensity and polarization properties of ATS reflections

To study the properties of ATS reflections we shall use the kinematical theory of diffraction. It is well known that in this theory the reflection intensity I_H is proportional to $|F_H|^2$ and for a nonpolarized incident beam we have

$$I_H = A_H |F_H|^2 (1 + \cos^2 2\theta_B)/2, \qquad (17)$$

where θ_B is the Bragg angle, A_H is a proportionality factor which depends on the incident beam intensity, the sample volume, *etc.** (Vainshtein, 1979). Equation (17) is valid when the anisotropy of $\tilde{\chi}(\mathbf{r})$ is absent and F_H is scalar. If the anisotropy of $\tilde{\chi}(\mathbf{r})$ is taken into account then it is convenient to introduce the reflection intensity of an $\boldsymbol{\alpha}$-polarized incident beam into a $\boldsymbol{\beta}$-polarized reflected one

$$I_{\alpha\beta} = |\boldsymbol{\beta}^+ \hat{F}^H \boldsymbol{\alpha}|^2, \qquad (18)$$

where $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the unit vectors of polarization, $\hat{F}^H$ is the tensorial structure amplitude [see (5) and Table 1] and the cross denotes Hermitian conjugation. Instead of arbitrary $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, the conventional normal and parallel vectors of polarization $\boldsymbol{\sigma}$ and $\boldsymbol{\pi}$ may be used. If the incident beam is $\boldsymbol{\sigma}$ or $\boldsymbol{\pi}$ polarized or nonpolarized then the reflection intensities for these three cases are given by the following expressions

$$I_\sigma = I_{\sigma\sigma} + I_{\sigma\pi} \qquad (19)$$

$$I_\pi = I_{\pi\sigma} + I_{\pi\pi} \qquad (20)$$

$$I_H = (I_\sigma + I_\pi)/2, \qquad (21)$$

where

$$\begin{aligned} I_{\sigma\sigma} &= |\boldsymbol{\sigma}\hat{F}^H \boldsymbol{\sigma}|^2 \\ I_{\pi\pi} &= |\boldsymbol{\pi}_H \hat{F}^H \boldsymbol{\pi}_0|^2 \qquad (22) \\ I_{\sigma\pi} = I_{\pi\sigma} &= |\boldsymbol{\pi}_H \hat{F}^H \boldsymbol{\sigma}|^2 = |\boldsymbol{\sigma}\hat{F}^H \boldsymbol{\pi}_0|^2 \end{aligned}$$

and $\boldsymbol{\pi}_0$ and $\boldsymbol{\pi}_H$ are the vectors of $\boldsymbol{\pi}$ polarization for incident and reflected beams. It may be easily proven that (21) transforms into (17) if the anisotropy of susceptibility is absent.

From the kinematical theory the polarization of the reflected beam can be obtained in the following way (Belyakov, 1975). If $\boldsymbol{\alpha}$ is the polarization vector of the incident beam then the polarization vector of the reflected beam $\boldsymbol{\beta}_H$ is that for which the right side of (18) has its maximum value. Thus, from (18) we have

$$\boldsymbol{\beta}_H = \mathbf{B}_H / |\mathbf{B}_H|, \qquad (23)$$

where $\mathbf{B}_H = \boldsymbol{\sigma}(\boldsymbol{\sigma}\hat{F}^H \boldsymbol{\alpha}) + \boldsymbol{\pi}_H(\boldsymbol{\pi}_H \hat{F}^H \boldsymbol{\alpha})$. Note that in general $\boldsymbol{\beta}_H$ depends on $\boldsymbol{\alpha}$ but in some cases does not (see below).

Let us consider the properties of the glide-plane ATS reflections. As above, we assume that the glide plane c is normal to axis x. For simplicity we consider the $00l$ ($l = 2n + 1$) ATS reflections only. From (11) and (19)–(22), the reflection intensities for $\boldsymbol{\sigma}$- and $\boldsymbol{\pi}$-polarized or nonpolarized incident beams are given by

$$\begin{aligned} I_\sigma = {} & |F_1|^2 (\sin^2\theta_B + \cos^2\theta_B \sin^2 2\varphi) \\ & + |F_2|^2 \cos^2\theta_B \sin^2\varphi \\ & + \mathrm{Re}(F_1 F_2^*) \sin\varphi \cos 2\varphi \sin 2\theta_B, \\ I_\pi = {} & |F_1|^2 \sin^2\theta_B (\sin^2\theta_B + \cos^2\theta_B \cos^2 2\varphi) \\ & + |F_2|^2 \sin^2\varphi \cos^2\theta_B \\ & - \mathrm{Re}(F_1 F_2^*) \sin\varphi \cos 2\varphi \sin 2\theta_B, \\ I_H = {} & |F_1|^2 (\sin^2\theta_B + \tfrac{1}{4}\sin^2 2\varphi \cos^4\theta_B) \\ & + |F_2|^2 \sin^2\varphi \cos^2\theta_B, \end{aligned} \qquad (24)$$

where φ is the azimuthal angle of the incident wave vector in the xy plane. Thus, studying experimentally the azimuthal dependence of I_σ, I_π and I_H, one can determine F_1 and F_2 and the tensor structure amplitude $\hat{F}^H$ [see (11)]. If $\varphi = 0$ or $\varphi = \pi/2$ then the $\boldsymbol{\sigma}$-polarized incident beam gives the $\boldsymbol{\pi}$-polarized reflected one and *vice versa*.

Now, let us discuss the properties of the screw-axis ATS reflections. There are two types of these reflections: type I – those reflections for which $F^H_{xx} = F^H_{yy} = F^H_{xy} = 0$ and type II – the rest (see Table 1). The type I ATS reflections have the most simple polarization properties. From (19)–(22) and Table 1 one obtains $I_{\sigma\sigma} = I_{\pi\pi} = 0$, $I_H = I_\sigma = I_\pi = I_{\pi\sigma} = I_{\sigma\pi}$ for these reflections and $I_{\sigma\pi}$ is given by

$$\begin{aligned} I_{\sigma\pi} = {} & [|F_1|^2 \sin^2\varphi + |F_2|^2 \cos^2\varphi \\ & - \mathrm{Re}(F_1 F_2^*) \sin 2\varphi] \cos^2\theta_B \end{aligned} \qquad (25)$$

for a 2_1 screw axis and

$$I_{\sigma\pi} = |F_1|^2 \cos^2\theta_B \qquad (26)$$

for 4_1, 4_3, 6_1 and 6_5 screw axes. Thus, in this case the $\boldsymbol{\sigma}$-polarized incident beam gives the $\boldsymbol{\pi}$-polarized reflected one and *vice versa*; the unpolarized incident beam gives the unpolarized reflected one. Then, the type I reflections vanish for the backward Bragg diffraction because in this case $\cos\theta_B = 0$.

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* For simplicity hereafter the factor A_H will be omitted.

The intensities of the type-II reflections can be obtained from (19)–(22) and are given by

$$\begin{aligned} I_\sigma &= |F_1|^2 (1 + \sin^2 \theta_B) + D(\varphi), \\ I_\pi &= |F_1|^2 \sin^2 \theta_B (1 + \sin^2 \theta_B) + D(\varphi), \\ I_H &= |F_1|^2 (1 + \sin^2 \theta_B)^2/2 + D(\varphi), \\ D(\varphi) &= |F_2|^2 \cos^2 \theta_B + \sin 2\theta_B [\mathrm{Re}(F_1 F_2^*) \\ &\quad \times \cos 3\varphi \mp \mathrm{Im}(F_1 F_2^*) \sin 3\varphi] \end{aligned} \tag{27}$$

for 3_1 and 3_2 screw axes;

$$\begin{aligned} I_\sigma &= |F_1|^2 B(\varphi) + |F_2|^2 C(\varphi) \\ &\quad + \mathrm{Re}(F_1 F_2^*) \cos^2 \theta_B \sin 4\varphi \\ I_\pi &= \sin^2 \theta_B [|F_1|^2 C(\varphi) + |F_2|^2 B(\varphi) \\ &\quad - \mathrm{Re}(F_1 F_2^*) \cos^2 \theta_B \sin 4\varphi] \\ I_H &= (I_\sigma + I_\pi)/2 \\ B(\varphi) &= 1 - \cos^2 \theta_B \sin^2 2\varphi \\ C(\varphi) &= 1 - \cos^2 \theta_B \cos^2 2\varphi \end{aligned} \tag{28}$$

for 4_1, 4_3 and 4_2 screw axes, and

$$\begin{aligned} I_\sigma &= |F_1|^2 (1 + \sin^2 \theta_B) \\ I_\pi &= |F_1|^2 \sin^2 \theta_B (1 + \sin^2 \theta_B) \\ I_H &= |F_1|^2 (1 + \sin^2 \theta_B)^2/2 \end{aligned} \tag{29}$$

for 6_1, 6_2, 6_4 and 6_5 screw axes. The $\mp$ sign in (27) corresponds to $F^H_{xy} = \pm iF^H_{xx}$ (see Table 1). It should be emphasized that the azimuthal patterns of ATS reflections given by (27) and (28) are connected with the crystal and do not depend on the choice of the coordinate axes in the xy plane. Unlike the type-I reflections the intensities of the type-II reflections are different for σ- and π-polarized incident beams, $I_\sigma \geq I_\pi$ and $I_\sigma - I_\pi \propto (1 - \sin^4 \theta_B)$. Then, from (18) it can be easily shown that the type-II reflections are 'chiral', *i.e.* their intensities are different for the right-hand and left-hand circularly polarized incident beams. For example, let us consider the backward type-II reflections ($\theta_B = \pi/2$) for 3- and 6-fold screw axes. We find from (18) and (23) that only the beams with definite circular polarization (right hand if $F^H_{xy} = iF^H_{xx}$ and left hand if $F^H_{xy} = -iF^H_{xx}$) are reflected and the reflected beams have the same polarization. For opposite polarization the reflection is absent. Thus, in this case the crystal may be regarded as a circular polarizer or analyser. If $\theta_B < \pi/2$ the polarizations are elliptic and the axial ratio of the polarization ellipse is equal to $\sin \theta_B$ for the 6-fold screw axes (for the 3- and 4-fold screw axes this ratio depends on the parameters F_1 and F_2).

Note that the screw-axis ATS reflections are similar to those Bragg reflections of light in some liquid crystals which have been studied both theoretically and experimentally by many authors (see, for example, the review paper by Belyakov, Dmitrienko & Orlov, 1979).

Examples and estimations

To illustrate the developed theory let us consider the $00l$ ($l = 2n + 1$) ATS reflections in crystals with TiO_2 (rutile) structure (the space group is D^4_{4h}, $P4_2/mnm$). One can imagine this structure as being constructed from successive layers with O—Ti—O bonds directed alternately at 45° and −45° to the crystal axis a (see Fig. 1). The distance between these layers is $c/2$ and they have the same electron density. Hence, the $00l$ reflections should be forbidden if l is odd. However, the tensor of susceptibility is different for neighbouring layers because the principal axes of the tensor have different orientations in accordance with the directions of O—Ti—O bonds. Thus, the scattering amplitudes of the neighbouring layers are also different and this difference makes the $00l$ ($l = 2n + 1$) reflections possible. From Table 1 one can obtain the tensor structure amplitude of these ATS reflections taking into account both the screw axis 4_2 and the glide plane n [for $00l$ ($l = 2n + 1$) reflections there is no difference between c and n glide planes]. It is clear from Table 1 that due to the combined action of the screw axis and the glide plane only $F^H_{xy} \neq 0$. Thus, the azimuthal dependences of these reflections are given by (24) with $F_2 = 0$ or by (28) with $F_1 = 0$. Note that the azimuthal dependences are stronger for the small θ_B. The polarization properties of these reflections are rather unusual: if $\varphi = 0$ or $\pi/2$ then the σ-polarized incident beam gives the π-polarized reflected one and *vice versa*; if $\varphi = \pi/4$ then the σ- or π-polarized incident beam gives the σ- or π-polarized reflected one.

Now, let us estimate the intensity of ATS reflections, *i.e.* the possible values of the structure amplitudes $\hat{F}^H$ of these reflections. The theoretical calculations of $\hat{F}^H$ are rather difficult (Kolpakov, Bushuyev & Kuz'min, 1978) and we shall estimate $\hat{F}^H$ from the experimental data. It is clear that the structure amplitude $\hat{F}^H$ may be of the same order of magnitude as the anisotropic part of $\hat{F}^0$ (we denote it $\hat{F}^0_a$). Then, $\hat{F}^0_a$ may be estimated from the anisotropy of the absorption coefficient μ. For example, it has been observed by Cox & Beaumont (1980) that in ZnF_2 (rutile structure) near the Zn K edge the anisotropic part of μ is approximately one-third of the

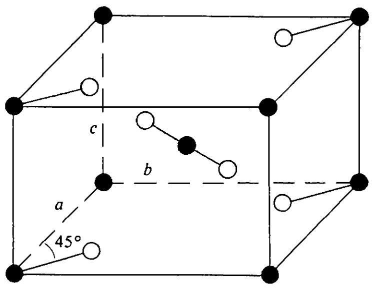

Fig. 1. The rutile structure (○ oxygen, ● titanium).

isotropic part. Taking into account that μ is proportional to Im($\hat{F}^0$), one obtains Im($\hat{F}^0_a$) $\simeq$ 2 because the isotropic part Im($\hat{F}^0_i$) $\simeq$ 6 near the Zn *K* edge (two Zn atoms in a unit cell). It is clear that Re($\hat{F}^0_a$) should be of the same order of magnitude due to the dispersion relations. In the region of the extended X-ray absorption fine structure (EXAFS) the anisotropy of μ is smaller and it is absent far from the *K* edge (Cox & Beaumont, 1980). Similar results have been obtained by Heald & Stern (1977) for selenium and by Templeton & Templeton (1980) for vanadium [the earlier works were reviewed by Azároff & Pease (1974)].

These estimations show that both $\hat{F}^0_a$ and the structure amplitude of ATS reflections $\hat{F}^H$ may be of the order of a few units in the close vicinity of an absorption edge; they are slightly less in the EXAFS region and vanish far from the edge. Thus, it seems that ATS reflections can be observed in suitable experimental conditions. Recently it has been reported by Templeton & Templeton (1982) that the anisotropic part of the structure amplitude of nonforbidden reflections may also be about a few units near the absorption edge.

Note that some glide-plane forbidden reflections have been observed in white tin by Field (1976). The observed values of $\hat{F}^H$ were about a few units for Mo $K\alpha$ radiation, *i.e.* rather far from the tin *K* edge. Our estimations show that these values are too large to be caused by the anisotropy of susceptibility.

It should be emphasized that forbidden reflections may also be excited *via* multiple diffraction (Renninger, 1937; Terminasov & Tuzov, 1964). If the wavelength is short then the integrated intensity of numerous Renninger reflections may strongly distort the true intensity of ATS reflections. To avoid this distortion the longest possible wavelengths should be used. For example, near the Ti *K* edge ($\lambda = 2{\cdot}5$ Å) the Renninger pattern of the TiO_2 crystal contains 48 Renninger reflections per 360° and these reflections can be easily excluded from the azimuthal pattern of the 001 ATS reflection. Note that there are many compounds with the rutile structure (VO_2, MnO_2, NiF_2, MnF_2, CoF_2, *etc.*) which have suitable *K*-edge wavelengths.

Conclusion

It is shown above that from the symmetry properties of the tensor of X-ray susceptibility one can obtain the main properties of the ATS reflections:

1. The tensorial structure amplitudes of ATS reflections are determined by at most two independent parameters (see Table 1).

2. The intensity of ATS reflections may have smooth azimuthal dependence, *i.e.* it may vary during crystal rotation around the diffraction vector.

3. The polarization properties of ATS reflections are very unusual (the transformation of **σ** polarization into **π** polarization and *vice versa* and the selective diffraction of the circularly polarized beam are possible). The polarization properties may also have azimuthal dependence.

The estimations, based on the experimental data, show that the structure amplitudes of the ATS reflections reach their maximum values near the absorption edges where they may be of the order of a few electrons atom^{-1}. Thus, the intensity of ATS reflections may be comparable with the intensity of those reflections which arise due to the asphericity of the atomic electron density. But it is worthwhile to emphasize once more that the anisotropy of susceptibility makes possible even those reflections (namely, the glide-plane and screw-axes forbidden reflections) which remain forbidden if only the asphericity of electron density and the atomic thermal motion are taken into account.

The ATS reflections give us a unique possibility to study the anisotropy of the periodic part of X-ray susceptibility. The anisotropy of susceptibility is caused by the chemical bonds and depends on the local environment of the atom in the crystal. Therefore, this anisotropy may be different for the same atom placed into different crystals. The ATS reflections may be also useful for the better understanding of the fine structure of X-ray spectra near absorption edges. In the structure analysis the screw-axis ATS reflections give a way of distinguishing the enantiomorphous pairs of crystals. It would be very interesting to study the ATS reflections in cubic crystals where the anisotropy of absorption is absent (the theory of ATS reflections in cubic crystals will be discussed elsewhere). Note that the developed methods may be applied to nonforbidden reflections too. These methods may also be useful for the description of the structure and properties of the 'blue phase' in liquid crystals (Belyakov, Dmitrienko & Osadchii, 1982).

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On the Application of Phase Relationships to Complex Structures. XX. *RANTAN* For Large Structures and Fragment Development

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Abstract

The *RANTAN* procedure has been used to solve an unknown structure with 100 atoms in the asymmetric unit. In a test of the power of the method a synthetic structure with 234 atoms in space group *P*1 was solved without difficulty. *RANTAN* is also very effective as a multisolution fragment-development procedure with as little as 10% of the structure in the fragment.

Introduction

The *RANTAN* procedure (Yao Jia-xing, 1981) assigns random initial phases to a large number of reflexions together with weights. Subsequent phase refinement is by a controlled use of the tangent formula, in which the weights play a role. *RANTAN* has already been shown to be competitive in power and efficiency with other multisolution methods and further work has now been undertaken to explore the full potentiality of the method and to find new ways of exploiting the general approach.

An unknown structure – complex 2 enniantin C: 1 KSCN

The data for this structure were provided by Dr G. Tischenko of the Institute of Crystallography, Moscow. The basic parameters were: formula $2[(C_{12}H_{21}NO_3)_3]$. KSCN; space group $P2_1$, $Z = 2$; $a = 20{\cdot}205$, $b = 8{\cdot}702$, $c = 25{\cdot}587$ Å and $\gamma = 97{\cdot}0°$. There were 100 atoms in the asymmetric unit.

MULTAN 80 was tried but did not solve the structure. *RANTAN* employed 400 reflexions ($E > 1{\cdot}62$) for the phase-determining process and 100 weak reflexions ($E < 0{\cdot}185$) for calculating the PSIZERO figure of merit. The number of strong triple-phase relationships was 4377. The convergence map chose three general reflexions for fixing the origin and enantiomorph. Another 247 reflexions in the bottom of the convergence map were assigned random phases with weights of 0·25 giving a total of 250 reflexions in the starting set.

RANTAN stopped at set 78 automatically and accepted this set as a true solution with figures of merit: ABSFOM 1·0521, PSIZERO 1·149, RESID 18·37, CFOM 2·8822. The *E* map showed two fragments which contained 40 and 45 atoms respectively. The group KSCN could not be found in the *E* map, except the carbon atom, since the group was disordered. Fig. 1 shows the molecular structure. The preliminary least-squares refinement was carried out by the *SHELX* 76 program (Sheldrick, 1976) and the *R* factor was 14·57%. The result showed that the potassium atom had two positions with low occupation factors and that the group SCN seemed to rotate around the heavy centre.

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