Resonant X-ray scattering in the presence of several anisotropic factors

E. N. Ovchinnikova[a]* and V. E. Dmitrienko[b]

[a]Moscow State University, Physical Department, 119899 Moscow, Russia, and [b]A. V. Shubnikov Institute of Crystallography, 117333 Moscow, Russia. Correspondence e-mail: eno@simmetry.phys.msu.su

The general form of the X-ray susceptibility tensor near absorption edges is found when several anisotropic factors, such as the anisotropy of local atomic environment, magnetic ordering and orbital ordering, simultaneously exist in a crystal. Different phenomenological approaches are used to obtain the explicit form of the susceptibility tensor and to find the contributions from each anisotropic factor separately as well as 'combined' terms owing to their simultaneous existence. The results of the theoretical treatment are applied to the resonant diffraction by $La_{0.5}Sr_{1.5}MnO_4$ below the Néel temperature, where charge and orbital ordering coexist with anisotropy of local atomic environment and magnetic ordering.

1. Introduction

Resonant X-ray diffraction has been proved to be a method sensitive to the local properties of a crystal, such as anisotropy of the local atomic environment or atomic magnetic moments orientation. The enhancement of the resonant X-ray scattering amplitude near absorption edges is closely related to anomalous dispersion and occurs when the energy of the incident radiation approaches the value required to excite an inner-shell electron into an empty state of a valence shell. The valence shells are strongly affected by the local environment and therefore the atomic scattering amplitude depends on the local crystal field, the atomic magnetic moment and other factors that influence the electronic states. If the degeneration of the valence-electron states is broken down owing to the various factors, the susceptibility of the crystal becomes anisotropic near the absorption edge. The anisotropic properties of the susceptibility provide effects like birefrigence and dichroism. In diffraction, it leads to the excitement of forbidden magnetic (Gibbs et al., 1985) and ATS (anisotropy of the tensor of susceptibility) (Templeton & Templeton, 1980; Dmitrienko, 1983) reflections, which possess complex azimuthal and polarization properties. Using the general properties of susceptibility, it was shown (Ovchinnikova & Dmitrienko, 1997) that the simultaneous existence of two kinds of anisotropic properties, for instance, anisotropy of the local atomic environment along with magnetic ordering, can stimulate the existence of extra reflections that are forbidden otherwise. Recently, the anisotropy owing to orbital ordering was studied with the help of resonant diffraction of synchrotron radiation (Murakami et al., 1998). The possibility of forbidden reflec-

tions caused by violation of local anisotropy by thermal vibrations was recently considered by Dmitrienko et al. (1999).

Different approaches can be used to calculate the scattering amplitude taking into account magnetic ordering together with anisotropy of local atomic environment and/or orbital ordering. One of them, using the spherical tensors technique, was developed by Hannon et al. (1988), Carra & Thole (1994), Carra et al. (1993), Rennert (1993), Fabrizio et al. (1998) and others. The Cartesian form of the susceptibility in the presence of a magnetic moment together with an axially symmetric local environment was considered for dipole transition by Blume (1994).

In the present paper, we develop an approach based on the explicit Cartesian form of the susceptibility tensor. This approach gives a simple way of treating several problems, such as the determination of the set of possible reflections and computation of their polarization properties. We use the phenomenological treatment, which allows one to obtain the explicit form of the susceptibility tensor taking into account various different anisotropic factors. Our treatment is based on the expansion of the susceptibility tensor in terms of small order parameters describing anisotropy of the local atomic environment, magnetic ordering and orbital ordering. This approach will be referred to as 'the weak anisotropy approximation'. It allows one to obtain the explicit form of the susceptibility for any kind of resonant transition, which contains the separate contributions from each anisotropic factor together with the terms describing the 'combined' effects owing to the simultaneous existence of different anisotropies. We discuss also forbidden reflections appearing due to these 'combined' terms in the susceptibility tensor.

2. The susceptibility tensor near the absorption edge

In the present paper, we shall consider all tensors in a Cartesian basis. This approach is widely used, *e.g.* by Blume (1994), Brouder (1990), Kirfel *et al.* (1991), Kissel *et al.* (1995) and Templeton (1998). The resonant part of the scattering factor $F_{res}(\mathbf{H})$, describing the resonant X-ray scattering into the reflection with $\mathbf{H} = (hkl)$ is equal to

$$F_{res}(\mathbf{H}) = -(V\omega^2/4\pi r_e c^2) \sum_s e_i'^* e_j \chi_{ij}^s \exp(i\mathbf{Hr}_s - W_s), \quad (1)$$

where s runs over the number of atoms in the unit cell, $\mathbf{k}$ and $\mathbf{k}' = \mathbf{k} + \mathbf{H}$ are the wave vectors of the incident and scattered radiation with the polarization vectors $\mathbf{e}$ and $\mathbf{e}'$, ω is the frequency of radiation, $r_e = e^2/mc^2$, V is the unit-cell volume, χ_{ij}^s is the resonant susceptibility tensor of the sth atom and W_s is the temperature factor. In (1), we used the usual relation between susceptibility and structure factor (see Pinsker, 1982). The resonant susceptibility tensor can be calculated as

$$\chi_{ij}^s(\omega, \mathbf{k}', \mathbf{k}) = (4\pi r_e c^2 m \omega_{ca}^3/\hbar\omega^3 V)$$
$$\times \sum_{ca} p_a[B_{ca,i}^{s0} B_{ca,j}^{s*}/(\omega_a - \omega_c + \omega - i\Gamma/2\hbar)], \quad (2)$$

where

$$B_{ca}^{s*} = \langle a \mid \mathbf{r}[1 - i\mathbf{k}'\mathbf{r} - (\mathbf{k}' \cdot \mathbf{r})^2 + \ldots] \mid c\rangle, \quad (3)$$

$$B_{ca}^{s0} = \langle c \mid \mathbf{r}[1 + i\mathbf{kr} - (\mathbf{k} \cdot \mathbf{r})^2 + \ldots] \mid a\rangle, \quad (4)$$

$\mid c\rangle$ describes the intermediate electronic state with the eigenvalue $E_c = \hbar\omega_c$, $\mid a\rangle$ the initial and final electronic states with the eigenvalue $E_a = \hbar\omega_a$, p_a is the probability that the incident state of the scatterer $\mid a\rangle$ is occupied, $\omega_{ca} = \omega_c - \omega_a$, Γ is the inverse lifetime of the intermediate state. The explicit form of the susceptibility tensor depends on the type of electronic transition and on the electronic states. The considered expansion differs from the usual multipole expansion in spherical harmonics, but the resulting tensors are usually classified in a similar way, that is as dipole–dipole, dipole–quadrupole, quadrupole–quadrupole and so on:

$$\chi_{ij} = \chi_{ij}^{dd} + \chi_{ijk}^{dq}(\mathbf{k}' - \mathbf{k}) + \chi_{ijkl}^{qq}\mathbf{k}'\mathbf{k} + \ldots. \quad (5)$$

The explicit forms of the susceptibility tensors in the Cartesian coordinates were calculated for magnetic and nonmagnetic crystals for dipole $E1$ and quadrupole transitions (Hannon *et al.*, 1988; Blume, 1994). The sum rules that allow the scattering amplitude to be calculated in terms of spherical tensors were represented by Carra *et al.* (1993) and Luo *et al.* (1993). In the dipole–dipole approximation, the explicit Cartesian form of susceptibility for the simultaneous existence of magnetic ordering and axially symmetric anisotropy of the local atomic environment was proposed by Blume (1994):

$$\chi_{ij}^+ = (n_i n_j - \tfrac{1}{3}\delta_{ij})[a_1 + b_1(\mathbf{n} \cdot \mathbf{m})^2] + c_1(m_i m_j - \tfrac{1}{3}m^2\delta_{ij})$$
$$+ d_1[n_i m_j + n_j m_i - \tfrac{2}{3}(\mathbf{n} \cdot \mathbf{m})\delta_{ij}](\mathbf{n} \cdot \mathbf{m}), \quad (6)$$

$$\chi_{ij}^- = i\delta_{ijk}[a_2 m_k + b_2 n_k(\mathbf{n} \cdot \mathbf{m})], \quad (7)$$

where χ^- is the antisymmetric part of χ_{ij}: $\chi^- = \frac{1}{2}(\chi_{ij} - \chi_{ji})$; $\chi^+ = \frac{1}{2}(\chi_{ij} + \chi_{ji}) - \frac{1}{3}\text{tr}(\hat{\chi})\delta_{ij}$ is the symmetric part, $a_1, b_1, c_1, d_1, a_2, b_2$ contain the resonant denominators, m_j and n_i denote the projections of the magnetic moment and the unit vector $\mathbf{n}$ along the local crystal field axis, corresponding to the sth atom in the unit cell, and δ_{ijk} is the completely antisymmetric third-rank pseudotensor. Equations (6) and (7) are only valid if the atom occupies a site with threefold, fourfold or sixfold symmetry of environment. It follows from (6) and (7) that the susceptibility consists of parts that separately describe the resonant scattering due to the magnetic moment (let us call it χ_{ij}^{mag}) or the anisotropy of the local atomic environment (χ_{ij}^{cryst}) and the 'combined' term χ_{ij}^{comb} following from the simultaneous existence of the two anisotropic factors. Hence, we can also represent the susceptibility as

$$\chi_{ij} = \chi_{ij}^{mag} + \chi_{ij}^{cryst} + \chi_{ij}^{comb}. \quad (8)$$

It was shown by Ovchinnikova & Dmitrienko (1997) that the combined term is responsible for the appearance of additional reflections. To consider crystal structures with non-uniaxial local symmetry (we shall call it biaxial), the general properties of the susceptibility relative to magnetic field inversion were used by the authors. This approach cannot be used to consider crystal structures in general. Hence, it is preferable to obtain an explicit form of the susceptibility for the case of the simultaneous existence of several anisotropic factor, including biaxial anisotropy of the local atomic environment. Below we shall find different ways to explicitly take into account several anisotropic factors.

3. Resonant susceptibility of a magnetic crystal with anisotropy of local atomic environment. Dipole transition

In this section, the susceptibility of a magnetic crystal with local crystal anisotropy will be considered with several approaches. Since the direct calculation of the susceptibility is very complicated, we will use a phenomenological way to find explicit expressions for the susceptibility tensor for each kind of local anisotropy.

3.1. Optical approach

For the visual optical band, a magnetic ordering (or an external magnetic field) leads to a variety of magnetooptical effects depending on the crystal symmetry (Landau & Lifshitz, 1953). To describe these effects, it is sufficient to consider the properties of the dielectric permeability in a weak magnetic field. A similar approach was also used when optical effects connected with the electric field or the tensor of mechanical tension are considered.

Further, we shall use the tensor $\hat{\chi}$, traditionally used in X-ray diffraction, instead of $\hat{\varepsilon} = 1 + \hat{\chi}$ usually used in optics. The resonant part of $\hat{\chi}$ for a single resonant transition can be written as $\chi_{ij} = \zeta_{ij}k_{res}$, where ζ_{ij} is a tensor describing the angular and polarization properties of scattering, k_{res} is the energy denominator. The tensor ζ_{ij} depends on the anisotropy

research papers

of the local atomic environment, the magnetic moment **m** and other anisotropic factors, which also influence the valence-electron state E_c, *i.e.* k_{res} and the position of the resonant line on the energy scale. In the following, we suppose this position fixed, *i.e.* we neglect the dependence of the resonant multiplier on the field parameters. Hence, only the tensor ζ_{ij} is responsible for the properties of X-ray anisotropic resonant scattering. Then, we will use the optical approach and represent the tensor ζ_{ij}^s for the separate resonant transitions in the following expansion:

$$\zeta_{ij}^s(\mathbf{m}) = \zeta_{ij}^{s0} + A_{ijk}^{s1} m_k^s + A_{ijkl}^{s2} m_k^s m_l^s + \ldots, \qquad (9)$$

where ζ_{ij}^{s0} is the susceptibility of the *s*th resonant atom in the presence of only anisotropy of the local atomic environment, excluding magnetic interaction. If we take into account spatial dispersion effects, we suppose the tensors to depend on the wave vectors. But for the dipole transition, where spatial dispersion is absent, all tensors in (9) are invariant under the point-group symmetry of the position of the *s*th resonant atom. In (9), **m** is considered to be a small parameter, hence this expansion in terms of **m** corresponds to the strong crystal-field approximation.

It is known that the symmetry of kinetic coefficients requires that $\chi_{ij}(\omega, \mathbf{m}) = \chi_{ji}(\omega, -\mathbf{m})$. Neglecting the dependence of the energy denominator on **m**, we obtain a similar expression for ζ: $\zeta_{ij}(\mathbf{m}) = \zeta_{ji}(-\mathbf{m})$. It also follows from (2) that $\zeta_{ij} = \zeta_{ji}^*$. Thus, all tensors in (9) being antisymmetric under *ij* are purely imaginary. Hence, A_{ijk}^1 is a third-rank imaginary pseudotensor and A_{ijkl}^2 is a fourth-rank symmetric tensor.

In correspondence with the results of visual optics, the third-rank pseudotensor $\hat{A}^1$ can be represented as $A_{ijk}^1 = i\varepsilon_{ijl} f_{lk}$, f_{lk} being a second-rank pseudotensor, ε_{ijk} is a completely antisymmetric third-rank tensor. As discussed by Landau & Lifshitz (1953), the asymmetric part of f_{lk} is not essential so that this tensor will be assumed to be symmetric. $f_{lk} m_k$ is called the gyration vector, its form together with the fourth-rank symmetric tensor A_{iklm}^2 was represented for example by Sirotin & Shaskolskaja (1975) and Agranovitch & Ginzburg (1984) for different point groups. Below, we will find the explicit forms of $\hat{\chi}$ for different kinds of anisotropy of local atomic environment using expansion (9).

3.2. The explicit form of the susceptibility for a biaxial magnetic crystal

To calculate the tensors in (9), we can use the standard forms of the third-, fourth- and higher-order tensors listed in the tables (see *e.g.* Sirotin & Shaskolskaja, 1975). The convolution of these tensors with the magnetic moment components gives the susceptibility for each specific case.

To obtain the explicit form of $\hat{\zeta}$, we can also construct the required tensors using the tensor invariants. The numbers of the invariants for various point groups are listed in the tables (see Sirotin & Shaskolskaja, 1975). Let us construct the susceptibility tensor for the monoclinic point group 2. The second-rank pseudotensor f_{lk} transforms as $\varepsilon[V^2]$ [here and below we shall use the notations by Jahn (1949)] in those

groups that allow its existence. In the cases of low symmetry ($\lambda_1 \neq \lambda_2 \neq \lambda_3$, where λ_i are the eigenvalues of the tensor), f_{lk} possesses three independent invariants and can be written as

$$f_{lk} = f'(a\delta_{lk} + b n_k^1 n_l^1 + c n_k^2 n_l^2), \qquad (10)$$

where a, b, c are arbitrary constants and f' is a pseudoscalar. The coordinates of the vectors $\mathbf{n}^1$ and $\mathbf{n}^2$ in the diagonal form are connected with the eigenvalues of the tensor (see Fedorov & Filippov, 1976). The substitution of (10) into (9) gives

$$A_{ijk}^1 m_k = i f' \varepsilon_{ijk} [a m_k + b(\mathbf{n}_k^1 \cdot \mathbf{m}) n_k^1 + c(\mathbf{n}^2 \cdot \mathbf{m}) n_k^2]. \qquad (11)$$

For the groups with tetragonal, hexagonal and rhombohedral symmetries where $\lambda_1 = \lambda_2$, $\mathbf{n}_1 = \mathbf{n}_2$, there are two invariants: $f_{lk} = f'[a\delta_{lk} + b n_k n_l]$, hence

$$A_{ijk}^1 m_k = i f' \varepsilon_{ijk} [a m_k + b n_k (\mathbf{n} \cdot \mathbf{m})], \qquad (12)$$

which coincides with the result given in (6). Here and further on, we shall use the letters $a_i, b_i, \ldots$ to denote arbitrary coefficients of the expansion. For the cubic and spherical symmetries, we have $\lambda_1 = \lambda_2 = \lambda_3$, hence $\mathbf{n} = 0$. Then, we obtain $A_{ijk}^1 = i f' a \varepsilon_{ijk} m_k$. This result corresponds to the purely magnetic crystal and coincides with the well known result given by Hannon *et al.* (1988).

Now, let us consider the second-order term. The tensor A_{ijkl}^2 transforms like $[V^2]^2$. The forms of such tensors are listed for different point groups in the tables (see Sirotin & Shaskolskaja, 1975) together with suitable numbers of invariants. As an example, let us consider the monoclinic groups 2, m, $2/m$. They possess 20 components that can be constructed from 19 invariants. Here, we will not represent the very long explicit expression for the invariant form of $\mathbf{A}^2$. One can obtain it using the tensor δ_{ij}, vectors $\mathbf{n}^1$, $\mathbf{n}^2$ and 19 arbitrary coefficients. The convolution of A_{ijkl}^2 with the magnetic moment components gives

$$\begin{aligned} A_{ijkl}^2 m_k m_l = {}& \alpha\delta_{ij} + 2b m_i m_j + [\gamma_1 n_i^1 n_j^1 + \gamma_2 n_i^2 n_j^2 \\ & + \gamma_3(n_i^1 n_j^2 + n_j^1 n_i^2)] + 2(p_{lj} m_l m_i + p_{li} m_l m_j), \end{aligned} \qquad (13)$$

where the coefficients α and $\gamma_{1,2,3}$ include the dependencies on m^2, $(\mathbf{n}^1 \cdot \mathbf{m})^2$, $(\mathbf{n}^2 \cdot \mathbf{m})^2$, $(\mathbf{n}^1 \cdot \mathbf{m})(\mathbf{n}^2 \cdot \mathbf{m})$ and 15 independent parameters.

$$p_{li} = e_1 n_l^1 n_i^1 + e_2 n_l^2 n_i^2 + e_3(n_l^1 n_i^2 + n_l^2 n_i^1)$$

is a second-rank tensor invariant under the anisotropy of the local atomic environment symmetry group. b and $e_{1,2,3}$ are the independent parameters. The first and third terms in (13) are the amendments to ζ_{ij}^0, the second one corresponds to the purely magnetic part of the scattering. The last term is the 'combined' part, which is the most interesting for us.

For the groups with higher symmetry, the number of invariants decreases. For groups 622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m, ∞/mmm, we need six invariants [*i.e.* there are 6 arbitrary coefficients instead of 19 in (13)], which can be constructed from only one vector **n**, *i.e.*

$$\mathbf{n}^1 = \mathbf{n}^2 = \begin{pmatrix} 0 \\ 0 \\ n_z \end{pmatrix}.$$

Then we obtain:

$$\begin{aligned}
A_{ijkl}^2 m_k m_l &= [a_1 m^2 + c_1 (\mathbf{m} \cdot \mathbf{n})^2]\delta_{ij} + 2b_1 m_i m_j \\
&\quad + [d_1 m^2 + f_1 (\mathbf{m} \cdot \mathbf{n})^2]n_i n_j \\
&\quad + 2e_1 (m_i n_j + n_i m_j)(\mathbf{m} \cdot \mathbf{n}).
\end{aligned} \tag{14}$$

Excluding the diagonal part of the tensor ζ_{ij}, we obtain the expression for $\hat{\chi}^+$ given in (6). The invariants for the rest of the point groups can be realized by choosing suitable arbitrary coefficients and vectors $\mathbf{n}$.

For a spherical symmetry of anisotropy of the local atomic environment, we have two independent invariants ($\mathbf{n} = 0$), then

$$\begin{aligned}
A_{ijkl}^2 m_k m_l &= [a\delta_{ij}\delta_{kl} + b(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il})]m_k m_l \\
&= a_1 m^2 \delta_{ij} + 2b_1 m_i m_j.
\end{aligned}$$

This expression describes the symmetric part of the scattering amplitude conforming with the known result given by Hannon *et al.* (1988).

The above expressions can be used to find the additional reflections that can appear near the absorption edge in a magnetic crystal with anisotropy of the local atomic environment. The considered case corresponds to a strong crystal field, hence the influence of the crystal field is greater than that of the magnetic interaction. As a result, the combined effects may be negligible compared with the effect from anisotropy of the local atomic environment. From this point of view, the most interesting effects may occur in the case of an intermediate field when the influence of the magnetic ordering is compatible with the effect from anisotropy of the local atomic environment. However, in this case, expansion (9) is not correct. Below, we shall therefore consider another approach which treats the case of the intermediate field.

4. The approach of weak anisotropy

The best situation for the 'combined' effects is when the energy of magnetic splitting of the valence-electron states is of the same order as that of the splitting due to the crystal field. Since this case cannot be described using the optical approach, another approximation will be used in this section.

The states of the valence electrons of a free atom are degenerated with respect to the spin- and orbital-moment projections. In this case, the susceptibility tensor has spherical symmetry, *i.e.* it is equal to $\chi_{ij}^0 \sim a\delta_{ij}$. The interaction of the atom with the crystal field and its magnetic interaction split the atomic electron levels, causing the anisotropy of the susceptibility. Let us consider cases when this anisotropy is sufficiently weak. These are: (i) far from the absorption edge, *i.e.* when $|E_a - E_c + \hbar\omega| \gg \Gamma$, so that the resonant scattering amplitude is small compared with the isotropic Thomson scattering; (ii) when the splitting Δ of the atomic resonant levels is small compared with the width of the resonant line,

$\Delta \ll \Gamma$. We shall denote both cases as a weak-anisotropy approximation. It is similar to the fast-collision approximation (Luo *et al.*, 1993). To explain the weakness of anisotropy in the latter case, let us suppose that the atomic resonant line is split into two levels described by the susceptibility tensors $\hat{\zeta}_1$ and $\hat{\zeta}_2$ and the resonant energies E_1 and E_2. The following condition must be satisfied to provide isotropy in the absence of the splitting: $\zeta_{ij}^1 + \zeta_{ij}^2 = a\delta_{ij}$. We can represent the susceptibility as a function of ω as follows:

$$\begin{aligned}
\chi_{ij} &= (\hbar\omega - E_2 + i\Gamma/2)^{-1}[a\delta_{ij} + \zeta_{ij}^1(E_1 - E_2) \\
&\quad \times (\hbar\omega - E_1 + i\Gamma/2)^{-1}].
\end{aligned} \tag{15}$$

If the splitting of the levels $\Delta = E_1 - E_2 \ll \Gamma$, the main part of the susceptibility is spherically symmetric corresponding to the susceptibility of the free atom. For example, if $\hbar\omega = E_1$, we have

$$\chi_{ij} = (E_1 - E_2 + i\Gamma/2)^{-1}[a\delta_{ij} + i\alpha\zeta_{ij}^1], \tag{16}$$

where $\alpha = 2\Delta/\Gamma \ll 1$. Hence the anisotropy can be considered to be weak.

Note that if a forbidden reflection appears owing to weak anisotropy, it still exists if the anisotropy is not weak. Hence, if we are not interested in the intensities of these reflections but only in the set of possible reflections, then all conclusions below may be used for cases when the anisotropy is not weak.

4.1. The susceptibility of a magnetic crystal with anisotropy of the local atomic environment

Now we shall consider the case of the resonant $E1$–$E1$ dipole transition. Let us suppose the crystal field and the magnetic moment are small parameters and apply the following expansion of $\hat{\zeta}$ similar to the one used in optics (s is omitted):

$$\begin{aligned}
\zeta_{ij}(\mathbf{E}, \mathbf{m}) &= A_{ij}^0 + A_{ikl}^1 m_k + A_{ikl}^2 E_k + A_{ijkl}^3 E_k E_l \\
&\quad + A_{ijkl}^4 m_k m_l + A_{ijkl}^5 m_k E_l + A_{ijklm}^6 n_{kl} m_m \\
&\quad + A_{ijklmn}^7 n_{kl} m_m m_n + \dots.
\end{aligned} \tag{17}$$

In this expansion, we consider only the largest terms depending on the magnetic moment $\mathbf{m}$ and electric field $\mathbf{E}$ and those terms that can describe the combined influence of magnetic ordering and anisotropy of the local atomic environment. As was remarked by Blume (1994), we must take into account the symmetry of the p_a [see equation (2)] under field inversion. For the magnetic moment, we have $|\bar{a}\rangle = |-m\rangle$. Hence, in a magnetically ordered system, *i.e.* when $p_a \neq p_{\bar{a}}$, those terms that linearly depend on the magnetic moment differ from zero. In contrast, because the Stark effect depends quadratically on the electric field, we have $p_a = p_{\bar{a}}$. Then, all the terms that linearly depend on the electric field vanish. Taking this fact into account, we shall further use a second-rank symmetric tensor $n_{kl} \sim E_k E_l$ as an ordering parameter (fourth- and higher-order terms are neglected) describing the anisotropy of the local atomic environment at the position of the sth resonant-atom location. All tensors $\hat{A}^i$ in (17) correspond to a free atom, *i.e.* are

invariant under the group $\infty\infty/m$. In the case of axially symmetric anisotropy of the local atomic environment, we can write $n_{kl} = n_k n_l$; for biaxial symmetry, we must introduce two vectors (see §3). There is no necessity at all to decompose this tensor.

It is known from the general theory (Gurewitch, 1948) that any isotropic tensor of rth rank can be represented as a linear combination of the isomers $\delta_{i_1 i_2}\delta_{i_3 i_4}\ldots\delta_{i_{r-1} i_r}$. In addition, we have $A^1_{ijk} = -A^1_{jik}$, $A^6_{ijklm} = -A^6_{jiklm}$. All other tensors are symmetric under permutation of i and j. Let us consequently consider all tensors.

A^0 characterizes the susceptiblity of the free atom, this tensor is isotropic, i.e. $A^0_{ij} = a_0\delta_{ij}$.

A^1 is an antisymmetric purely imaginary pseudotensor, hence it can be represented in the form $A^1_{ikl}m_l = i\delta_{ijl}m_l$, similar to those considered above for the system with spherical symmetry. Here and below we shall use the antisymmetric pseudotensor δ_{ijk} instead of $f'\varepsilon_{ijk}$.

A^3 and A^4 are symmetric tensors invariant under the full group of rotations. Their general form is $[V^2]^2$. In this case, they have two independent components and can be represented as the following sum of isomers (Sirotin & Shaskolskaja, 1975):

$$A^3_{ijkl} = a_3\delta_{ij}\delta_{kl} + b_3(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \tag{18}$$

With a similar expression for A^4, we get:

$$A^4_{ijkl}m_k m_l = a_4\delta_{ij}m^2 + 2b_4 m_i m_j, \tag{19}$$

$$A^3_{ijkl}n_{kl} = a_3\delta_{ij}n_{ll} + 2b_3 n_{ij}. \tag{20}$$

A^6 is an antisymmetric pseudotensor, transformed as $\varepsilon\{V^2\}V[V^2]$ and $\varepsilon V[V^2]^2$. A^6 can be represented as

$$A^6_{ijklm} = b_6\delta_{ijk}\delta_{lm} + c_6(\delta_{ijl}\delta_{km} + \delta_{ijm}\delta_{kl}). \tag{21}$$

The convolution of this tensor with the field components gives

$$A^6_{ijklm}n_{kl}m_m = b_6 n_{ll}\delta_{ijk}m_k + c_6(\delta_{ijl}n_{lm}m_m + \delta_{ijm}n_{lm}m_l). \tag{22}$$

For axially symmetric anisotropy of the local atomic environment, we have $n_{lm} = n_l n_m$, so that

$$A^6_{ij} = \delta_{ijk}[b_6 n^2 m_k + 2c_6(\mathbf{n}\cdot\mathbf{m})n_k]. $$

A^7 is an isotropic tensor. It can be represented as a sum of isomers with the internal symmetry $[V^2]^3$. It has five independent components, yielding

$$\begin{aligned}
A^7_{ijklmn}m_k m_l n_{mn} &= [a_7\delta_{ij}\delta_{kl}\delta_{mn} + b_7\delta_{ij}(\delta_{km}\delta_{ln} + \delta_{kn}\delta_{lm}) \\
&\quad + c_7\delta_{kl}(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jl}) \\
&\quad + d_7\delta_{mn}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \\
&\quad + e_7(\delta_{ik}\delta_{jm}\delta_{ln} + \delta_{ik}\delta_{jn}\delta_{lm} + \delta_{il}\delta_{jm}\delta_{kn} \\
&\quad + \delta_{il}\delta_{jn}\delta_{km} + \delta_{im}\delta_{jk}\delta_{ln} + \delta_{im}\delta_{jl}\delta_{kn} \\
&\quad + \delta_{in}\delta_{jk}\delta_{lm} + \delta_{in}\delta_{jl}\delta_{km})]m_k m_l n_{mn} \\
&= (a_7 m^2 n_{ll} + 2b_7 m_k m_l n_{kl})\delta_{ij} \\
&\quad + 2c_7 n_{ll}m_i m_j + 2d_7 m^2 n_i n_j \\
&\quad + 4e_7(m_i m_l n_{jl} + m_j m_l n_{il}). \tag{23}
\end{aligned}$$

A^6 and A^7 contain the parts that depend both on the magnetic moments and on anisotropy of the local atomic environment, i.e. are responsible for 'combined' effects.

As a result, we obtain the following forms for $\hat{\zeta}^+$ and $\hat{\zeta}^-$:

$$\begin{aligned}
\zeta^+_{ij} &= [n_{ij} - \tfrac{1}{3}\mathrm{tr}(\hat{n})\delta_{ij}](2b_3 + 2c_7 m^2) + (m_i m_j - \tfrac{1}{3}m^2\delta_{ij}) \\
&\quad \times [b_4 + 2d_6\mathrm{tr}(\hat{n})] + 4e_7[m_i m_l n_{lj} + m_j m_l n_{li} \\
&\quad - \tfrac{2}{3}(n_{ij}m_i m_j)\delta_{ij}] \tag{24}
\end{aligned}$$

$$\zeta^-_{ij} = i\delta_{ijk}\{[a_1 + b_6\mathrm{tr}(\hat{n})]m_k + 2c_6 n_{kl}m_l\}, \tag{25}$$

which are correct for the biaxial symmetry. In the case of the axial anisotropy of the local atomic environment, we suppose $n_{ij} = n_i n_j$, and we obtain the expression given by Blume (1994). The numerical coefficients in this tensor expansion are unknown and included in them are the resonant denominators. The considered approach can be useful when the resonant scattering in the presence of several anisotropic factors is considered. It allows one to find the set of possible reflections and to determine their azimuthal and polarization properties.

4.2. The susceptibility in the case of several anisotropic factors

Recently, the resonant scattering of synchrotron radiation was studied in a crystal with orbital ordering. In this case, there are three simultaneous anisotropic factors, i.e. anisotropy of the local atomic environment, anisotropy due to orbital ordering and magnetic ordering. If we take into account the anisotropy due to orbital ordering together with that due to magnetic ordering, we obtain a result similar to that in §4.1. Instead of the tensor n_{kl}, we should, however, introduce in this case the order-parameter tensor $\boldsymbol{\Delta}_{ij} = \tau_i\tau_j$, where τ means pseudospin (see Kugel & Homsky, 1982). If we take into account all three types of local anisotropies simultaneously and apply the approach developed above, we obtain:

$$\begin{aligned}
\zeta_{ij}(n_{kl}, \mathbf{m}, \tau_p\tau_q) &= A^0\delta_{ij} + A^1_{ijk}m_k + A^2_{ijkl}n_{ij} \\
&\quad + A^3_{ijkl}m_k m_l + A^4_{ijkl}\tau_k\tau_l + A^5_{ijklm}n_{kl}m_m \\
&\quad + A^6_{ijklm}\tau_k\tau_l m_m + A^7_{ijklmn}n_{kl}m_m m_n \\
&\quad + A^8_{ijklmn}\tau_k\tau_l m_m m_n + \ldots. \tag{26}
\end{aligned}$$

Thus, we see that the terms $A^0 - A^4$ describe the resonant scattering due to each of the independent anisotropic factors. Hence, the diffraction pattern will contain additional reflections that are 'purely magnetic', 'purely ATS' and 'purely orbital'. The terms A^{5-8} describe the possible 'combined' effects. Calculations similar to those made above give the following expressions for the susceptibility tensor:

$$\begin{aligned}
\zeta^+_{ij} &= b_1[n_{ij} - \tfrac{1}{3}\mathrm{tr}(\hat{n})\delta_{ij}] + b_2(m_i m_j - \tfrac{1}{3}m^2\hat{\delta}_{ij}) \\
&\quad + b_3[\tau_i\tau_j - \tfrac{1}{3}\mathrm{tr}(\Delta)\delta_{ij}] + 4\{(b_4 n_{im} + b_5\tau_i\tau_m)m_j m_m \\
&\quad + (b_4 n_{jm} + b_5\tau_j\tau_m)m_i m_m - \tfrac{2}{3}[b_4 n_{ij}m_i m_j + b_5(\boldsymbol{\tau}\cdot\mathbf{m})^2]\delta_{ij}\}, \tag{27}
\end{aligned}$$

$$\zeta^-_{ij} = i\delta_{ijk}[c_1 m_k + (c_2 n_{km} + c_3\tau_k\tau_m)m_m]. \tag{28}$$

In (27) and (28), all the coefficients are unknown. Several terms that are not essential for the anisotropy are omitted.

These expressions show that different types of anisotropy with the same internal symmetry (for example, anisotropy both of the local atomic environment and of orbital ordering, which are decribed by the second-order symmetric tensors) can be summarized and give no 'combined' effects. Moreover, these two contributions cannot be distinguished physically by a resonance measurements. The 'combined' terms appear in the susceptibility tensor only when anisotropic factors with different internal symmetries exist for resonant atoms.

4.3. Dipole–quadrupole term

If a resonant electronic transition has a mixed multipole order, then the cross terms can appear, for example the dipole–quadrupole term. The consideration of the magnetic type transitions adds new tensors, their general forms were discussed by Templeton (1998). We will not discuss this question. As shown by Blume (1994), the dipole–quadrupole term can be represented as

$$\zeta_{ij}^{dq} \sim (g_{ijk}^{++} + g_{ijk}^{--})(k_k - k_k') + (g_{ijk}^{+-} + g_{ijk}^{-+})(k_k + k_k'),$$

where

$$
\begin{aligned}
g_{ijk}^{\mu\nu} = \tfrac{1}{2}\sum_{ac}(p_a' + \mu p_a')[&(\langle a \mid R_i \mid c\rangle\langle c \mid Q_{jk} \mid a\rangle \\
&+ \mu\nu\langle a \mid Q_{ik} \mid c\rangle\langle c \mid R_j \mid a\rangle) \\
&+ \nu(\langle a \mid R_j \mid c\rangle\langle c \mid Q_{ik} \mid a\rangle \\
&+ \mu\nu\langle a \mid Q_{jk} \mid c\rangle\langle c \mid R_i \mid a\rangle)],
\end{aligned}
$$
(29)

$\mu, \nu = \pm 1$. The terms with $\mu = 1$ are time-reversal, *i.e.* they are not sensitive to the magnetic structure. We are interested in the 'combined' effects that require the crystal to be magnetic. Hence, we will consider only the terms with $\mu = -1$. g_{ijk}^{-+} and g_{ijk}^{--} correspond to the symmetric and antisymmetric parts of $\hat{g}^-$.

Let us consider the expansion of $\hat{g}^-$ over the anisotropic factors.

$$
\begin{aligned}
g_{ijk}^{-}(n_{mn}, \mathbf{m})l_k = \{&g_{ijk}^0 + g_{ijkl}^1 m_l + g_{ijklm}^2 n_{lm} + g_{ijklm}^3 m_l m_m \\
&+ g_{ijklmn}^4 m_l n_{mn} + g_{ijklmnp}^5 m_l m_m n_{np} \\
&+ \ldots\}l_k,
\end{aligned}
$$
(30)

where l_k means $-H_k = k_k - k_k'$ for g^{--} and $k_k + k_k'$ for g^{-+}. In (30), only the terms $\hat{g}^4$ and $\hat{g}^5$ are essential for the 'combined' effects.

Taking into account the general property of the susceptibility $\chi_{ij}(\mathbf{k}, \mathbf{m}) = \chi_{ji}(-\mathbf{k}, -\mathbf{m})$, we obtain g_{ijklmn}^4 to be symmetric under i, j permutation. Hence, it describes the symmetric part g_{ijk}^{-+}, which transforms like $\varepsilon V^2[V^2]^2$, possessing five independent invariants. Its convolution with the ordering parameters gives the following expression:

$$
\begin{aligned}
g_{ijklmn}^{-+} = \delta_{ij}[&a_4(\mathbf{l} \cdot \mathbf{m})n_{ll} + 2b_4 l_k m_n n_{kn}] \\
&+ 2c_4(\mathbf{l} \cdot \mathbf{m})n_{ij} + d_4 n_{nn}(l_i m_j + l_j m_i) \\
&+ 2e_4(l_i n_{jm} m_m + l_j n_{im} m_m + m_i n_{jm} l_m + m_j n_{im} l_m),
\end{aligned}
$$
(31)

where the diagonal part is not excluded.

$g_{ijklmnp}^5$ is a seventh-rank tensor antisymmetric under i, j permutation, $\varepsilon\{V^2\}V[V^2]^2$ type. To obtain its invariant form, we can use the duality relation $\varepsilon\{V^2\} \sim V$. Then, $g_{ijklmnp}^5 = \delta_{ijq}g_{qklmnp}^4$, which was considered above. The convolution of this tensor with the order parameters gives

$$
\begin{aligned}
g_{ijklmnp}^{--} l_k m_l m_m n_{np} = i\delta_{ijk}\{&(a_5 m^2 n_{pp} + 2b_5 n_{np} m_m m_p)l_k \\
&+ 2c_5 m^2 z_k + 2d_5[n_{pp}(\mathbf{l} \cdot \mathbf{m}) \\
&+ 4e_5(\mathbf{m} \cdot \mathbf{z})]m_k + 4e_5(\mathbf{m} \cdot \mathbf{l})n_{km} m_m\},
\end{aligned}
$$
(32)

where $z_k = n_{kp}l_p$.

5. Quadrupole transition

Let us consider the quadrupole–quadrupole term. It is known that the extinction rules in the resonant diffraction pattern corresponding to the quadrupole transition can differ from those for the dipole transition (Finkelstein *et al.*, 1993). In this section, we consider the susceptibility tensor for the quadrupole transition in the presence of two anisotropic factors. We have:

$$\chi_{ij}^{qq} = k_{\mathrm{res}} U_{iljk} k_l' k_k.$$
(33)

The following symmetry relation describes the tensor $\hat{U}$: $U_{iljk} = U_{lijk} = U_{ilkj} = U_{likj}$ (see Blume, 1994). Let us consider the following expansion:

$$
\begin{aligned}
\zeta_{ij}^{qq}(n_{pq}, m_m) = &U_{iljk}^0 k_l' k_k + U_{iljkm}^1 k_l' k_k m_m + U_{iljkpq}^2 k_l' k_k n_{pq} \\
&+ U_{iljkpq}^3 k_l' k_k m_p m_q + U_{iljkmpq}^4 k_l' k_k m_m n_{pq} \\
&+ U_{iljkmnpq}^5 k_l' k_k m_m m_n n_{pq} + \ldots,
\end{aligned}
$$
(34)

where all tensors $\hat{U}$ are isotropic and can be represented as a linear combination of the isomers. We see that the first four terms describe the resonant scattering of X-rays similar to those cases for which there are only anisotropy of the local atomic environment or magnetic ordering. Below we shall represent only the term responsible for the resonant scattering in the presence of only anisotropy of the local atomic environment, which is correct for the biaxial case, and those terms that correspond to the combined symmetry of anisotropy of the local atomic environment together with magnetic ordering. For pure biaxial anisotropy of the local atomic environment, we must consider U^2, which transforms like $[V^2]^3$ and possesses five independent parameters [see equation (23)]. Its convolution with the wave-vector components together with the order parameters is equal to

$$U^2_{iljkpq}k'_l k_k n_{pq} = \delta_{ij}[d_2 n_{pp}(\mathbf{k} \cdot \mathbf{k}') + 2e_2 k'_i k_k n_{kl}]$$
$$+ e_2 n_{ij}(\mathbf{k} \cdot \mathbf{k}') + (a_2 + d_2)k'_i k_j n_{pp}$$
$$+ 2b_2 k'_i n_{jp} k_p + 2e_2 k_i n_{lj} k'_l$$
$$+ 2c_2 k_j n_{ip} k'_p + 2e_2 k'_j n_{ik} k_k. \tag{35}$$

For axial anisotropy of the local atomic environment, we have

$$U^2_{iljkpq}k'_l k_k n_{pq} = \delta_{ij}[d_2 n^2(\mathbf{k} \cdot \mathbf{k}') + 2e_2(\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{k}')]$$
$$+ 2e_2 n_i n_j(\mathbf{k} \cdot \mathbf{k}') + (a_2 + d_2)k'_i k_j n^2$$
$$+ 2b_2 k'_i n_j(\mathbf{n} \cdot \mathbf{k}) + 2c_2 k_j n_i(\mathbf{n} \cdot \mathbf{k}')$$
$$+ 2e_2 k_i n_j(\mathbf{k}' \cdot \mathbf{n}) + 2e_2 k'_j n_i(\mathbf{k} \cdot \mathbf{n}). \tag{36}$$

The convolution of these tensors with the polarization vectors of the incident and scattered radiation gives expressions conforming with the terms involving the square of $\mathbf{n}$ in the scattering amplitude obtained by Blume (1994).

To obtain the terms that may be responsible for 'combined' effects, we must consider U^4 and U^5. Using U^4, which transforms like $V[V^2]^3$, we have:

$$\zeta^-_{ij} = U^4_{iljkmnp}k'_l k_k m_m n_{np}$$
$$= a_4 n_{pp}\{\delta_{ijm} m_m(\mathbf{k} \cdot \mathbf{k}') + [\mathbf{m} \times \mathbf{k}']_j k_i + [\mathbf{m} \times \mathbf{k}]_i k'_j$$
$$+ [\mathbf{m} \times \mathbf{k}]k' \delta_{ij}\} + 2b_4([\mathbf{m} \times \mathbf{z}']k_j - [\mathbf{m} \times \mathbf{k}']_p n_{ip} k_j)$$
$$+ 2c_4([\mathbf{m} \times \mathbf{z}]_j k'_i - [\mathbf{m} \times \mathbf{k}]_p n_{ip} k'_i), \tag{37}$$

where $z_k = n_{kl}k_l$, $z'_k = n_{kl}k'_l$. The last two terms describe $\zeta^{-,\text{comb}}$.

Similarly, we can obtain the expression for $\zeta^{+,\text{comb}}$:

$$\zeta^{+,\text{comb}}_{ij} = 2k_i\{b_1 k'_j m_m m_n n_{mn} + c_1 z'_j m^2 + d_1 n_{pp}(\mathbf{m} \cdot \mathbf{k}')m_j$$
$$+ e_1[m_j(\mathbf{m} \cdot \mathbf{z}') + (\mathbf{m} \cdot \mathbf{k}')m_n n_{jm}]\}$$
$$+ 2k'_j\{b_2 k_i m_m m_n n_{nm} + c_2 m^2 z_i + d_2 n_{pp}(\mathbf{k} \cdot \mathbf{m})m_i$$
$$+ e_2[m_i(\mathbf{m} \cdot \mathbf{z}) + (\mathbf{m} \cdot \mathbf{k})m_n n_{im}]\}, \tag{38}$$

where the diagonal part is not excluded.

Comparing the expressions for $\chi^{-,dd}$ and $\chi^{-,qq}$, we see that in dipole transition the 'combined' terms in susceptibility disappear when $\mathbf{n} \perp \mathbf{m}$, not so, however, for the quadrupole transition. Hence, near the absorption edge, extra forbidden combined reflections caused by the quadrupole transition can appear in the diffraction pattern.

6. Susceptibility tensor in a crystal with orbital ordering

In the previous sections, we have found phenomenological expressions that describe the resonant X-ray diffraction in the presence of two different anisotropic factors. Now we will discuss an example when three anisotropic factors simultaneously exist in a system. This is the crystal of $La_{0.5}Sr_{1.5}MnO_4$, where anisotropy of the local atomic environment coexists with magnetic ordering and orbital ordering. Forbidden reflections were recently experimentally observed by Murakami et al. (1998) near the K edge of Mn^{3+}. At first, they were classified as dipole ATS reflections. Their azimuthal

dependence is in accordance with such an assumption. In the following, the theory describing the properties of the resonant scattering in systems with orbital ordering was developed by Ishihara & Maekawa (1998a,b) and Fabrizio et al. (1998). Here we develop a phenomenological method aiming to find possible effects that can appear in the presence of three anisotropic factors compared with one or two.

In the considered system, charge ordering is also observed together with the above listed ordering types (see Miozakawa & Fujimori, 1995; Sternlieb et al., 1996). The charge ordering describes the symmetry of the Mn^{3+}/Mn^{4+} superlattice and does not produce additional anisotropy.

At room temperature, the considered structure is described by the space group $I4/mmm$. In the region of orbital and charge ordering, the symmetry becomes orthorhombic, though close to tetragonal with lattice parameters $(2\mathbf{a})^{1/2} \times (2\mathbf{a})^{1/2} \times \mathbf{c}$. The resonant atoms are on the fourfold axes, hence the symmetry of the local environment causes an anisotropy described by the tensor ζ_{ij}, where $\zeta_{xx} = \zeta_{yy} = n_{xx}$, $\zeta_{zz} = n_{zz}$ (the other tensor components are zero). Such symmetry cannot cause the appearance of any ATS reflections in the diffraction pattern near the absorption edge of Mn^{3+}.

An additional reflection $(\frac{3}{4}\frac{3}{4}0)$ associated with orbital ordering was found by Murakami et al. (1998) at 29.5 K. At this temperature, all magnetic ordering, charge ordering, orbital ordering and anisotropy of the local atomic environment can exist.

Let us apply the results of the previous sections to the resonant diffraction in $La_{0.5}Sr_{1.5}MnO_4$. To this purpose, we write the tensors n_{ij}, $\Delta_{ij} = \tau_i \tau_j$ and vectors $\mathbf{m}$ corresponding to four resonant atoms in a unit cell.

Atom(1):

$$n^1_{xx} = n_{zz}, n^1_{yy} = n^1_{zz} = n_{xx}, \Delta^1_{xx} = \Delta_{zz}, \Delta^1_{yy} = \Delta^1_{zz} = \Delta_{xx},$$
$$\mathbf{m}_1 = (m_x, m_y, 0).$$

Atom (2):

$$n^2_{ij} = n^1_{ij}, \Delta^2_{yy} = \Delta_{zz}, \Delta^2_{xx} = \Delta^2_{zz} = \Delta_{xx}, \mathbf{m}_2 = (m_x, m_y, 0).$$

Atom (3):

$$n^3_{ij} = n^1_{ij}, \Delta^3_{yy} = \Delta_{zz}, \Delta^3_{xx} = \Delta^3_{zz} = \Delta_{xx},$$
$$\mathbf{m}_3 = (-m_x, -m_y, 0).$$

Atom (4):

$$n^4_{ij} = n^1_{ij}, \Delta^4_{xx} = \Delta_{zz}, \Delta^4_{yy} = \Delta^4_{zz} = \Delta_{xx},$$
$$\mathbf{m}_4 = (-m_x, -m_y, 0).$$

The other tensor coefficients are zero. Substitution of these values into (24) and (25) shows that no 'combined' contribution appears in the reflection $(\frac{3}{4}\frac{3}{4}0)$, hence it can be considered as purely ATS type.

Let us consider the $h0l$ reflections in detail. In this case,

$$\hat{\chi}(\{[2n+1]/2\}0\{[2m+1]/2\})$$
$$\sim \hat{\chi}^{3+}_1 - \hat{\chi}^{3+}_2 + \hat{\chi}^{3+}_3 - \hat{\chi}^{3+}_4 + 2\hat{\chi}^{4+}_1 - 2\hat{\chi}^{4+}_2, \tag{39}$$

where $\hat{\chi}_i^{3+}$, $i = 1, 2, 3, 4$, describe the scattering by Mn^{3+} ions, $\hat{\chi}_{1,2}^{4+}$ correspond to the scattering by Mn^{4+} ions. There is no orbital ordering on the ions Mn^{4+} for which e_g electrons are absent. If only one anisotropic factor is taken into account, the susceptibility for these reflections is completely defined by the magnetic ordering on Mn^{4+} ions, consistent with the results by Sternlieb et al. (1996). Let us take into account three aniso-tropic factors on the Mn^{3+} ions. We see that anisotropy of the local atomic environment together with magnetic ordering gives nothing new, but magnetic ordering together with orbital ordering gives the contribution to the susceptibility tensor.

Hence, for the reflection $h0l$ with $h = (2n + 1)/2$, $l = (2m + 1)/2$, we have

$$\hat{\chi}^-(h0l) = 2i\alpha_3(\Delta_{xx} - \Delta_{zz})$$
$$\times k_{res}^{3+} \begin{bmatrix} \begin{pmatrix} 0 & 0 & m_y^{(3)} \\ 0 & 0 & m_x^{(3)} \\ -m_y^{(3)} & -m_x^{(3)} & 0 \end{pmatrix} \end{bmatrix}$$
$$+ 4i k_{res}^{4+} \begin{pmatrix} 0 & 0 & m_y^{(4)} \\ 0 & 0 & -m_x^{(4)} \\ -m_y^{(4)} & m_x^{(4)} & 0 \end{pmatrix} \end{bmatrix}, \quad (40)$$

where α_3 is an unknown coefficient, describing the ratio of the 'strengths' corresponding to the local anisotropy and magnetic interaction.

This reflection, which was considered by Sternlieb et al. (1996) as purely magnetic owing to the scattering by the Mn^{4+} sublattice, contains the contribution from the Mn^{3+} sublattice, which is neither purely magnetic nor purely ATS. Taking into account the difference of about 4 eV between the resonant energies corresponding to Mn^{3+} and Mn^{4+}, an interference form of resonant line must occur. The interference between the resonant lines can either enhance or weaken the intensity of a resonant peak. In the considered case, the interference form of the resonant line cannot be resolved owing to the small distance between the resonant energies corresponding to Mn^{3+} and Mn^{4+} compared with the line width. The coeffi-cient α_3 seems to be small, thus the weak peak corresponding to the 'combined' reflection from the Mn^{3+} sublattice may be negligible compared with the magnetic peak from the sublattice Mn^{4+}. We will consider a possibility that allows us to characterize the weak reflection.

Let us look at the azimuthal dependence. Calculations show that for the $h0l$ reflections the intensity of the scattered radiation within the kinematical approach of diffraction theory is equal to

$$I(\{[2n + 1]/2\}0\{[2m + 1]/2\})$$
$$= 2\{|\chi_{xz} \cos \beta - \chi_{yz} \sin \beta|^2 \cos^2 \theta_B$$
$$+ |\chi_{xz} \sin \beta + \chi_{yz} \cos \beta|^2 \sin^2 \theta_B$$
$$+ |\chi_{xz} \sin \beta + \chi_{yz} \cos \beta|^2 \sin^2 \theta_B \cos 2\theta_B \sin^2 \varphi\}, \quad (41)$$

where φ is the azimuthal angle, β the angle between the scattering plane and the a axis, θ_B is the Bragg angle, χ_{xz} and χ_{yz} are the components of the susceptibility tensor, repre-sented by (40).

The azimuthal dependence of the usual ATS reflection is not energy dependent. I.e., if we represent the azimuthal function given by (41) in the form $I \sim a + b \sin^2 \varphi$ and intro-duce a typical parameter, for example $p = a/b$, then we can see that for a purely ATS or magnetic reflection belonging to only one resonant line the ratio a/b will be the same at all points of the energy scale. In contrast, the typical parameter for the azimuthal dependence described by (41) with $\hat{\chi}$ equal to (40) has to be energy dependent.

7. Conclusions

When the wavelength of the incident radiation is close to the absorption edge of an element in a crystal, then different kinds of forbidden reflections, i.e. reflections that are absent far from the absorption edge, can appear in the diffraction pattern. We have shown that, besides the well known magnetic and ATS reflections, the diffraction pattern may also contain reflections that only appear when several anisotropic factors exist in a crystal. The phenomenological expressions that describe the susceptibility tensor in the presence of several kinds of anisotropy are developed. These expressions allow evaluation of the set of possible reflections in the resonant X-ray diffraction. For example, they show that additional reflections may appear in resonant diffraction near the absorption edge in the presence of the magnetic ordering together with anisot-ropy of the local atomic environment or together with orbital ordering. Also, we have shown that the set of forbidden (combined) reflections for quadrupole resonant transition can differ from that for the dipole transition.

In this paper, the approximations for strong and inter-mediate crystal fields were considered. Similarly, we can obtain the approximation for a weak crystal field. To this purpose, we must use an expansion of the susceptibility tensor in terms of the crystal field order parameter n_{kl} supposing the tensors to be invariant under the magnetic field symmetry group ∞/m. This expansion gives nothing new compared with the case of the intermediate field.

We have neglected the dependence of k_{res} on the aniso-tropic factors. It is really not essential for the anisotropic properties of scattering when we consider the separate reso-nant atom. It becomes essential, however, when we consider a unit cell that includes several resonant atoms. If there is only one anisotropic factor, then the resonant denominator does not depend on its orientation in crystal space, i.e. k_{res} depends only on the value of the magnetic moment or crystal field. The situation may be more complicated when there are several anisotropic factors simultaneously. In this case, k_{res} may depend on the mutual orientations of the anisotropic fields. This fact must then be taken into account in the study of diffraction patterns because the difference in k_{res}, for example for different atomic species located on the same crystal-lographic position, can lead to the appearance of additional reflections.

References

Agranovitch, V. M. & Ginzburg, V. L. (1984). *Crystal Optics with Spatial Dispersion and Exitons. Springer Series on Solid-State Sciences*, Vol. 42. Berlin: Springer Verlag.

Blume, M. (1994). *Resonant Anomalous X-ray Scattering*, edited by G. Materlik, C. J. Spark & K. Fisher, pp. 495–515. Amsterdam: North-Holland.

Brouder, C. (1990). *J. Phys. Condens. Matter*, **2**, 701–793.

Carra, P. & Thole, B. T. (1994). *Rev. Mod. Phys.* **66**, 1509–1515.

Carra, P. L., Thole, B. T., Altareli, M. & Wang, X. (1993). *Phys. Rev. Lett.* **70**, 694–697.

Dmitrienko, V. E. (1983). *Acta Cryst.* A**39**, 29–37.

Dmitrienko, V. E., Ovchinnikova, E. N. & Ishida, K. (1999). *Pis'ma JETP*, **69**, 885–889.

Fabrizio, M., Altarelli, M. & Benfatto, M. (1998). *Phys. Rev. Lett.* **80**, 3400–3403.

Fedorov, F. I. & Filippov, V. V. (1976). *Reflection and Refraction of Light by Transparent Crystals.* Moscow: Nauka i Tekhnika. (In Russian.)

Finkelstein, K. D., Shen, Q. & Shastri, S. (1993). *Phys. Rev. Lett.* **69**, 1612–1615.

Gibbs, D., Moncton, D. E. & D'Amico, K. L. (1985). *J. Appl. Phys.* **57**, 3619–3622.

Gurewitch, G. B. (1948). *The Basics of the Algebraic Invariants Theory.* Moscow: Gostehizdat. (In Russian.)

Hannon, J. P., Trammell, G. T., Blume, M. & Gibbs, D. (1988). *Phys. Rev. Lett.* **61**, 1245–1248.

Ishihara, S. & Maekawa, S. (1998a). *Phys. Rev. Lett.* **80**, 3799–3802.

Ishihara, S. & Maekawa, S. (1998b). *Phys. Rev. B*, **58**, 13442–13451.

Jahn, H. A. (1949). *Acta Cryst.* **2**, 30–33.

Kirfel, A., Petcov, A. & Eichhorn, K. (1991). *Acta Cryst.* A**47**, 180–195.

Kissel, L., Zhou, B., Roy, S. C., Sen Gupta, S. K. & Pratt, R. H. (1995). *Acta Cryst.* A**51**, 271–288.

Kugel, K. I. & Homsky, D. I. (1982). *Usp. Phys. Nauk*, **136**, 621–664; Engl. Transl: *Sov. Phys. Usp.* **25**, 231–270.

Landau, L. D. & Lifshitz, E. M. (1953). *Electrodynamics of Continuous Media.* Moscow: Gostehizdat.

Luo, J., Trammell, G. T. & Hannon, J. P. (1993). *Phys. Rev. Lett.* **71**, 287–290.

Miozakawa, T. & Fujimori, A. (1995). *Phys. Rev. B*, **51**, 12880–12883.

Murakami, Y., Kawada, H., Kawata, H., Tanaka, M., Arima, T., Morimoto, Y. & Tokura, Y. (1998). *Phys. Rev. Lett.* **80**, 1932.

Ovchinnikova, E. N. & Dmitrienko, V. E. (1997). *Acta Cryst.* A**53**, 388–395.

Pinsker, Z. G. (1982). *X-ray Crystallooptics.* Moscow: Nauka. (In Russian.)

Rennert, P. (1993). *Phys. Rev. B*, **48**, 13559–13568.

Sirotin, Yu. I. & Shaskolskaja, M. P. (1975). *The Foundation of Crystallophysics.* Moscow: Nauka. (In Russian.)

Sternlieb, B. J., Hill, J. P., Wildgruber, U. C., Luke, G. M., Nachumi, B., Morimoto, Y. & Tokura, Y. (1996). *Phys. Rev. Lett.* **76**, 2169–2172.

Templeton, D. H. (1998). *Acta Cryst.* A**54**, 158–162.

Templeton, D. H. & Templeton, L. K. (1980). *Acta Cryst.* A**36**, 237–241.