

Anisotropy of X-ray Susceptibility and Bragg Reflections in Cubic Crystals

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Abstract

The previous theory of X-ray diffraction in crystals with anisotropic X-ray susceptibility [Dmitrienko (1983). *Acta Cryst.* A39, 29–35] is applied to cubic crystals. Such a theory is needed if the X-ray wavelengths are near the absorption edges because in this case the X-ray susceptibility may be anisotropic. The most general form of the spatially dependent tensor of X-ray susceptibility is obtained for all cubic space groups. This tensor is anisotropic at any point of a unit cell except those with cubic point symmetry (being averaged over a unit cell the tensor becomes isotropic providing the macroscopic isotropy of cubic crystals). From the tensor of susceptibility the structure amplitudes and new extinction rules are derived for the glide-plane and screw-axis forbidden reflections (such reflections are forbidden if the susceptibility is isotropic). For example, the *hhh* forbidden reflections remain extinguished even if the anisotropy is taken into account. Further restrictions on the structure amplitudes of forbidden reflections are obtained with the natural assumption that the anisotropy of susceptibility is localized at the special atomic positions. The tensor form of the structure amplitudes of nonforbidden reflections is also discussed. The general methods are illustrated by their application to the A15 structure (space group $Pm\bar{3}n$).

Introduction

Structurally forbidden Bragg reflections are commonly used as direct indications of the thermal motion and chemical binding of atoms in crystals (Dawson, 1967; Belyakov, 1971; Borie, 1981). The chemical binding and thermal motion lead to the asphericity of atomic electron density and, therefore, the conventional extinction rules may be violated. However, in this case the extinction rules obtained for general atomic positions remain valid; for example, the glide-plane and screw-axis forbidden reflections remain extinguished. Besides, the chemical binding and the anisotropy of the local atomic environment lead to the polarization anisotropy of X-ray susceptibility which makes a crystal locally birefringent and dichroic (especially for the X-ray wavelengths near the absorption edges; see a review

paper by Kolpakov, Bushuyev & Kuz'min, 1978). If this anisotropy is taken into account then the glide-plane and screw-axis extinction rules are no longer valid (Templeton & Templeton, 1980; Dmitrienko, 1981). Thus, the glide-plane and screw-axis forbidden reflections may be excited and the intensity of these reflections depends on the anisotropy of susceptibility alone (to emphasize this, hereafter these reflections will be called ATS reflections, where ATS denotes the anisotropy of the tensor of susceptibility).^{*} New extinction rules and the structure amplitudes of ATS reflections have been obtained from the symmetry considerations in the previous paper (Dmitrienko, 1983; referred to hereafter as paper I). It was shown in paper I that the properties of ATS reflections are very unusual.

The present paper contains a detailed description of ATS reflections in cubic crystals. In this case the macroscopic dichroism and birefringence are absent [we neglect the possible effects of spatial dispersion (Agranovich & Ginzburg, 1966)]. Thus, ATS reflections give us unique information about the local anisotropy of susceptibility and, hence, about the anisotropy of chemical bonds, crystal fields, *etc.* The effect of the anisotropy of susceptibility on the properties of nonforbidden reflections is also described below and it is shown that even in the most symmetrical cubic crystals the structure amplitudes of the most symmetrical reflections can contain an asymmetric part.

The tensor of X-ray susceptibility of cubic crystals

As in paper I, we shall use the symmetry considerations to obtain the most general form of the spatially dependent tensor of X-ray susceptibility $\hat{\chi}(\mathbf{r})$ which 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 $\mathbf{P}(\mathbf{r})$:

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

The tensor $\hat{\chi}(\mathbf{r})$ should be invariant under all symmetry transformations which belong to the space

^{*} The glide-plane and screw-axis forbidden reflections may be also excited in the case of Mössbauer γ -ray diffraction (see a review paper by Belyakov, 1975).

group of the crystal. The common feature of all cubic space groups is a threefold rotation axis directed along a cubic diagonal. Requiring the invariance of $\hat{\chi}(\mathbf{r})$ under this rotation and using the methods developed in paper I, one obtains the following general form of $\hat{\chi}(\mathbf{r})$ in cubic crystals

$$\hat{\chi}(x, y, z) = \begin{pmatrix} a_1(x, y, z) & a_2(z, x, y) & a_2(y, z, x) \\ a_2(z, x, y) & a_1(y, z, x) & a_2(x, y, z) \\ a_2(y, z, x) & a_2(x, y, z) & a_1(z, x, y) \end{pmatrix}, \quad (2)$$

where $a_1(\mathbf{r})$ and $a_2(\mathbf{r})$ are the arbitrary functions of \mathbf{r} with the periodicity of the Bravais lattice of the crystal; $a_i(\mathbf{r})$ may be complex-valued functions because of the X-ray absorption; the system of axes used in (2) is the one conventional for cubic space groups (*International Tables for X-ray Crystallography*, 1952). One can easily prove that $\hat{\chi}(\mathbf{r})$ is really invariant under 120° rotation around a threefold cubic axis, that is

$$\hat{\chi}(\mathbf{r}) = \hat{R}_3 \hat{\chi}(\mathbf{r}') \hat{R}_3^{-1}, \quad (3)$$

where $\mathbf{r}' = \hat{R}_3^{-1} \mathbf{r}$; \hat{R}_3 is the matrix of 120° rotation around the cubic axis,

$$\hat{R}_3 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \quad (4)$$

[see also the paper by Belyakov, Dmitrienko & Osadchii (1982)].

Other symmetry operations lead to some additional properties of functions $a_i(\mathbf{r})$. For example, let us consider the crystals with the space group O_h^3 , $Pm\bar{3}n$. To provide the invariance of $\hat{\chi}(\mathbf{r})$ under the mirror reflection m , the functions $a_i(\mathbf{r})$ should have the following properties:

$$a_1(x, y, z) = a_1(\bar{x}, y, z) = a_1(x, \bar{y}, z) = a_1(x, y, \bar{z}) \quad (5a)$$

$$a_2(x, y, z) = a_2(\bar{x}, y, z) = -a_2(x, \bar{y}, z) = -a_2(x, y, \bar{z}). \quad (5b)$$

Then, to provide the invariance of $\hat{\chi}(\mathbf{r})$ under the glide plane n (Belov, Zagal'skaya, Litvinskaya & Egorov-Tismenko, 1980), the functions $a_i(\mathbf{r})$ should also have the additional property

$$a_i(x, y, z) = a_i(\frac{1}{2} + x, \frac{1}{2} + z, \frac{1}{2} + y). \quad (6)$$

Thus, being determined by (2), (5) and (6), the susceptibility $\hat{\chi}(\mathbf{r})$ is invariant under all symmetry operations which are included into the crystallographic symbol $Pm\bar{3}n$. All the other symmetry operations of this space group may be regarded as some combination of those already considered and they give no additional properties of $a_i(\mathbf{r})$. Hence, we obtain the most general form of the tensor of X-ray susceptibility for this space group. Note that $\hat{\chi}(\mathbf{r})$ is isotropic (*i.e.* $\hat{\chi}(\mathbf{r}) \propto \hat{I}$, \hat{I} is the unit matrix) at the points $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ with cubic point symmetry $m\bar{3}$ because at these points $a_1(x, y, z) = a_1(y, z, x) =$

$a_1(z, x, y)$ and $a_2(x, y, z) = 0$ [see (5b) and (6)]. The similar properties of $a_i(\mathbf{r})$ can be easily obtained for all cubic crystals (see Appendix). Naturally, these properties are not sufficient for the unique determination of $a_i(\mathbf{r})$ but they impose strong restrictions on the structure amplitudes of both forbidden and non-forbidden reflections.

Forbidden reflections

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

$$\hat{F}^H = B \int \hat{\chi}(\mathbf{r}) \exp(2\pi i \mathbf{H} \mathbf{r}) d\mathbf{r}, \quad (7)$$

where $B = -v/(r_e \lambda^2)$; v is the volume of the unit cell; r_e is the classical electron radius; λ is the X-ray wavelength; \mathbf{H} is the reciprocal-lattice vector. From (2) and (7) one obtains the general form of \hat{F}^H in cubic crystals

$$\hat{F}^{hkl} = \begin{pmatrix} F_1^{hkl} & F_2^{lhk} & F_2^{klh} \\ F_2^{lhk} & F_1^{klh} & F_2^{hkl} \\ F_2^{klh} & F_2^{hkl} & F_1^{lhk} \end{pmatrix}, \quad (8)$$

where

$$F_j^{hkl} = B \int a_j(x, y, z) \exp[2\pi i(hx + ky + lz)] d\mathbf{r}. \quad (9)$$

For example, let us determine the structure amplitudes of the hhl ATS reflections for space group $Pm\bar{3}n$ ($l = 2n + 1$). Taking into account (5) and (6), one can obtain from (9) the following expressions for the elements of \hat{F}^{hhl}

$$F_1^{hhh} = F_2^{lhh} = 0 \quad (10a)$$

$$\begin{aligned} F_1^{hhl} &= -F_1^{lhh} = F_1 \\ &\equiv \frac{B}{2} \int a_1(x, y, z) (\cos 2\pi hy \cos 2\pi lz \\ &\quad - \cos 2\pi ly \cos 2\pi hz) \cos 2\pi hx d\mathbf{r} \end{aligned} \quad (10b)$$

$$\begin{aligned} F_2^{hhl} &= -F_2^{lhl} = F_2 \\ &\equiv \frac{B}{2} \int a_2(x, y, z) (\sin 2\pi hy \sin 2\pi lz \\ &\quad - \sin 2\pi ly \sin 2\pi hz) \cos 2\pi hx d\mathbf{r}. \end{aligned} \quad (10c)$$

Here and below we denote as F_1 and F_2 the nonzero elements of the structure amplitudes of ATS reflections; F_1 and F_2 are complex valued because $a_i(\mathbf{r})$ are complex-valued functions.

Thus, for space group $Pm\bar{3}n$, the structure amplitudes of ATS reflections have the following tensor form:

$$\hat{F}^{hhl} = \begin{pmatrix} F_1 & 0 & F_2 \\ 0 & -F_1 & -F_2 \\ F_2 & -F_2 & 0 \end{pmatrix}. \quad (11)$$

Returning to the general case, note that those ATS reflections, which are connected with the glide planes inclined at 45° to coordinate axes, have the structure amplitudes given by (11) in all cubic crystals with such glide planes. If the glide plane is parallel to a cube face then the consequent ATS reflections have the following structure amplitudes (see paper I):

$$\hat{F}^{0kl} = \begin{pmatrix} 0 & F_1 & F_2 \\ F_1 & 0 & 0 \\ F_2 & 0 & 0 \end{pmatrix}. \quad (12)$$

Finally, the screw-axis ATS reflections have the structure amplitudes given by

$$\hat{F}^{00l} = \begin{pmatrix} 0 & 0 & F_1 \\ 0 & 0 & F_2 \\ F_1 & F_2 & 0 \end{pmatrix} \quad (13)$$

or by

$$\hat{F}^{00l} = \begin{pmatrix} F_1 & F_2 & 0 \\ F_2 & -F_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (14)$$

(see paper I). Note that the permutation of the Miller indices in (11)–(14) should be accompanied by the permutation of the elements of \hat{F}^{hkl} in accordance with (8).

Table 1 contains the indices and the tensor form of the structure amplitudes of ATS reflections for all cubic crystals having ATS reflections. From Table 1 it follows that some restrictions on parameters F_1 and F_2 may arise from the combined action of different glide planes. For instance, $F_1 = F_2 = 0$ for the hhh forbidden reflections and, hence, these reflections remain extinguished even if the anisotropy of susceptibility is taken into account; then, F_1 or F_2 (or even both of them) may be equal to zero in the case of the $00l$ ATS reflections. All these restrictions are the direct consequence of the symmetry properties of functions $a_i(\mathbf{r})$ (see Appendix); for the $Pm\bar{3}n$ space group, these restrictions are evident from (10). Besides these purely symmetrical restrictions, some additional restrictions arise if one makes certain assumptions about the real distribution of the anisotropy of susceptibility inside a unit cell.

Additional restrictions on the structure amplitudes

Until now it has been assumed that inside a unit cell the anisotropy of susceptibility has some unknown distribution which could be invariant under the symmetry transformations. To obtain further restrictions on the tensor structure amplitudes we can use the well known fact that the anisotropic part of X-ray susceptibility is connected mainly with the dispersion corrections to the tensor of atomic scattering factor \hat{f} ; tensor \hat{f} may be written as

$$\hat{f} = f\hat{I} + \hat{f}^a, \quad (15)$$

Table 1. The tensor form of the structure amplitudes and indices of ATS reflections in cubic crystals

Space group	Indices of ATS reflections	Equations for \hat{F}^{hkl} and symmetry restrictions on \hat{F}^{hkl} for special ATS reflections
$P2_13$	$00l; l = 2n + 1$	(13)
$Pn\bar{3}$	$0kl; k + l = 2n + 1$	(12); $00l: F_2 = 0$
$Fd\bar{3}$	$0kl; k, l = 2n;$ $k + l = 4n + 2$	(12); $00l: F_2 = 0$
$Pa\bar{3}$	$0kl; k = 2n + 1$	(12); $0k0: F_2 = 0$
$Ia\bar{3}$	$0kl; k, l = 2n + 1$	(12)
$P4_232$	$00l; l = 2n + 1$	(14)
$F4_32$	$00l; l = 4n + 2$	(14)
$P4_332$	$00l; l = 4n \pm 1$	(13); $F_2 = \mp iF_1$
	$00l; l = 4n + 2$	(14)
$P4_132$	$00l; l = 4n \pm 1$	(13); $F_2 = \pm iF_1$
	$00l; l = 4n + 2$	(14)
$I4_132$	$00l; l = 4n + 2$	(14)
$P43n$	$hhl; l = 2n + 1$	(11); $hhh: F_1 = F_2 = 0;$ $00l: F_2 = 0$
$F43c$	$hhl; h, l = 2n + 1$	(11); $hhh: F_1 = F_2 = 0$
$I43d$	$hhl; 2h + l = 4n + 2$	(11); $hhh: F_1 = F_2 = 0;$ $00l: F_2 = 0$
$Pn\bar{3}n$	$0kl; k + l = 2n + 1$	(12); $00l: F_1 = F_2 = 0$
	$hhl; l = 2n + 1$	(11); $hhh: F_1 = F_2 = 0$
$Pm\bar{3}n$	$hhl; l = 2n + 1$	(11); $hhh: F_1 = F_2 = 0$
$Pn\bar{3}m$	$0kl; k + l = 2n + 1$	(12); $00l: F_2 = 0$
$Fm\bar{3}c$	$hhl; h, l = 2n + 1$	(11); $hhh: F_1 = F_2 = 0$
$Fd\bar{3}m$	$0kl; k, l = 2n;$ $k + l = 4n + 2$	(12); $00l: F_2 = 0$
$Fd\bar{3}c$	$0kl; k, l = 2n;$ $k + l = 4n + 2$	(12); $00l: F_2 = 0$
$Ia\bar{3}d$	$hhl; h, l = 2n + 1$	(11); $hhh: F_1 = F_2 = 0$
	$0kl; k, l = 2n + 1$	(12); $0kk: F_2 = -F_1$
	$hhl; 2h + l = 4n + 2$	(11); $hhh: F_1 = F_2 = 0;$ $00l: F_2 = 0$

where f is a conventional scattering factor which includes the isotropic part of the dispersion corrections; \hat{I} is the unit matrix; \hat{f}^a is the anisotropic part of the dispersion corrections [for uniqueness, we put $Sp(\hat{f}^a) = 0$]. The discussion of the validity of (15) was given by Kolpakov, Bushuev & Kuz'min (1978). For our purposes, it is most important that the symmetry properties of \hat{f}^a are determined by the point symmetry of the atomic position. Assuming (15) and taking into account the proportionality between the atomic scattering factors and X-ray susceptibility, one can easily realize that \hat{f}^a has the same tensor form as the anisotropic part of $\hat{\chi}(\mathbf{r}_0)$, where \mathbf{r}_0 is the position of the atom in the crystal. Thus, one can use (2) to obtain the general tensor form of \hat{f}^a for any atomic position in cubic crystals. For example, $\hat{f}^a = 0$ for positions with cubic point symmetry; for positions at the three-fold axes, \hat{f}^a contains only off-diagonal elements:

$$\hat{f}^a = \begin{pmatrix} 0 & f_{xy} & f_{xz} \\ f_{xy} & 0 & f_{yz} \\ f_{xz} & f_{yz} & 0 \end{pmatrix}, \quad (16)$$

where all f_{ik} are equal (except for sign); for positions with tetragonal point symmetry, \hat{f}^a contains only diagonal elements, etc. Note that even if some atoms occupy the crystallographically equivalent positions \mathbf{r}_j , their tensor \hat{f}_j^a may be different; for such atoms,

the principal values of \hat{f}_j^a are the same but the orientations of the principal axes of \hat{f}_j^a may be different if the atomic positions \mathbf{r}_j are connected *via* rotation or mirror reflection. One can obtain the relationships between \hat{f}_j^a from the equations for $a_i(\mathbf{r}_j)$ [see (5), (6) and Appendix].

Assuming (15) we obtain a conventionally looking expression for the tensor structure amplitude:

$$\hat{F}^H = \sum_m \hat{f}_m \exp(2\pi i \mathbf{H} \mathbf{r}_m) = F_H \hat{I} + \hat{F}^{aH}, \quad (17)$$

where \hat{f}_m is the atomic scattering factor for the m th atom in a unit cell; F_H is the conventional structure amplitude; \hat{F}^{aH} is the anisotropic part of the structure amplitude which arises from the anisotropic parts of atomic scattering factors.

If the tensor form of \hat{f}_m is restricted by the point symmetry of atomic positions then the tensor form of \hat{F}^H may be restricted too. Consider, as above, the A15 structure [general chemical formula A_3B (V_3Si , Nb_3Ge , *etc.*)]. In a unit cell of this structure two B atoms occupy special positions (a) with cubic point symmetry $m\bar{3}$; hence, $\hat{f}^a(B) = 0$ and B atoms make no contribution to the X-ray anisotropy. Six A atoms occupy special positions (c) (point symmetry $\bar{4}2m$). For these positions, the atomic scattering factors are determined by two parameters f_{\parallel} and f_{\perp} ; f_{\parallel} and f_{\perp} are the principal values parallel and perpendicular to the fourfold axes respectively. It follows from (2), (5) and (6) that

$$\hat{f}(A) = \begin{pmatrix} f_{\parallel} & 0 & 0 \\ 0 & f_{\perp} & 0 \\ 0 & 0 & f_{\perp} \end{pmatrix} \quad (18a)$$

for A atoms occupying the sites $(\frac{1}{4}, 0, \frac{1}{2}; \frac{3}{4}, 0, \frac{1}{2})$; then,

$$\hat{f}(A) = \begin{pmatrix} f_{\perp} & 0 & 0 \\ 0 & f_{\parallel} & 0 \\ 0 & 0 & f_{\parallel} \end{pmatrix} \quad (18b)$$

for the sites $(0, \frac{1}{2}, \frac{1}{4}; 0, \frac{1}{2}, \frac{3}{4})$ and

$$\hat{f}(A) = \begin{pmatrix} f_{\perp} & 0 & 0 \\ 0 & f_{\parallel} & 0 \\ 0 & 0 & f_{\perp} \end{pmatrix} \quad (18c)$$

for the sites $(\frac{1}{2}, \frac{1}{4}, 0; \frac{1}{2}, \frac{3}{4}, 0)$. From (17) and (18) we obtain the tensor structure amplitude of ATS reflections in the A15 structure:

$$\hat{F}^{hhl} = 2(-1)^{h/2}(f_{\perp} - f_{\parallel}) \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (19)$$

if l is odd and h is even; $\hat{F}^{hhl} = 0$ if both l and h are odd. Note that A atoms in the sites $(0, \frac{1}{2}, \frac{1}{4}; 0, \frac{1}{2}, \frac{3}{4})$ make no contribution to the structure amplitudes of ATS reflections.

Comparing (19) with the general expression (11) one can see that $F_1 = 0$ if h is odd and $F_2 = 0$ for any h . Thus, assuming the localization of the anisotropy of susceptibility at the special atomic positions, one obtains additional restrictions on the tensor form and value of the structure amplitudes of ATS reflections. These restrictions significantly simplify the expressions for the intensity and polarization properties of ATS reflections (see paper I); besides, the physical meaning of the elements of the tensor structure amplitudes becomes more evident.

Nonforbidden reflections

It is clear that the anisotropic parts of structure amplitudes are of the same order of magnitude both for forbidden and for nonforbidden reflections. In the latter case the anisotropic parts may be even more important (Templeton & Templeton, 1982) because the corrections to the intensity of nonforbidden reflections are of the order of $F_H \hat{F}^{aH}$ rather than $|\hat{F}^{aH}|^2$ as in the case of ATS reflections (for nonforbidden reflections, we suppose that the anisotropic part \hat{F}^{aH} is much smaller than the conventional part F_H).

In the general case the tensor structure amplitude is given by (8) and (9) and is determined by six complex parameters: F_1^{hkl} , F_2^{hkl} and the circular permutations of hkl . The number of independent parameters decreases for special reflections because in this case some restrictions on F_i^{hkl} arise from (9) owing to the symmetry properties of $a_i(\mathbf{r})$. For example, for the space groups $Pm\bar{3}m$, $Fm\bar{3}m$ and $Im\bar{3}m$, (8) may be reduced to:

$$\hat{F}^{hhl} = \begin{pmatrix} F_1^{hhl} & F_2^{lhh} & F_2^{hhl} \\ F_2^{lhh} & F_1^{hhl} & F_2^{hhl} \\ F_2^{hhl} & F_2^{hhl} & F_1^{lhh} \end{pmatrix} \quad (20)$$

(four independent parameters);

$$\hat{F}^{hhh} = \begin{pmatrix} F_1^{hhh} & F_2^{hhh} & F_2^{hhh} \\ F_2^{hhh} & F_1^{hhh} & F_2^{hhh} \\ F_2^{hhh} & F_2^{hhh} & F_1^{hhh} \end{pmatrix} \quad (21)$$

(two parameters);

$$\hat{F}^{0kk} = \begin{pmatrix} F_1^{0kk} & 0 & 0 \\ 0 & F_1^{k0k} & F_2^{0kk} \\ 0 & F_2^{0kk} & F_1^{k0k} \end{pmatrix} \quad (22)$$

(three parameters);

$$\hat{F}^{00l} = \begin{pmatrix} F_1^{00l} & 0 & 0 \\ 0 & F_1^{00l} & 0 \\ 0 & 0 & F_1^{l00} \end{pmatrix} \quad (23)$$

(two parameters). Thus, even in the most symmetrical cases, the structure amplitudes can contain an anisotropic part. If only the symmetry properties of $\hat{\chi}(\mathbf{r})$ are taken into account then all F_i^{hkl} in (8), (20)–

(23) are different for different reflections and the total number of independent parameters is very large. But using the physical restrictions on the tensor form of atomic scattering factors (see the previous section) one obtains strong additional restrictions on F_i^{hkl} too. Namely, if the atoms of some chemical element occupy one set of general positions in a unit cell then, for the j th atom of the set, the anisotropic part of the scattering factor \hat{f}_j^a contains at most five independent elements because \hat{f}_j^a is a symmetrical tensor and $Sp(\hat{f}_j^a) = 0$. For the n th atom of the set, all elements of \hat{f}_n^a are expressible *via* those five of \hat{f}_j^a because \hat{f}_n^a and \hat{f}_j^a are mutually connected by symmetry transformations. Hence, the anisotropic parts of all structure amplitudes depend on at most $5N$ independent complex parameters, where N is the number of the sets of positions occupied by the atoms of the same chemical element. These parameters are the same for different reflections because the dispersion corrections, which make the main contribution to \hat{f}_j^a , weakly depend on the scattering angle. The atoms of different elements make their contributions to the anisotropy in different parts of the X-ray spectrum (except for an occasional overlap of the absorption edges of different elements).

It is clear that the number of independent parameters is less than $5N$ if the atoms are in special positions with high point symmetry: the anisotropic part of \hat{F}^{aH} is absent if all the atoms occupy the positions with cubic symmetry, *etc.* (see the previous section). Considering again the A15 structure, one can obtain from (17) and (18) that the anisotropic part of the structure amplitude is expressible *via* the only parameter $f_{\parallel} - f_{\perp}$ for any reflection:

$$\hat{F}^{aH} = \frac{1}{3}(f_{\parallel} - f_{\perp}) \begin{pmatrix} B_{hkl} & 0 & 0 \\ 0 & B_{klh} & 0 \\ 0 & 0 & B_{lkh} \end{pmatrix}, \quad (24)$$

where $B_{hkl} = 2C_{hl} - C_{kh} - C_{lk}$ and

$$C_{hl} = [1 + \exp(\pi ih)] \exp[\pi i(l + h/2)]. \quad (25)$$

It is very important that the difference $f_{\parallel} - f_{\perp}$ is approximately of the same value for all reflections because the dispersion corrections, which give the main contribution to $f_{\parallel} - f_{\perp}$, are almost independent on the reflection vector.

Note that the tensor structure amplitudes were calculated earlier by Templeton & Templeton (1982) for space group $P2_13$ and by Belyakov, Dmitrienko & Osadchii (1982) for the space groups of 23 and 432 crystal classes.

Possible applications

As was noted earlier, the anisotropy of X-ray susceptibility reaches its maximum value near X-ray absorption edges where the anisotropic part of the atomic

scattering factor may be of the order of a few electrons/atom (Templeton & Templeton, 1982; Dmitrienko, 1983). This anisotropy makes the structure analysis more complicated (Templeton & Templeton, 1982). At the same time it provides new opportunities to study the atomic and electron structure of crystals. For these purposes, the selectivity of ATS reflections may be especially useful. For example, changing the X-ray wavelength one can study the selective contribution to the anisotropy from the atoms of different elements. Moreover, the contributions from the atoms of the same element may be also distinguished if these atoms occupy the positions with different point symmetry (see previous sections).

Consider, as above, the A15 structure (A_3B). Some crystals with this structure (V_3Si , Nb_3Al) demonstrate superconductivity at rather high temperatures and it is theoretically supposed that their superconductivity may be connected with the presence of the quasi-one-dimensional chains of A atoms. The electronic structure of such crystals may be sensitive to their quasi-one-dimensionality and, therefore, the atomic scattering factor of A atoms may be anisotropic near the absorption edge of these atoms. Because of the global cubic symmetry the absorption is isotropic and X-ray diffraction is the unique method to observe the anisotropy of the scattering factor. As it was shown above [see (19) and (24)], the anisotropic part of the structure amplitudes is proportional to $f_{\parallel} - f_{\perp}$ where f_{\parallel} and f_{\perp} are the scattering factors of A atoms for X-rays linearly polarized parallel and perpendicular to a quasi-one-dimensional chain respectively (the scattering factors of B atoms should be isotropic because of the local cubic symmetry of their positions). Thus, the observation of the anisotropy of structure amplitudes may be useful for a better understanding of the nature of superconductivity in crystals with A15 structure.

In some cases the ATS reflections may be used in structure analysis. Consider, for example, a crystal with the space group $P2_13$ containing four atoms in special positions (a) (point symmetry 3); $x, x, x; \frac{1}{2} + x, \frac{1}{2} - x, \bar{x}; \bar{x}, \frac{1}{2} + x, \frac{1}{2} - x; \frac{1}{2} - x, \bar{x}, \frac{1}{2} + x$. For $00l$ ($l = 2n + 1$) ATS reflections, one obtains from (13), (16) and (17) that $F_1/F_2 = i \tan(2\pi lx)$. The intensity of these reflections (for unpolarized incident beam) is proportional to $1 - \cos(4\pi lx) \cos(2\varphi)$, where φ is the angle of rotation around the diffraction vector (see paper I); thus, parameter x can be determined from the azimuthal dependence of the intensity of ATS reflections.

It should be also emphasized that the wavelength dependence of the intensities of ATS reflections contains even more detailed information about the atomic environment than the fine structure of X-ray absorption spectra which is usually used for the environment study. It is especially important that owing to their selectivity the ATS reflections may be used in those

cases when the observation of the absorption fine structure is practically impossible because of the strong background absorption from heavy atoms or from a great number of light atoms, as in the case of biological molecules.

Conclusion

It is shown above that both global and local symmetry of cubic crystals may impose some restrictions on the anisotropic parts of tensor structure amplitudes. From purely symmetrical considerations it follows that the glide-plane forbidden reflections remain extinguished if $|h| = |k| = |l|$; for $00l$ ATS reflections, some restrictions may also arise from the simultaneous action of two different glide planes (see Table 1). More strong restrictions may be obtained under the natural assumption that the tensor form of atomic scattering factors is completely determined by the point symmetry of atomic positions. But it is worth emphasizing that the latter assumption should be proved both experimentally and theoretically. The theoretical proof should be based on the detailed microscopic theory of X-ray susceptibility which has not been developed yet.

The general properties of ATS reflections have been discussed in paper I; in cubic crystals they are the same. In particular, the polarization properties of ATS reflections are very unusual: in some cases, a σ -polarized incident beam can give a π -polarized diffracted one and *vice versa*; then, both the polarization properties and the intensities of ATS reflections may vary during crystal rotation around the diffraction vector. For nonforbidden reflections, similar effects should arise from the anisotropic part of structure amplitudes but these effects will be small in comparison with the full intensity of the reflections. To observe them careful experiments are needed and in this case as in the case of ATS reflections synchrotron radiation seems to be the most appropriate tool because of its tunable wavelength and its polarization properties.

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APPENDIX

In general, the tensor of X-ray susceptibility of cubic crystals depends on two functions $a_i(\mathbf{r})$ [see (2)]. Below, the properties of functions $a_i(\mathbf{r})$ are given for all cubic space groups. Those functions, which determine the general form of the tensorial scattering factor of an atom placed at the point $\mathbf{r} = (x, y, z)$, have the same properties. These properties are the direct consequence of the space-group symmetry [see, as examples, (5) and (6)].

$P23, F23, I23$:

$$a_1(x, y, z) = a_1(x, \bar{y}, \bar{z}) = a_1(\bar{x}, \bar{y}, z) = a_1(\bar{x}, y, \bar{z}) \quad (\text{A.1})$$

$$a_2(x, y, z) = a_2(x, \bar{y}, \bar{z}) = -a_2(\bar{x}, \bar{y}, z) = -a_2(\bar{x}, y, \bar{z}).$$

$P2_13, I2_13$:

$$\begin{aligned} a_1(x, y, z) &= a_1(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}) = a_1(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z) \\ &= a_1(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z) \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} a_2(x, y, z) &= a_2(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}) = -a_2(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z) \\ &= -a_2(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z). \end{aligned}$$

$Pm\bar{3}, Fm\bar{3}, Im\bar{3}$: (A.1) and

$$a_i(x, y, z) = a_i(\bar{x}, \bar{y}, \bar{z}). \quad (\text{A.3})$$

$Pn\bar{3}$: (A.1) and

$$a_i(x, y, z) = a_i(\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z). \quad (\text{A.4})$$

$Fd\bar{3}$: (A.1) and

$$a_i(x, y, z) = a_i(\frac{1}{4} - x, \frac{1}{4} - y, \frac{1}{4} - z). \quad (\text{A.5})$$

$Pa\bar{3}, Ia\bar{3}$: (A.2) and (A.3).

$P432, F432, I432$: (A.1) and

$$a_i(x, y, z) = a_i(\bar{x}, \bar{z}, \bar{y}). \quad (\text{A.6})$$

$P4_232$: (A.1) and

$$a_i(x, y, z) = a_i(\frac{1}{2} - x, \frac{1}{2} - z, \frac{1}{2} - y). \quad (\text{A.7})$$

$F4_132, P4_332, I4_132$: (A.2) and

$$a_i(x, y, z) = a_i(\frac{1}{4} - x, \frac{1}{4} - z, \frac{1}{4} - y). \quad (\text{A.8})$$

$P4_132$: (A.2) and

$$a_i(x, y, z) = a_i(\frac{3}{4} - x, \frac{3}{4} - z, \frac{3}{4} - y). \quad (\text{A.9})$$

$P\bar{4}3m, F\bar{4}3m, I\bar{4}3m$: (A.1) and

$$a_i(x, y, z) = a_i(x, z, y). \quad (\text{A.10})$$

$P\bar{4}3n, F\bar{4}3c$: (A.1) and

$$a_i(x, y, z) = a_i(\frac{1}{2} + x, \frac{1}{2} + z, \frac{1}{2} + y). \quad (\text{A.11})$$

$I\bar{4}3d$: (A.2) and

$$a_i(x, y, z) = a_i(\frac{1}{4} + x, \frac{1}{4} + z, \frac{1}{4} + y). \quad (\text{A.12})$$

$Pm\bar{3}m, Fm\bar{3}m, Im\bar{3}m$: (A.1), (A.3) and (A.10).

$Pn\bar{3}n$: (A.1), (A.4) and (A.6).

$Pm\bar{3}n, Fm\bar{3}c$: (A.1), (A.3) and (A.11).

$Pn\bar{3}m$: (A.1), (A.4) and (A.10).

$Fd\bar{3}m$: (A.1), (A.5) and (A.10).

$Fd\bar{3}c$: (A.1), (A.5) and (A.11).

$Ia3d$: (A.2), (A.3) and (A.12).

Note that the obvious equations should be added for body-centred or face-centred groups respectively:

$$a_i(x, y, z) = a_i(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z) \quad (\text{A.13})$$

or

$$\begin{aligned} a_i(x, y, z) &= a_i(\frac{1}{2} + x, \frac{1}{2} + y, z) = a_i(\frac{1}{2} + x, y, \frac{1}{2} + z) \\ &= a_i(x, \frac{1}{2} + y, \frac{1}{2} + z). \end{aligned} \quad (\text{A.14})$$

In all equations for $a_i(\mathbf{r})$, the set of coordinates is chosen as in *International Tables for X-ray Crystallography* (1952); if the tables give two alternative origins (of coordinates) then the first one is adopted.

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How to Choose OD Layers

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Abstract

A method for choosing OD layers in a structure is given. For any structure one of four cases is possible: 1. the structure cannot be interpreted as an OD structure consisting of layers; 2. the OD layers are uniquely determined; 3. the limits between OD layers may be changed with keeping the OD groupoid family; and 4. the limits may be changed with changing the OD groupoid family.

Introduction

Since OD theory has been developed it has proved its worth for the investigation of disordered structures and for the explanation of relations between polytypes (for some references see, for example, Table 1 in Dornberger-Schiff, 1979).

OD theory is based on the principle that interatomic forces decrease with increasing distance. A local arrangement of atoms occurring equivalently again and again in a structure does not necessarily enforce a three-dimensional periodicity of the total arrangement of all atoms in the structure. Because of the possible absence of three-dimensional periodicity, the symmetry relations within structures with (possible) disorder cannot be adequately described in the usual way by total symmetry operations which form space

groups. The geometrical means used instead by Dornberger-Schiff are partial coincidence operations which in their turn form groupoids (Brandt, 1926; Ehresmann, 1957). The partial coincidence operations refer to parts of the structure occurring equivalently again and again in the structure. These parts may be aperiodic blocks, one-dimensionally periodic rods, or two-dimensionally periodic layers. In the case of polytypes which differ in layer stacking sequence (Bailey *et al.*, 1977) these parts are two-dimensionally periodic layers. OD theory is a geometrical approach and therefore these layers, called OD layers, are not identical with crystallochemical layers, although they often refer to the same region of the structure. OD layers reflect predominantly symmetry properties of two-dimensionally periodic parts. With the knowledge about the OD layers and about the pairs of adjacent OD layers all possible polytypes of a substance may be deduced, especially the MDO structures, called simple or regular by other authors, disordered and periodic polytypes of any length may be deduced as well. All these theoretically possible structures consisting of the same kinds of OD layers and the same kinds of layer pairs are said to belong to a family of OD structures (Dornberger-Schiff, 1964; Dornberger-Schiff & Đurovič, 1975). Until now there have been no exact methods for choosing OD layers