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Chirality-induced 'forbidden' reflections in X-ray resonant scattering

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It is shown that additional Bragg reflections can appear exclusively owing to the local chirality associated with the left–right asymmetric environment of scattering atoms in non-magnetic crystals. The structure amplitude of these reflections depends on the antisymmetric part of a third-rank tensor describing the spatial dispersion effects. It enhances for resonant near-edge scattering through a mixed multipole transition, which includes a dipole–quadrupole contribution. It is shown that this mechanism works even for centrosymmetric crystals, and some realistic examples are considered in detail (α-Fe_2O_3, $LiNbO_3$ *etc.*). For instance, the interference between the dipole–quadrupole and quadrupole–quadrupole terms may be responsible for the threefold symmetry of the azimuthal dependence of the *hhh*, $h = 2n + 1$, reflections observed recently in hematite.

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1. Introduction

The effects of X-ray gyrotropy and circular dichroism have been of growing interest in recent years (we will use for phenomena of this type the general term chirality). The third generation of synchrotrons allows the measurement of these effects near the absorption edges of different elements and the study of the element-specific chirality. X-ray natural optical activity and circular dichroism have been tentatively investigated for many years by several authors (Siddons *et al.*, 1990; Hart, 1994) but the corresponding effects have been unambiguously established only quite recently (Alagna *et al.*, 1998; Goulon *et al.*, 1998, 2000). They provide non-trivial information on the fundamental properties of crystals, for example on the even–odd parity of the excited-state wave function.

Chirality can be considered as a particular case of environment-induced anisotropy of the X-ray atomic susceptibility in crystals. It is reasonable to distinguish the global anisotropy/chirality of a crystal, studied by conventional optics, and the local atomic anisotropy/chirality accessible only *via* X-ray diffraction. The former and latter are restricted correspondingly by the point and space symmetry groups of the crystal. For example, atomic environments can be locally anisotropic even in cubic crystals and locally chiral even in centrosymmetric structures. According to the optical classification, the chiral effects are associated with the antisymmetric part of a third-rank tensor, and its real and imaginary parts correspond to rotatory power and circular dichroism. In optics, this tensor may differ from zero in non-centrosymmetric crystal classes exclusively. For the Bragg scattering, however, in contrast with optics, not only the chiral properties of scatterers themselves are essential but also the ordering of the scatterers in a unit cell. If atoms are not in inversion centres, their scattering amplitudes can include third-rank antisymmetric tensors, and we will show that their special ordering can cause additional reflections (chirality-induced reflections).

There is quite a close similarity between this effect and the anisotropy-induced reflections which were predicted by Templeton & Templeton (1980), theoretically developed by Dmitrienko (1983, 1984), and experimentally observed for the first time by Templeton & Templeton (1985) for the dipole–dipole transition in $NaBrO_3$. They are usually called 'forbidden reflections' or ATS (anisotropy of the tensor of the susceptibility) reflections, because in the absence of the anisotropy they are strictly forbidden by the glide-plane and/or screw-axis selection rules. The anisotropy of the X-ray susceptibility has significant value only in resonant conditions near absorption edges of atoms, where excited electronic states are strongly influenced by the anisotropic local environment. In the dipole approximation, it is described by the symmetric traceless part of a second-rank tensor. Therefore these 'forbidden' reflections can be observed near the absorption edges of atoms if there are glide planes or screw axes in the symmetry group of the crystal. Up to now they have been found for many crystals, among them $NaBrO_3$ (Templeton & Templeton, 1985), CuO_2, $LiHSeO_3$ (Kirfel, 1994), FeS_2 (Nagano *et al.*, 1996). The electric dipole–dipole contribution was usually dominant.

In some cases, however, the ATS reflections are absent for dipole transitions. For example, they are absent if the scattering vector is directed along the threefold, fourfold or sixfold rotation axis (not to be confused with screw axes). Then, ATS reflections are also absent when resonant atoms are in special positions with high point symmetry (for instance cubic) and for which the dipole anisotropy vanishes. If the reflections are nevertheless observed, the high-rank dipole–quadrupole (Templeton & Templeton, 1994) and quadrupole–quadrupole (Finkelstein *et al.*, 1992) terms are supposed to be relevant. In optics, similar terms are associated with the first- and second-order spatial dispersion correspondingly. The gyrotropic chiral contribution, which is also the first-order spatial dispersion effect, is responsible for the natural circular dichroism in X-ray optics, but it was never observed for X-ray diffraction. This contribution was included in the general formulae (Hannon *et al.*, 1988; Blume, 1994; Templeton, 1998) as the antisymmetric part of the third-rank tensor describing the dipole–quadrupole transitions, but no specific diffraction effects for its observation were suggested.

There is an important difference between symmetric and antisymmetric high-rank contributions to the structure factor of 'forbidden' reflections. It was found recently that the reflections caused by the symmetric part of the high-rank tensors might also appear for dipole–dipole transitions owing to thermal atomic motion or point defects (Dmitrienko *et al.*, 1999; Dmitrienko & Ovchinnikova, 2000). In particular, the forbidden reflections in Ge, originally attributed to the third-rank symmetric contribution (Templeton & Templeton, 1994), are caused mainly by the thermal motion effect (Kokubun *et al.*, 2001). The antisymmetric part cannot be imitated this way.

In the present paper, we show how the local chirality can lead to the appearance of the reflections, which are forbidden in the absence of chirality. From the mathematical point of view, those additional reflections appear owing to the antisymmetric part of the third-rank tensor corresponding to the chirality of resonant atom positions. Hence, in this case one can be sure that the effect is induced by the first-order spatial dispersion of the susceptibility. We also discuss several crystal structures where this term is accompanied by the symmetric third-rank and fourth-rank tensors.

2. Tensor atomic factor and tensor structure factor

To consider the spatial dispersion effects in resonant X-ray scattering, we will use the most general form of the tensoral atomic factor f_{jm} allowed by symmetry (Blume, 1994). In this paper, we take into account only time-reversal terms neglecting spin and orbital ordering. The considered expansion differs from the mulitpole expansion in spherical harmonics, but the tensors appearing are usually classified in a similar way, that is, as dipole–dipole, *dd*, dipole–quadrupole, *dq*, quadrupole–quadrupole, *qq*, and so on,

$$f_{jm} = f_{jm}^{dd} + i f_{jmn}^{dqs}(k'_n - k_n) + i f_{jmn}^{dqa}(k'_n + k_n) + f_{jnmp}^{qq} k'_n k_p + \ldots . \tag{1}$$

The dipole–dipole and quadrupole–quadrupole terms are symmetrical over the index permutation, whereas for the dipole–quadrupole contribution there are two terms, symmetrical and antisymmetrical,

$$\begin{aligned} f_{jm}^{dd} &= f_{mj}^{dd}, \\ f_{jmn}^{dqs} &= f_{mjn}^{dqs}, \\ f_{jmn}^{dqa} &= -f_{mjn}^{dqa}, \\ f_{jnmp}^{qq} &= f_{njmp}^{qq} = f_{jnpm}^{qq} = f_{mpjn}^{qq}. \end{aligned} \tag{2}$$

In general, all these terms are complex and include resonant denominators. Note that the symmetrical third-rank tensor is absent in optics because $\mathbf{k}' = \mathbf{k}$. This term was discussed in detail by Templeton & Templeton (1994). In addition to this permutation symmetry, each tensor should be symmetric over the point group of the corresponding atomic position. This produces strong restrictions on the number of independent non-zero components. All these restrictions can be found in the crystallography textbooks (Sirotin & Shaskolskaya, 1975; Nye, 1985). Each of these independent components may be resonant and for the most general description they should be considered as independent complex parameters. For all the atoms occupying the same orbit of equivalent positions, however, the set of those complex parameters is the same (because the atoms' environment is the same); only orientations or signs (in the case of inversion) of the corresponding tensors may be different.

In particular, the antisymmetric third-rank tensor differs from zero only for the point groups without an inversion centre. This means that all considered effects are possible only in the case of non-reversal time-invariant transitions. This was studied in detail in connection with the chiral effects in X-ray resonant optics (Goulon *et al.*, 1998; Natoli *et al.*, 1998) similar to conventional optics (Chiu, 1970; Buckingham & Dunn, 1971; Barron, 1971).

To find the possible reflections in the diffraction pattern, one should find the tensor structure amplitudes $F_{jm}(\mathbf{H})$ for reflection vectors $\mathbf{H}$,

$$F_{jm}(\mathbf{H}) = \sum_s f_{jm}^s \exp(2\pi i\, \mathbf{H}\mathbf{r}^s), \tag{3}$$

where $\mathbf{r}^s$ is the position of the sth atom in the unit cell and f_{jm}^s is given by (1).

If the atomic factor is scalar (as it is usually supposed) then the structure factor (3) must be zero for some reflections related by screw axes and/or glide planes [so-called general reflection conditions in *International Tables for Crystallography* (1996)]. Because tensors are changed under the rotation and mirror operations, they can violate those general conditions and produce 'forbidden' reflections. In order to illustrate this point, we calculate in §§3 and 4 the tensor structure factors of 'forbidden' reflections for cases of increasing complexity. We will select space groups for which a number of ATS reflections are forbidden in the dipole–dipole (or even in quadrupole–quadrupole) approximation but become allowed owing to the antisymmetric and symmetric parts of the tensor f_{jmn}^{dq}.

3. A simple example: cubic symmetry of resonant atom positions

Let us start with a simple illustrative example when the symmetry of resonant atom positions is so high, 432, that it does not allow any anisotropy of scattering in the dipole–dipole approximation. This cubic symmetry also forbids the symmetric third-rank tensor, but allows the antisymmetric third-rank tensor f^{dqa}_{jmn} and the fourth-rank tensor f^{qq}_{jmnp}. Such a situation exists in the $Pn\bar{3}n$ space group with the resonant atoms in the 2(a) position with 432 symmetry and coordinates (i) 0, 0, 0 and (ii) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

For isotropic susceptibility, the Bragg reflections $0kl$, $k + l = 2n + 1$, and hhl, $l = 2n + 1$, are forbidden according to the general reflection conditions (*International Tables for Crystallography*, 1996). For the forbidden reflections, atom (i) and atom (ii) scatter X-rays in antiphase so that the tensor structure factor is given by $F_{jm}(\mathbf{H}) = f^{(1)}_{jm} - f^{(2)}_{jm}$. Because the positions (i) and (ii) are related by inversion, the fourth-rank tensors are the same for the two atoms and their contributions vanish. On the contrary, the third-rank tensors have opposite signs and their contributions give the following structure amplitude:

$$F_{jm}(\mathbf{H}) = 2ig\varepsilon_{jmn}(k'_n + k_n), \tag{4}$$

where it is taken into account that for the 432 symmetry the antisymmetric third-rank tensor should be proportional to the tensor ε_{jmn} antisymmetric over all indices (ε_{xyz} = 1); g is a complex coefficient which includes a resonant denominator.

Multiplying the structure amplitude by polarization vectors of incident and diffracted waves, $\mathbf{e}$ and $\mathbf{e}'$, we have

$$\mathbf{e}'\hat{\mathbf{F}}(\mathbf{H})\mathbf{e} = 2ig(\mathbf{k}' + \mathbf{k})(\mathbf{e}' \times \mathbf{e}). \tag{5}$$

Here, and hereafter, a circumflex (ˆ) above a letter signifies a tensor and the sign × signifies the vector product. For the conventional $\boldsymbol{\sigma}$ and $\boldsymbol{\pi}$ polarization vectors it is easy to see that $\boldsymbol{\sigma}\hat{\mathbf{F}}\boldsymbol{\sigma} = \boldsymbol{\pi}'\hat{\mathbf{F}}\boldsymbol{\pi} = 0$ and $\boldsymbol{\sigma}\hat{\mathbf{F}}\boldsymbol{\pi} = -\boldsymbol{\pi}'\hat{\mathbf{F}}\boldsymbol{\sigma} = 2ig(1 + \cos 2\theta_{\rm B})$. Therefore, the initial $\boldsymbol{\pi}$ polarization transforms into $\boldsymbol{\sigma}$ polarization of the diffracted wave and *vice versa* for all forbidden reflections. It is unusual that the structure amplitudes $\boldsymbol{\sigma} \Rightarrow \boldsymbol{\pi}$ and $\boldsymbol{\pi} \Rightarrow \boldsymbol{\sigma}$ have opposite signs. Furthermore, we shall see that this sign difference can lead to interesting effects in less symmetrical situations.

Note that for this case the scattering amplitude is spherically symmetrical, without any anisotropy, and depends only on the scattering angle $2\theta_B$. Nevertheless, we have non-zero 'forbidden' reflections (in this case ATS should be read as antisymmetric tensor of susceptibility). The only bad point with this example is that there are no good crystals with $Pn\bar{3}n$ symmetry. The same situation exists, however, in the $Fm\bar{3}c$ structures for resonant atoms in the 8(a) position. There are many crystals of the cF112 Pearson type with this structure but their large unit cell makes the observation of forbidden reflections very difficult because of the multiple-wave reflections. Similar examples may be found in the $P\bar{4}3n$ structures where resonant atoms can be at the 2(a) positions with 23 point symmetry. There are also many suitable less-symmetrical crystals with few atoms per unit cell (for some of them the space group is a subgroup of $Pn\bar{3}n$) and now we will consider these more realistic structures.

4. Resonant atoms in special positions with non-cubic symmetry

We will again concentrate on those cases where the ATS reflections vanish for the dipole–dipole transition. In the previous section, we considered an example of a crystal without any anisotropy in the dipole–dipole approximation. In some cases, however, the dipole–dipole contribution to ATS reflections is absent in spite of the local anisotropy of atomic positions. For example, the dipole–dipole transitions give no contribution to ATS reflections from the crystal planes normal to threefold, fourfold and sixfold axes. Therefore, it is interesting to study the cases of rhombohedral, tetragonal and hexagonal crystals.

4.1. Rhombohedral crystals with $R\bar{3}c$ and $R3c$ symmetries

Let us consider first the hematite crystal, α-Fe_2O_3, where quadrupole–quadrupole terms were supposed to be responsible for the hhh, $h = 2n + 1$, reflections observed near the iron K edge (Finkelstein *et al.*, 1992; Watanabe *et al.*, 2000). We will neglect the magnetic ordering and, strictly speaking, our results will be valid for the paramagnetic phase of α-Fe_2O_3 or other crystals with the same structure, like V_2O_3. Here we will consider more carefully the nature of these reflections.

The space group of hematite is rhombohedral, $R\bar{3}c$, with four Fe atoms per unit cell in the 4c sites at the threefold axes (Fig. 1). The coordinates of Fe atoms will be enumerated in the order of their positions at the threefold axis: (i) $\bar{x}\bar{x}\bar{x}$, (ii) xxx, (iii) $\bar{x} + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{x} + \frac{1}{2}$, (iv) $x + \frac{1}{2}, x + \frac{1}{2}, x + \frac{1}{2}$, where x = 0.105. The point symmetry is 3 and the atom environment is

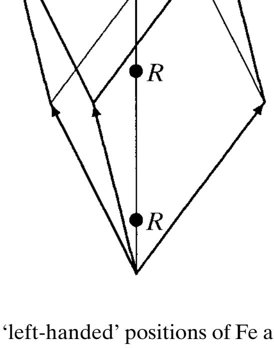

Figure 1
The 'right-handed' and 'left-handed' positions of Fe atoms in a unit cell of hematite.

chiral: if we assume that atom (i) is left-handed then atom (iv), related to atom (i) by twofold rotation, is also left-handed, whereas atoms (ii) and (iii), related to atoms (i) and (iv) by inversion, should be right-handed (hence, inside a unit cell the sequence of atoms along the threefold axis is *RRLL*, Fig. 1).

If any anisotropy is neglected, then the glide-plane-forbidden reflections are hhl, $l = 2n+1$, and hhh, $h = 2n+1$, because for these reflections atoms (i) and (iii) scatter in antiphase as well as atoms (ii) and (iv). For any tensor part of the susceptibility, it is obvious that only those components of the tensors that change sign under the glide-plane operation can contribute to the forbidden reflections. This is a necessary condition but not sufficient; the contribution can vanish because of the special orientation of the polarization and wave vectors.

In the case of the dipole–dipole resonant transition, the second-rank susceptibility tensors of Fe atoms are uniaxial and oriented along threefold axes. Therefore, the second-rank tensors are the same for all the atoms and the forbidden reflections remain forbidden in this approximation.

Contrary to the second-rank tensors, the third-rank tensors are different for different Fe atoms but related by corresponding symmetry operations. For atoms related by inversion, (i) and (ii) or (iii) and (iv), the third-rank tensors have opposite sign. We will write all tensor components in crystallophysical Cartesian coordinates with the z axis along the 3 symmetry axis of the rhombohedron and the x axis normal to the glide plane. For reflections, however, we will use notations in rhombohedral coordinates. In the Cartesian coordinates, the symmetric part of the third-rank tensor, $f^{dqs}_{jmn} = f^{dqs}_{mjn}$, has the following non-zero components for the threefold symmetry: $xxx = -yyx = -xyy$; $yyy = -xyx = -xxy$; $zxy = -yzx$; $yzy = zxx$; $xxz = yyz$; zzz (six independent constants). It is easy to see that only two types of components, $xxx = -yyx = -xyy$ and $zxy = -yzx$, change their sign under the glide-plane operation $x \Rightarrow -x$ and can contribute to the forbidden reflections. Let us denote $f^{dqs}_{xxx} = f^{dqs}_1$ and $f^{dqs}_{zxy} = f^{dqs}_2$ for atom (ii). For the structure factor of forbidden reflections we obtain

$$\hat{\mathbf{F}}^{dqs}(hhl) = 4i\sin[2\pi(2h+l)x]\begin{pmatrix} f^{dqs}_1 H_x & -f^{dqs}_1 H_y & f^{dqs}_2 H_y \\ -f^{dqs}_1 H_y & -f^{dqs}_1 H_x & -f^{dqs}_2 H_x \\ f^{dqs}_2 H_y & -f^{dqs}_2 H_x & 0 \end{pmatrix}. \tag{6}$$

According to the usual convention for hhh reflections that the vector $\mathbf{H} = \mathbf{k}' - \mathbf{k}$ is directed along the z axis, we find that $\hat{F}(hhh)$ vanishes. This means that there is no symmetrical dipole–quadrupole contribution to the hhh, $h = 2n+1$, forbidden reflections. The third-rank symmetric tensor can contribute only in the hhl, $l = 2n+1$, $h \neq l$, reflections but a similar contribution can also appear owing to thermal-motion-induced anisotropy in the dipole–dipole approximation.

The antisymmetric part of the third-rank tensor, $f^{dqa}_{jmn} = -f^{dqa}_{mjn}$, contains three independent non-zero components: xyz; $yzx = zxy$; $yzy = -zxx$. Only two of them, xyz and $yzx = zxy$, change their sign under the glide-plane symmetry operation and can contribute to the forbidden reflections. If we denote $f^{dqa}_{xyz} = f^{dqa}_1$ and $f^{dqa}_{zxy} = f^{dqa}_2$ for atom (ii), then the structure factor of forbidden reflections is given by the following equation:

$$\hat{\mathbf{F}}^{dqa}(hhl) = 4i\sin[2\pi(2h+l)x]\begin{pmatrix} 0 & f^{dqa}_1 k^+_z & -f^{dqa}_2 k^+_y \\ -f^{dqa}_1 k^+_z & 0 & f^{dqa}_2 k^+_x \\ f^{dqa}_2 k^+_y & -f^{dqa}_2 k^+_x & 0 \end{pmatrix}, \tag{7}$$

where $k^+ = k' + k$. Both types of forbidden reflections, hhh, $h = 2n+1$, and hhl, $l = 2n+1$, $h \neq l$, can be excited owing to the antisymmetric third-rank tensor.

The quadrupole–quadrupole contribution is described by the symmetric fourth-rank tensor (magnetism is neglected). For the atoms related by inversion, this tensor is the same (seven independent components). Only one of these components is odd relative to x: $xxxz = -yyxz = -xyyz$ (*i.e.* it changes its sign under the glide-plane operation). This component can contribute to forbidden reflections and, denoting $f^{qq}_{xxxz} = f^{qq}_1$ for atom (ii), we obtain the following structure factor of forbidden reflections:

$$\begin{aligned} \hat{\mathbf{F}}^{qq}(hhl) &= 4\cos[2\pi(2h+l)x]\,f^{qq}_1 \\ &\quad\times\begin{pmatrix} k_x k'_z + k_z k'_x & -k_y k'_z - k_z k'_y & k_x k'_x - k_y k'_y \\ -k_y k'_z - k_z k'_y & -k_x k'_z - k_z k'_x & -k_x k'_y - k_y k'_x \\ k_x k'_x - k_y k'_y & -k_x k'_y - k_y k'_x & 0 \end{pmatrix}. \end{aligned} \tag{8}$$

It is easy to see that $\hat{\mathbf{F}}^{qq}(hhl) \neq 0$ for both types of forbidden reflections, hhh, $h = 2n+1$, and hhl, $l = 2n+1$, $h \neq l$.

Let us consider more carefully the hhh, $h = 2n+1$, reflections. In this case, the tensor structure amplitudes are strongly simplified,

$$\hat{\mathbf{F}}^{dqa}(hhh) = 8ikf^{dqa}_2 \sin(6\pi hx)\cos\theta\begin{pmatrix} 0 & 0 & -\sin\varphi \\ 0 & 0 & \cos\varphi \\ \sin\varphi & -\cos\varphi & 0 \end{pmatrix}, \tag{9}$$

$$\begin{aligned} \hat{\mathbf{F}}^{qq}(hhh) &= 4\cos(6\pi hx) f^{qq}_1 k^2 \cos^2\theta \\ &\quad\times\begin{pmatrix} 0 & 0 & \cos 2\varphi \\ 0 & 0 & -\sin 2\varphi \\ \cos 2\varphi & -\sin 2\varphi & 0 \end{pmatrix}. \end{aligned} \tag{10}$$

The polarization properties of the reflections are simple: the σ-polarized incident beam transforms into the π-polarized diffracted beam and *vice versa*. The structure amplitudes for these two channels are given by the following expressions calculated from (9) and (10):

$$\begin{aligned} \boldsymbol{\pi}'\hat{\mathbf{F}}(hhh)\boldsymbol{\sigma} &= 8ikf^{dqa}_2 \sin(6\pi hx)\cos^2\theta \\ &\qquad + 4\cos(6\pi hx) f^{qq}_1 k^2 \cos^3\theta \sin 3\varphi, \\ \boldsymbol{\sigma}\hat{\mathbf{F}}(hhh)\boldsymbol{\pi} &= -8ikf^{dqa}_2 \sin(6\pi hx)\cos^2\theta \\ &\qquad + 4\cos(6\pi hx) f^{qq}_1 k^2 \cos^3\theta \sin 3\varphi. \end{aligned} \tag{11}$$

An unusual feature is that the intensities of the $\boldsymbol{\sigma} \Rightarrow \boldsymbol{\pi}$ and $\boldsymbol{\pi} \Rightarrow \boldsymbol{\sigma}$ channels may be different owing to interference between dipole–quadrupole and quadrupole–quadrupole contributions. If $f_2^{dqa} = 0$ (*i.e.* only the quadrupole–quadrupole term differs from zero), then the azimuthal dependence is sixfold for both channels. For $f_1^{qq} = 0$, the azimuthal dependence given by the antisymmetric third-rank tensor is trivial. In the presence of both terms the interference influences the azimuthal dependence of the reflections. For both channels, the azimuthal dependence has a threefold symmetry, but a phase shift of 60° appears between $I_{\pi\sigma}(\varphi)$ and $I_{\sigma\pi}(\varphi)$.

Note that just the threefold azimuthal dependence was recently observed in hematite by Watanabe *et al.* (2000). However, there may be another explanation of the threefold azimuthal symmetry supposing the orbital ordering in hematite (Lovesey & Knight, 2000). The difference is that in the case of the orbital ordering the intensities of the $\boldsymbol{\sigma} \Rightarrow \boldsymbol{\pi}$ and $\boldsymbol{\pi} \Rightarrow \boldsymbol{\sigma}$ channels are equal. The dependences of the intensities on θ and hx are also very different for these two physical mechanisms and perhaps it would be not too difficult to distinguish them experimentally.

In other $R\bar{3}c$ crystals, like $FeCO_3$ and $FeBO_3$, the third-rank contribution vanishes for Fe atoms because they are at the inversion centres [$x = 0$ in (11)] and the azimuthal dependence should be sixfold. For C or B atoms ($x = \frac{1}{4}$), the fourth-rank contribution vanishes and the third-rank contribution reaches its maximum, but the energies of their absorption edges are too small for diffraction. The same situation occurs in the high-temperature $R\bar{3}c$ structure of the $LiNbO_3$ crystal. The low-temperature ferroelectric phase has $R3c$ symmetry and two Nb atoms are at x, x, x and $x+\frac{1}{2}, x+\frac{1}{2}, x+\frac{1}{2}$ positions with point symmetry 3, exactly like atoms (ii) and (iv) in the hematite structure. Therefore, near the Nb absorption edges the tensor structure factor of the hhh, $h = 2n+1$, forbidden reflections is similar to (11),

$$\boldsymbol{\pi}'\hat{\mathbf{F}}(hhh)\boldsymbol{\sigma} = 2\exp(6\pi ihx)[if_2^{dqa}k\cos^2\theta + f_1^{qq}k^2\cos^3\theta\sin 3\varphi], \tag{12}$$

$$\boldsymbol{\sigma}\hat{\mathbf{F}}(hhh)\boldsymbol{\pi} = 2\exp(6\pi ihx)[-if_2^{dqa}k\cos^2\theta + f_1^{qq}k^2\cos^3\theta\sin 3\varphi].$$

The value of f_2^{dqa} differs from zero because $x \neq 0$, *i.e.* because of the ferroelectric polarization. Hence, when the temperature T is near the temperature T_c of the phase transition into the paraelectric phase, one can expect that $f_2^{dqa} \propto x \propto (T_c - T)^{1/2}$.

4.2. Tetragonal crystals

Let us consider the $P4/nnc$ structure with the resonant atoms in the $2(a)$ position: (i) 0, 0, 0 and (ii) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Far from the absorption edge, the reflections $0kl$, $k0l$, $k+l = 2n+1$, are forbidden according to the general reflection conditions. In the dipole–dipole approximation, the local 422 symmetry allows only the diagonal form of the scattering amplitude tensor, which is the same for both atomic positions. Hence, no ATS reflections appear near absorption edges owing to the dipole–dipole transition.

Now let us calculate the dipole–quadrupole contribution to the scattering amplitude, which is equal to

$$F_{ijk}^{dq}(0kl, k+l = 2n+1) = f_{ijk}^{dq,1} - f_{ijk}^{dq,2}. \tag{13}$$

The point symmetry of the resonant-atom sites allows two types of non-zero components for the antisymmetric part of a third-rank tensor and one type for the symmetric part. For atom (i), the antisymmetric part of a third-rank tensor contains the following non-zero components: $f_{yzx}^{dqa} = f_{zxy}^{dqa} = f_1^{dqa}$, $f_{xyz}^{dqa} = f_2^{dqa}$. The non-zero components of the symmetric third-rank tensor on atom (i) are equal to $f_{yzx}^{dqs} = f_{zyx}^{dqs} = -f_{xzy}^{dqs} = -f_{zxy}^{dqs} = f_1^{dqs}$. The atoms (i) and (ii) are connected by the inversion (hence $f_{ijk}^1 = -f_{ijk}^2$) and also by the glide plane $(m_{-x-y} \mid 00\frac{1}{2})$, which causes the following coordinate transformation: $y \to -x$, $x \to -y$, $z \to z+\frac{1}{2}$. The calculation of the third-rank tensor components taking into account the structure factors shows that the symmetric part of $F_{ijk}^{dqs}(0kl, k+l = 2n+1)$ possesses the following non-zero components: $F_{yzx}^{dqs}(0kl) = -F_{xzy}^{dqs}(0kl) = f_{yzx}^{dqs,1} - f_{yzx}^{dqs,2} = f_{yzx}^{dqs} - f_{xzy}^{dqs} = 2f_1^{dqs}$. The antisymmetric part $F_{ijk}^{dqa}(0kl, k+l = 2n+1)$ has the components $F_{yzx}^{dqa}(0kl) = -F_{xzy}^{dqa}(0kl) = f_{yzx}^{dqa} - f_{xzy}^{dqa} = 2f_1^{dqa}$, $F_{xyz}^{a}(0kl) = f_{xyz}^{a} - f_{yzx}^{a} = 2f_2^{a}$.

An interesting case occurs for the reflection $00l$, $l = 2n+1$. The convolution of $F_{ijk}^{dq}(00l, l = 2n+1)$ with the components of the vectors $\mathbf{H}$ and $\mathbf{k}^+$ gives the scattering amplitude for the $00l$, $l = 2n+1$, reflection,

$$F_{ij}^{dq}(00l, l = 2n+1) = 2if_1^{dqa}\begin{pmatrix} 0 & 0 & -k_y^+ \\ 0 & 0 & k_x^+ \\ k_y^+ & -k_x^+ & 0 \end{pmatrix}. \tag{14}$$

We see that only the antisymmetric part of a third-rank tensor contributes to the scattering amplitude, *i.e.* $F_{ij}^{dqs}(00l, l = 2n+1) = 0$, but $F_{ij}^{dqa}(00l, l = 2n+1) \neq 0$.

It is easy to see that there is no contribution to this reflection from the quadrupole–quadrupole transition. Indeed, the considered atomic sites are related by inversion; therefore, any fourth-rank tensors are the same for both sites. Neglecting the higher-order terms, we find that only the antisymmetric part of a third-rank tensor can be the reason for the $00l$, $l = 2n+1$, reflections near the absorption edge of a resonant atom in the $2(a)$ position of the space group $P4/nnc$.

In several other tetragonal groups, we find the situation when the high tetragonal symmetry of resonant atomic positions forbid ATS reflections in the dipole–dipole and quadrupole–quadrupole transitions, but allows both the symmetric and antisymetric parts of a third-rank tensor.

4.3. Resonant atoms in a general position

The symmetry properties of a structure amplitude depend on two factors: (i) the transformation properties of a space group itself, and (ii) the local symmetry of the resonant atoms position. In the present section, we will consider the first factor. We will concentrate on forbidden reflections with the diffraction vectors directed along threefold, fourfold and sixfold axes because all other reflections can be excited even in the dipole–dipole approximation. If a space group contains a threefold, fourfold or sixfold axis together with the glide-plane c, then the structure amplitude for $00l$, $l = 2n+1$, reflections satisfy the relation

$$\hat{\mathbf{F}}(00l) = \exp(il\varphi)\hat{\mathbf{g}}\hat{\mathbf{F}}(00l), \tag{15}$$

where $\varphi = \pi$ for the glide plane $(\hat{\mathbf{g}} \mid \mathbf{c}/2)$ and $\varphi = 2\pi$ for point-symmetry elements $(\hat{\mathbf{g}} \mid 0)$. It essentially restricts the number of non-zero tensor elements: only those tensor components differ from zero that are allowed by point groups 3, 4 and 6 [they may be found in the textbooks by Sirotin & Shaskolskaya (1975); Nye (1985)] and change their sign under the mirror reflection.

Let us consider tetragonal space groups $P4nc$, $P4cc$, $P4/mcc$, $P4/mnc$ and $P4/nnc$. In all of these, the second-rank tensors contain only the components $F_{xx}^{dd} = F_{yy}^{dd}$ and F_{zz}^{dd}. They are invariant under the mirror reflections, hence $00l$, $l = 2n+1$, ATS reflections are absent in the dipole–dipole resonant transition.

The following third-rank tensor components differ from zero and change their sign under the mirror transformation $y \to -y$: $F_{yzx}^{dqs} = -F_{zxy}^{dqs}$, $F_{yzx}^{dqa} = F_{zxy}^{dqa} = F_1^{dqa}$, $F_{xyz}^{dqa} = F_2^{dqa}$. Fourth-rank tensors contain the components $F_{xxxy} = -F_{yyyx} = F^{qq}$. For the considered reflections $00l$, $l = 2n+1$, the symmetric part of a third-rank tensor provides no contribution to the scattering amplitude, similar to the considered case above of special resonant atoms positions. Hence the forbidden reflections contain the antisymmetric third-rank and fourth-rank contributions even if resonant atoms belong to a general position. The tensor structure amplitude is equal to

$$\hat{\mathbf{F}}(00l) = ikF_2^{dqa}\cos\theta \begin{pmatrix} 0 & 0 & -\sin\varphi \\ 0 & 0 & \cos\varphi \\ \sin\varphi & -\cos\varphi & 0 \end{pmatrix} + F^{qq}k^2\cos^2\theta\sin 2\varphi \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{16}$$

The azimuthal dependence of the pure quadrupole term is fourfold. The intensity turns to be zero at $\varphi = (\pi/2)n$ ($n = 1, 2, \ldots$). For the pure dipole–quadrupole contribution, the azimuthal dependence is trivial and the intensity differs from zero for any angles.

Additional restrictions on the tensor components occur when resonant atoms are in special positions with 2_x, 2_y, 222 or 422 local symmetry. In this case, the quadrupole–quadrupole tensor vanishes. Therefore, the forbidden reflection $00l$, $l = 2n+1$, are induced only by the antisymmetric part of a third-rank tensor.

The tetragonal groups listed above describe the symmetry of several minerals, among them iragite, turkestanite ($P4/mcc$); apophylite, chiolite, hydroromachite ($P4/mnc$); and cuprorivaite, effenbergite and urancircite ($P4/nnc$). In all these substances, $00l$, $l = 2n+1$, reflections appear near the absorption edges owing to the local chirality.

Now we pay attention to the hexagonal space groups which contain a 6 axis and a glide plane c. In these groups, similar to the tetragonal case, ATS reflections $00l$, $l = 2n+1$, remain forbidden for dipole–dipole resonant transitions. To find non-zero components of a tensor structure amplitude, we again look for the terms which are invariant under the sixfold rotation and change sign under mirror reflection owing to the c glide plane. The components which satisfy these demands are $F_{yzx}^{dqs} = F_{zxy}^{dqs}$, $F_{yzx}^{dqa} = F_{zxy}^{qda}$. A fourth-rank tensor does not contain the proper components. The symmetric part of a third-rank tensor gives no contribution to $00l$, $l = 2n+1$, reflections. Hence we find that, in the space groups $P6cc$, $P6/mcc$, $P\bar{6}c2$ and $P\bar{6}2c$, only the antisymmetric part of the third-rank tensor makes a contribution to the forbidden chirality-induced reflections. It is correct even for crystals with resonant atoms in general positions.

Special consideration has to be made for space groups with screw axis 6_3 because $00l$, $l = 2n+1$, ATS reflections are forbidden in the dipole–dipole approximation (Dmitrienko, 1983; Belyakov & Dmitrienko, 1989). The same is true for the $00l$, $l = 6n+3$, reflections in the presence of the 6_1 and 6_5 axes. Because there are no point-symmetry elements, it is more suitable to calculate tensor components as a sum under the atoms inside the position. The coordinates of the atoms on the orbit of the 6_3 group are equal to: (i) $x - y/2, 3^{1/2}y/2, z$; (ii) $-(x+y)/2, 3^{1/2}(x-y)/2, z$; (iii) $y - x/2, -3^{1/2}x/2, z$; (iv) $y/2 - x, -3^{1/2}y/2, z + \frac{1}{2}$; (v) $(x+y)/2, 3^{1/2}(y-x)/2, z + \frac{1}{2}$; (vi) $x/2 - y, 3^{1/2}x/2, z + \frac{1}{2}$. We can calculate $F_{ijk}^{dq}(00l,\ l = 2n+1) = \sum_i f_{ijk}^{dqi}$ and find that the antisymmetric part of the third-rank tensor is equal to zero. The symmetric part has non-zero components F_{xyx}^{dqs}, F_{xxx}^{dqs} *etc*., but it vanishes after convolution with the components of the corresponding reciprocal vector. Hence, there is no chirality-induced reflections of type $00l$, $l = 2n+1$, in the space groups with a 6_3 axis.

It is also easy to prove that the $00l$, $l = 2n+1$, forbidden reflections in the $Pn\bar{3}n$ crystals can be induced exclusively by the antisymmetric part of a third-rank tensor (without any contribution from the quadrupole–quadrupole mechanism) even if the resonant atoms are in general positions. The only position which cannot contribute to the $00l$, $l = 2n+1$, reflections is $8(c)$ because its point symmetry is $\bar{3}$.

5. Conclusions

We have found symmetry restrictions on the components of the antisymmetric part of the X-ray susceptibility in different space groups. They show that some additional reflections can appear near absorption edges, which are induced by local chirality of the atomic structure. We have identified those cases where only dipole–quadrupole resonant transitions provide a significant contribution. A prerequisite for this is the absence of ATS reflections in dipole–dipole transitions. It is shown that the chirality-induced reflections occur in cubic, rhombohedral, tetragonal and hexagonal crystals for the diffraction vectors directed along threefold, fourfold or sixfold axes. All other reflections can be excited even in the dipole–dipole approximation either because of general atomic positions or because of thermal atomic motion. In the presence of different contributions, interference between chirality-induced and other terms can provide additional information about the local chirality.

The chirality-induced effects in resonant X-ray diffraction correspond to the non-reversal time-invariant electronic transitions in atoms, which are also responsible for chiral effects in X-ray optics of non-magnetic crystals. Nevertheless, the resonant diffraction exhibits some properties of crystal chirality, never observed in the transmitted direction. The most interesting result concerns the existence of the chirality-induced reflections in centrosymmetric crystals which are not gyrotropic in optics. This demonstrates the difference between microscopic and macroscopic chirality of crystals.

If we refer to experimental results, the amplitude of the dipole–quadrupole contribution to dichroism is rather weak but can be of the order of a few 10^{-2} in favourable cases (Goulon *et al.*, 1998). The intensity of the chirality-induced reflections depends on both the imaginary and real parts of the scattering amplitude, which are related by the Kramers–Kronig dispersion relation generalized for the scattering process (Goldberger & Watson, 1964; Cross *et al.*, 1998). One may anticipate that the detection of the chirality-induced reflections will be rather difficult because of their small intensity. Nevertheless, the magnetic reflections owing to non-resonant scattering (Gibbs *et al.*, 1985) with a scattering amplitude of about 10^{-3} were successfully observed with synchrotron radiation as far as the quadrupole–quadrupole forbidden reflections (Finkelstein *et al.*, 1992; Watanabe *et al.*, 2000). This must encourage the experimental attempts to study the chirality-induced reflections.

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