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Combined Effects of Magnetic Structure and Local Crystal Fields in Anisotropic X-ray Anomalous Scattering

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. E-mail: eno@runar.phys.msu.su*

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Abstract

The X-ray extinction conditions are studied for the cases when both magnetic interaction and crystalline fields cause the anisotropy of X-ray scattering amplitudes near the absorption edge. It is demonstrated that the simultaneous existence of those two anisotropies, referred to as the combined anisotropy, can result in excitation of additional Bragg reflections otherwise forbidden by extinction rules. To show this, the structure amplitudes of reflections are computed and two Laue (L) groups are compared: one, L_m, which corresponds to the anomalous X-ray scattering in the presence of magnetic structure and another one, L_q, which takes into account the anisotropic atomic environment. Both groups can contain additional reflections and differ from the Laue group, L_p, associated with the usual potential X-ray scattering. The cross of these groups is considered and it is shown that several extinctions, typical for the L_p group, still remain in L_q and L_m. Nevertheless, the new reflections may appear instead of those extinctions when the combined anisotropy is taken into account. In this case, the diffraction pattern is characterized by the L_c group. Then, the transformation of L_q into L_c under the phase transition is studied. It is shown that the additional reflections, not typical for L_m, can appear in the diffraction pattern below the magnetic ordering temperature T_M. Two cases are discussed: (i) L_q above T_M contains the same reflections as L_c and (ii) L_q contains the extinctions corresponding to the additional reflections in L_c. Several examples are considered for real magnetic crystals.

1. Introduction

Recently, a rich variety of phenomena related to different types of crystal anisotropy was revealed and surveyed in resonant X-ray absorption (Brouder, 1990) and scattering (Belyakov & Dmitrienko, 1989; Blume, 1994; Carra & Thole, 1994) near absorption edges of atoms. These phenomena occur when the energy of the incident radiation approaches those values that are required to excite an inner-shell electron to an empty state of a valence shell. The valence shells are strongly affected by the atomic environment and therefore the atomic scattering amplitude can depend on the local crystal fields and (or) the atomic magnetic moments. One of the phenomena is the excitation of forbidden reflections, which are absent in the potential (Thomson) X-ray scattering. The forbidden magnetic reflections and those that exist even in non-magnetic crystals owing to an anisotropic atomic environment have been studied both theoretically and experimentally (Gibbs, Moncton & D'Amico, 1985; Hannon, Trammel, Blume & Gibbs, 1988; Templeton & Templeton, 1980; Dmitrienko, 1983).

The natural language for the description of possible reflections is group theory. The homomorphic correspondence between 230 space groups and 122 diffraction (Laue) groups is a fundamental fact for X-ray potential scattering. Each Laue group contains a set of extinctions, listed in *International Tables for X-ray Crystallography* (1965). The anisotropic character of the anomalous diffraction violates the extinction rules computed for isotropic scattering. Hence, in the case of anomalous scattering, the diffraction group $L_{\rm anom}$ may differ from a group L_p describing only the potential scattering. The difference between the Laue groups may be classified as a difference in the symmetry of structures studied by the anomalous diffraction method compared with the space-group symmetry. This statement is clear for magnetic structures, for which symmetry is described by magnetic groups and the diffraction pattern can be characterized by the Laue group L_m. But the crystal fields and electrical multipole moments should be invariant under space-group transformations. Nevertheless, the extinction rules of the L_p group can be violated when a resonant interaction with an electromagnetic field occurs because the crystallographically equivalent atoms may become non-equivalent scatterers owing to the local crystal anisotropy. In this case, the resonant X-ray diffraction pattern is characterized by the Laue group L_q, which differs from L_p and contains additional reflections excited owing to the local crystalline environment of the scattering atom (Templeton & Templeton, 1980; Dmitrienko, 1983). The local crystal-field anisotropy violates the screw-axis and glide-plane extinction rules, whereas the magnetic moments can violate the translation symmetry too.

The extinction rules for these groups, L_m and L_q, can differ from each other, but some extinctions may coincide. The simultaneous existence of two types of

anisotropy gives a diffraction pattern that is described by the L_c Laue group. In the present paper, we study this question in more detail for several crystal structures and compare the extinction rules corresponding to L_m and L_q. Then, we determine whether L_c contains some additional reflections in comparison with L_m and L_q. It is demonstrated that the simultaneous existence of these two anisotropies, referred to as the combined anisotropy, can result in excitation of the additional Bragg reflections otherwise forbidden by extinction rules. In other words, our conclusion is that the symmetry under the magnetic space group (including crystal anisotropy) allows reflections that are not permitted under the crystal space group or under the symmetry of potential scattering plus magnetic scattering. There may also be a difference in polarization properties of reflections corresponding to L_q, L_m and L_p groups (Belyakov & Dmitrienko, 1989); however, this is not a subject of the present work.

2. Different representations of X-ray scattering amplitudes

Because of the complexity of the phenomena, it is important to have general considerations that could predict new extinction rules. There are several approaches that can be used for the proper representation of X-ray scattering near the absorption edges taking into account the symmetry of investigated structures. An atomic scattering amplitude, which is the main parameter for the scattering process description, has been studied in detail [see surveys by Blume (1994) and Carra & Thole (1994)]. The most general form of the resonant coherent elastic scattering amplitude for any electric 2^L-pole transition in a spherically symmetric atom was given by Carra & Thole (1994) and Luo, Trammell & Hannon (1993). It was represented as a linear combination of pairs of tensors with increasing rank μ, which transform according to the irreducible representations of the spherical group (SO_3):

$$f^{\mathrm{EL}}(\omega) = 2\lambda \sum_{\mu=0}^{2L} \sum_{m=-\mu}^{\mu} T_m^{(\mu)*}(\mathbf{e}_f^*, \mathbf{k}_f, \mathbf{e}_i, \mathbf{k}_i)_{\mathrm{EL}} \times \langle \psi_0 | F_m^{(\mu)}(\omega)_{\mathrm{EL}} | \psi_0 \rangle, \quad (1)$$

where the spherical tensors $T_m^{(\mu)}$ determine the angular parts, $F_m^{(\mu)}$ are the frequency-dependent transition operators (spectrum), $\mathbf{e}_i$ and $\mathbf{e}_f$ are the polarization vectors of the incident and scattered radiation with the wave vectors $\mathbf{k}_i$ and $\mathbf{k}_f$, EL denotes the electrical multipole transitions, which are responsible for the discussed kind of scattering (see Hannon, Trammell, Blume & Gibbs, 1988). Any basis can be used to take into account the symmetry of the system, for example a point-group basis (when the local symmetry of the atom environment is considered) or SO_2 (cylindrical symmetry group) for the magnetic atom. This approach was used (Carra & Thole, 1994) to study the transformations of $T_m^{(\mu)}$ corresponding to glide planes and screw axes for arbitrary scattering geometry vectors. Several extinction rules were formulated in terms of μ and m. There are also strong symmetry restrictions on the tensor form of the structure amplitude (Dmitrienko, 1983) but we will not consider this subject here. A disadvantage of the scattering amplitude technique for the symmetry analysis is its dependence on the radiation properties (polarizations and wave vectors).

There is another approach, developed by Blume (1994), that allows separation of the dependence on polarizations and wave vectors from the 'material' part determined only by the properties of matter. The scattering amplitude is linked with the atomic polarizability tensors $\chi_s^{\alpha\beta}$ in the following way:

$$F_{\mathrm{res}}(\mathbf{H}) = -(e^2/mc^2)(m\omega_0^3/\hbar\omega) \times \sum_s \exp(i\mathbf{H}\cdot\mathbf{r}_s - W_s) e_f'^{*\alpha} e_i^{\beta} \chi_s^{\alpha\beta}, \quad (2)$$

where $\mathbf{H}$ is a reciprocal-lattice vector, $\mathbf{r}_s$ is the position of the sth atom in a unit cell and W_s is the temperature factor.

For the dipole transition, the equation for $\hat{\chi}_s$ has the form

$$\chi_s^{\alpha\beta} = \sum_{ca} p_a \frac{\langle a|\mathbf{R}_s^{\alpha}|c\rangle\langle c|\mathbf{R}_s^{\beta}|a\rangle}{\omega - \omega_0 - i\Gamma/2\hbar}, \quad (3)$$

where $|a\rangle$ and $|c\rangle$ are the ground and excited states of the atom, p_a are the occupation numbers and $\mathbf{R}_s^{\alpha} = \sum_i^{(s)} \mathbf{r}_i^{\alpha}$.

For quadrupole and higher transitions, $\hat{\chi}$ can be expressed as a convolution of $2L$-rank tensors with the wave vectors of incident and scattered radiation. The Cartesian form of $\hat{\chi}$ has been presented (Blume, 1994). It is easy to see that the polarizability tensors can be subdivided into parts with different internal symmetry:

$$\chi_s^{\alpha\beta} = \chi_{0s}\delta^{\alpha\beta} + \chi_{-s}^{\alpha\beta} + \chi_{+s}^{\alpha\beta}, \quad (4)$$

where $\chi_{0s} = \mathrm{tr}(\chi)/3$, $\chi_-^{\alpha\beta} = (\chi^{\alpha\beta} - \chi^{\beta\alpha})/2$, $\chi_+^{\alpha\beta} = (\chi^{\alpha\beta} + \chi^{\alpha\beta})/2 - \chi_{0s}\delta^{\alpha\beta}$.

The expressions for $\hat{\chi}$ are known for the cases of Templeton scattering (Templeton & Templeton, 1980; Dmitrienko, 1983), for magnetic dipole scattering (Hannon, Trammel, Blume & Gibbs, 1988) and for the quadrupole transition (Blume, 1994). The case of simultaneous existence of magnetic moments and crystal-field anisotropy was considered for the dipole transitions and $\hat{\chi}$ was expressed as (Blume, 1994)

$$\chi_+^{\alpha\beta} = (n^{\alpha}n^{\beta} - \tfrac{1}{3}\delta^{\alpha\beta})[a_1 + b_1(\mathbf{n}\cdot\mathbf{m})^2] + c_1(m^{\alpha}m^{\beta} - \tfrac{1}{3}m^2\delta^{\alpha\beta}) + d_1[n^{\alpha}m^{\beta} + n^{\beta}m^{\alpha} - \tfrac{2}{3}(\mathbf{n}\cdot\mathbf{m})\delta^{\alpha\beta}](\mathbf{n}\cdot\mathbf{m}), \quad (5)$$

$$\chi_-^{\alpha\beta} = i\varepsilon^{\alpha\beta\gamma}[a_2 m^{\gamma} + b_2 n^{\gamma}(\mathbf{n}\cdot\mathbf{m})]. \quad (6)$$

Here, a_1, b_1, c_1, d_1, a_2, b_2 contain the resonant denominators, m^α and n^α denote the projections of the magnetic moment and the unit vector along the local crystal-field axis corresponding to the sth atom in a unit cell. Equations (5) and (6) are correct when the polarizability tensors corresponding to the local crystal anisotropy are invariant under rotation around the axis, characterized by one unit vector **n**, *i.e.* in the cases of special symmetry of atomic positions.

We want to point out that the technique used for the description of the anomalous resonant X-ray scattering is just like that known in Mössbauer diffraction (Hannon & Trammell, 1969). It was shown (Andreeva & Kuz'min, 1982) that the polarizabiliy tensors describing the scattering of Mössbauer radiation by a nuclear subsystem can be written as

$$\hat{\chi}_s \sim \mathbf{u}_f \otimes \mathbf{u}_f \otimes \ldots \otimes \mathbf{u}_f : [L-1] : g_s^{(2L)} : [L-1] \otimes \mathbf{u}_i \otimes \mathbf{u}_i \otimes \ldots \otimes \mathbf{u}_i, \quad (7)$$

$$\hat{g}^{(2L)} = \sum_M A(M)\hat{Q}^L(M) \otimes \hat{Q}^L(M), \quad (8)$$

$$\hat{Q}^{(L)}(M) = \{(2L-1)!!/[(L+1)(L-1)!!]\}^{1/2} \times \sum_{\lambda,\mu,\ldots,\nu,\rho,m_1,m_2,\ldots} \langle 1\nu L - 1m_1 | LM\rangle \ldots \times \langle 1\mu L - 2m_2 | L - 1m_1\rangle \ldots \langle 1\nu 1\rho | 2m\rangle \times \mathbf{h}_\lambda \otimes \mathbf{h}_\mu \otimes \ldots \otimes \mathbf{h}_\nu \otimes \mathbf{h}_\rho, \quad (9)$$

where $\hat{g}^{(2L)}$ are the multipole polarizability tensors corresponding to the material parts (excluding the wave vectors) of $\hat{\chi}$, the $A(M)$'s contain the resonant denominators, $\ldots : [L-1] \ldots : [L-1]$ denote $[L-1]$-fold convolution of the $\hat{g}^{(2L)}$ tensor with the unit vectors $\mathbf{u}_i$ and $\mathbf{u}_f$ parallel to the wave vectors $\mathbf{k}_i$ and $\mathbf{k}_f$; $\mathbf{h}_{\pm 1} = \mp(i\mathbf{h}_x \pm i\mathbf{h}_y)/2^{1/2}$; $\mathbf{h}_0 = -i\mathbf{h}_z$; $\mathbf{h}_{x,y,z}$ are the unit vectors connected with the magnetic field and/or the electrical field gradient and $\otimes$ denotes the direct product of vectors. For the dipole transition in the case of cylindrical symmetry, $\hat{\chi}$ contains three parts with different resonant denominators, α_i, corresponding to the transitions with different $M = m_e - m_g$:

$$\chi_{\rm res}^{dd} \sim \alpha_1 \mathbf{h}_1 \otimes \mathbf{h}_1^* + \alpha_0 \mathbf{h}_0 \otimes \mathbf{h}_0^* + \alpha_{-1}\mathbf{h}_{-1} \otimes \mathbf{h}_{-1}^*. \quad (10)$$

It is easy to show that this form of $\hat{\chi}$, being expressed in the Cartesian form, coincides with (5) and (6).

A knowledge of $\hat{\chi}$ is needed to find a set of possible reflections and a corresponding set of tensor structure amplitudes. For this purpose, $\hat{\chi}(\mathbf{H})$ must be calculated:

$$\hat{\chi}(\mathbf{H}) = \sum_s \hat{\chi}(\mathbf{r}_s)\exp(i\mathbf{H}\cdot\mathbf{r}_s). \quad (11)$$

$\hat{\chi}(\mathbf{H}) = 0$ is the extinction condition for any polarization of incident radiation.

The above general formulas allow us to describe the sets of possible reflections in the anomalous X-ray scattering near absorption edges for different kinds of local fields in crystals. We will use them together with group theory to study the diffraction patterns, taking into account both the magnetic moments and the crystal local anisotropic environments of atoms.

3. The combined effects caused by the magnetic moments and local crystal anisotropy

Let us compare the extinction rules in anomalous X-ray scattering for a crystal above and below the temperature T_M of magnetic ordering. We consider the electric dipole transition and suppose the local symmetry of a probe atom to be lower than $T23$. Therefore, the Templeton reflections can be observed above T_M, except for several special cases when extinctions still remain (Dmitrienko, 1983). Below T_M, the magnetic ordering may lead to the occurrence of magnetic reflections. We consider only the structures where the magnetic cell coincides with the crystal cell. In this case, the sets of magnetic reflections and reflections due to a local crystal anisotropy are integral and fill only reciprocal-lattice centres. First, we compare those parts of these reflection sets that are forbidden for the usual X-ray potential scattering, *i.e.* the extinctions corresponding to Laue groups L_q, L_m and L_p. Then we discuss the question whether the combined magnetic and anisotropic local crystal symmetry gives any effects that cannot exist when these systems are considered separately.

3.1. *The combined reflections that are present in L_q and absent in L_m*

In recent years, many theoretical papers have appeared concerned with X-ray resonant arbsorption and scattering in magnetic crystals with local anisotropy. They have discussed the possibility of obtaining site-specific information on the magnetic anisotropy, sum rules and other questions (see Luo, Trammell & Hannon, 1993; Carra & Thole, 1994; Carra, Thole, Altarelli & Wang, 1993; Rennert, 1993; Hill & McMorrow, 1996; Lippmann, Kirfel & Fischer, 1996, and references therein). We would like to discuss only the extinction rules that follow from symmetry considerations.

For the analysis of crystal symmetry effects, let us compare the 'spectra' (which contain the resonant denominators) and then the angular parts of polarizabilities, corresponding to the different crystallographically equivalent resonant atoms with $\mathbf{r}_s$ coordinates in a unit cell.

Simplification of a 'spectrum' structure, corresponding to a single atom, was considered by Luo, Trammell & Hannon (1993). It was shown that $F_m^{(\mu)}$ [see (1)] operators are simplified when either a linewidth Γ or a deviation $\Delta\omega = E_f^s - E_0 - h\omega$ is large compared with the splitting Δ_s of the excited-state configuration. Then

it is possible to characterize the transition by an average value, $\bar{E}_l^s$, describing the single-atom excited state. In this approximation, operators $F_m^{(\mu)}(s)$ can be expressed as

$$F_m^{(\mu)}(\omega, s) = R(l_1 j_\pm; L; l_2; s)[(2L+1)/(2\mu+1)]^{1/2} \times M_m^{(\mu)}(l_1 j_\pm; L; l_2; s), \quad (12)$$

where only the R's contain an energy resonant denominator, depending on $\bar{E}_l^s$. This case was called 'the fast collision approximation'. In (12), we have added the s indices, which characterize the atoms inside one crystallographical position. The forms of M_m^μ operators for the $E1$ transition are given by (16) and (17) from the work of Luo, Trammell & Hannon (1993), where the exchange splitting between spin-up and spin-down valence states is taken into account. It is essential that even in this approximation the scattering amplitude depends on the mutual orientations of the magnetic moments and the local crystal-field directions.

The fast collision approximation is rather good for resonant scattering near the L_2 and L_3 edges in the rare earths and near the M_4 and M_5 edges in actinides. However, for the M_4 and M_5 transitions in the rare earths, $\Delta_s > \Gamma$ and the multiplet structure can be resolved. Experimental results have shown that the fast collision approximation is not good for the iron $L_{2,3}$ edges in hematite, where $\Gamma \approx 1.5$ eV and atoms have the octahedral environment with $10Dq \approx 1.45$ eV (Finkelstein, Shen & Shastry, 1992; Kuiper, Searle, Rudolf, Tjeng & Chen, 1993).

The forbidden reflection may occur if $F_m^{(\mu)}(s_1) \neq F_m^{(\mu)}(s_2)$ inside one equivalent position. There are two possible reasons for this inequality: (i) $R(s_1) \neq R(s_2)$ and/or (ii) $M_m^{(\mu)}(s_1) \neq M_m^{(\mu)}(s_2)$. The condition (i) may be realized even in the fast collision approximation if the different mutual orientations of the atomic magnetic moment $\mathbf{m}_s$ and local crystal-field axes $\mathbf{n}_s$ produce the different splittings Δ_s of the excited-state configurations of these atoms. Then the excited states of the atoms inside one crystallographic position can be characterized by E_l^s and $\bar{E}_l^s$ in the fast collision approximation. If a difference $|E_l^{s_1} - E_l^{s_2}|$ is comparable with the line halfwidth $\Gamma/2$, the possibility of additional reflection owing to the difference in the 'spectra' may be discussed. The condition (ii) may be fulfilled for various crystal structures. We try to find those cases when $M_m^{(\mu)}(s_1) = M_m^{(\mu)}(s_2)$ for purely magnetic structure (or purely local crystal anisotropy) but $M_m^{(\mu)}(s_1) \neq M_m^{(\mu)}(s_2)$ if both kinds of anisotropy are taken into account. Let us call the last case the combined anisotropy. Naturally, the effects corresponding to the combined anisotropy will vanish when the local crystal anisotropy is negligible compared with the magnetic one or *vice versa*. So the good condition for the considered reflections is that the splitting due to the spin–orbital interaction would be of the same order as that due to the crystal-field anisotropy. This case corresponds to an intermediate crystal field (see Ballhausen, 1962). The following examples will explain the idea.

3.1.1. *The forbidden reflections in YIG caused by different mutual orientations of magnetic moments and local crystal axes.* Let us consider a crystal with a symmetry described by the space group $O_h^{10} = Ia3d$. It is a typical group for rare-earth garnets, for instance, the yttrium iron garnet (YIG). Fe atoms occupy the positions 16(a) and 24(d) with point symmetries $\bar{3}$ and $\bar{4}$. Near the absorption edge of iron, the atomic polarizabilities are described (for dipole transitions) by the second-rank tensors invariant under the local position groups. It follows from the crystal symmetry that the main axes of those tensors coincide with threefold axes for the 16(a) positions and with fourfold axes for the 24(d) positions.

All the 24 atoms of (d) positions can be subdivided into three groups with the orientations of the local crystal-field axes along the [100], [010] and [001] directions correspondingly. They are connected to each other by the threefold axes. The directions of the local field axes coincide with the main axes of electric field gradients, which were determined with the help of Mössbauer spectroscopy (Winkler, Eisberg, Alp, Rüffer, Gerdau, Lauer, Trautwein, Grodzicki & Vera 1983).

In ferrimagnetic YIG below the Curie temperature T_C, the magnetic moments inside the 24(d) position are coupled ferromagnetically and they are collinear to the external magnetic field when it is applied to the crystal. This type of magnetic ordering cannot cause any new reflections in X-ray resonant anomalous scattering. Hence, the magnetic Laue group, L_m, coincides with L_p, *i.e.* keeps all the extinctions intrinsic to potential scattering.

Consideration of the polarizability tensors shows that there are reflections, absent in a usual potential scattering, that correspond to a resonant scattering only by atoms in position (a) or (d). The (d) sites yield new reflections with $h = 4n + 2$, $k = l = 4n'$, whereas, for the (a) sites, $h = 2n + 1$, $k = 2n' + 1$, $l = 0$ and $h = k = 2n + 1$, $l = 4n'$.

Let us consider the $h00$ ($h = 4n + 2$) reflections, generated by 24(d) positions. The polarizability tensor for it is equal to

$$\hat{\chi}(h00) = 8(\hat{\chi}_2 - \hat{\chi}_1), \quad (13)$$

where $\hat{\chi}_1$ and $\hat{\chi}_2$ correspond to the atoms that lie on the $\bar{4}$ axes parallel to [010] or [001]. The atoms with the [100] direction of the local field axis do not participate in scattering into this reflection.

For our discussion, it is essential that all the magnetic moments would be aligned, hence the crystal has to be a single domain. For this purpose, a weak external magnetic field (~0.01 T) may be applied to provide the full alignment. Suppose that the external magnetic field is directed along the [010] axis, which is the easy

magnetization axis, then all the magnetic moments are parallel to the b axis of a crystal. In this case, the atoms of the 24(d) position split into two subgroups (see Fig. 1a). For the first one, the angle θ_1 between the magnetic field and the main axis of the local crystal field is equal to zero ([010] subgroup). For the second subgroup, $\theta_2 = 90°$ ([001] subgroup). Let us write the projections of the local field axes $\mathbf{n}_{1,2}$ (they coincide with the fourfold axes) and the magnetic moments $\mathbf{m}$ onto the crystal axes and their scalar products for two atoms. They are equal to:

$$(a)\ \mathbf{n}_1 = (0, n, 0);\quad \mathbf{m}_1 = (0, m, 0);\quad (\mathbf{n}_1 \cdot \mathbf{m}_1) = nm;$$
$$(b)\ \mathbf{n}_2 = (0, 0, n);\quad \mathbf{m}_2 = (0, m, 0);\quad (\mathbf{n}_2 \cdot \mathbf{m}_2) = 0.$$

The calculation of the polarizability tensor above the Curie temperature shows that it can differ from zero, hence the extinction of the $h00$ ($h = 4n + 2$) reflection is absent in the L_q Laue group. The invariance of the polarizability tensors, caused by the local crystal-field anisotropy under the inversion of coordinates, is shown in Fig. 1 by the double-ended arrows.

The polarizability below T_C, computed from (5) and (6), shows that there are two reasons that can lead to the extra reflections. As discussed above, the first one gives $\hat{\chi}(\mathbf{H}) \neq 0$ if the energy denominators for atoms (1) and (2) are not equal to each other, *i.e.* $a_i^{(1)} \neq a_i^{(2)}$, $b_i^{(1)} \neq b_i^{(2)}$, $c_i^{(1)} \neq c_i^{(2)}$, $d_i^{(1)} \neq d_i^{(2)}$ (here the upper indices correspond to the atomic numbers). If the difference between the energies $\overline{E}_l[010] - \overline{E}_l[001]$ is comparable with the linewidth Γ, these extra reflections can be pronounced. Their frequency dependence is determined by the interference between the spectrum lines, corresponding to the atoms with the local axes oriented along [010] and [001]. A similar effect was predicted for Mössbauer diffraction (Grigoryan & Belyakov, 1971; Winkler, Eisberg, Alp, Rüffer, Gerdau, Lauer, Trautwien, Grodzicki & Vera 1983; Ovchinnikova & Kuz'min, 1988) and was observed experimentally (Labushkin, Ovchinnikova, Smirnov, Sarkisov & Uspensky, 1995). In the case of X-ray resonant diffraction near the L edges of iron, when the resonant lines are not resolved, we suppose this effect to be small.

Condition (ii) can be more essential for the appearence of the forbidden reflections. It is connected with the difference of the angular parts of the polarizability tensors, corresponding to atoms (1) and (2). This follows from the difference of the projections $\mathbf{n}_1$, $\mathbf{n}_2$ and the scalar products $(\mathbf{n}_1 \cdot \mathbf{m}_1) \neq (\mathbf{n}_2 \cdot \mathbf{m}_2)$, which were written above. Therefore, $\hat{\chi}_1 \neq \hat{\chi}_2$ and the reflection $h00$ ($h = 4n + 2$) may exist in the diffraction pattern.

3.1.2. *The combined reflections in YIG with magnetization along [100].* Let a weak external magnetic field be applied to the considered YIG crystal along [100], providing full alignment of the atomic magnetic moments along **a**, so that $\mathbf{m}'_{1,2} = (m, 0, 0)$. The mutual orientation of the magnetic moments and the local crystal axes are shown in Fig. 1(b). The energy denominators for all the resonant atoms are the same, as far as the scalar products $(\mathbf{n}_1 \cdot \mathbf{m}) = (\mathbf{n}_2 \cdot \mathbf{m}) = 0$. However, the angular parts of [010] and [001] atom polarizabilities are different because of the different orientations of the local crystal fields. An application of the Cartesian form of polarizability [(5) and (6)] gives the following value of the polarizability tensor:

$$\hat{\chi}_+(h00) = 8a_1 \begin{pmatrix} 0 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (14)$$

It shows a possibility of reflections caused by the crystal-field anisotropy below the Curie temperature. The discussed reflections are forbidden in an ordinary X-ray diffraction pattern and in the case when only magnetic structure is taken into account.

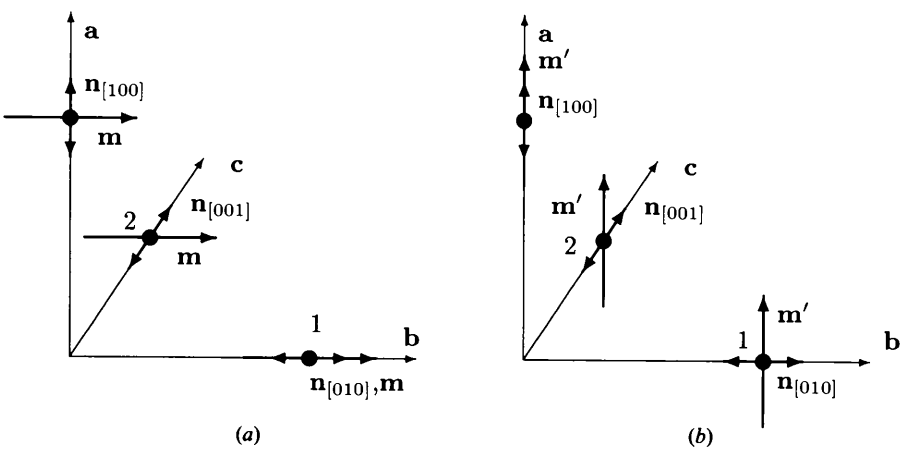

Fig. 1. The directions of the local crystal-field axes $\mathbf{n}_i$ (double-ended arrows) and the magnetic moments $\mathbf{m}_j$ (arrows) of the Fe atoms in 24(d) positions of the YIG crystal.

Thus, it is shown that the Laue group L_c contains in the magnetically ordered phase the $h00$ ($h = 4n + 2$) reflections, which belong to L_q but are forbidden for L_m and L_p.

It is worth considering one more interesting case when the resonantly scattered atoms occupy two or more crystallographically nonequivalent positions. Then, the form of the resonant spectra is determined by interference of radiation scattered by atoms in different positions. Those atoms can possess both different 'spectrum' and angular parts. Extremely complex polarization effects occur in this case.

3.2. *The combined reflections absent in both L_q and L_m*

In the previous subsections, we have discussed situations when the Templeton reflections are allowed above the magnetic ordering temperature. Now let us consider an example when both magnetic and crystal symmetries, applied separately, forbid some group of reflections, whereas the combined action of magnetic and crystalline fields can allow extra reflections. In other words, both L_q and L_m contain several extinctions, which are absent in L_c. In our example, the crystal is described by the D_{2h}^{16} = *Pnma* space group and the resonant atoms belong to the special position 4(c) with the following coordinates: (1) $x, 1/4, z$; (2) $-x, 3/4, -z$; (3) $1/2 - x, 3/4, 1/2 + z$; (4) $1/2 + x, 1/4, 1/2 - z$ (Fig. 2).

The polarizability tensor for the $0k0$ ($k = 2n + 1$) reflection is

$$\hat{\chi}(0k0) = \hat{\chi}_1 - \hat{\chi}_2 - \hat{\chi}_3 + \hat{\chi}_4. \qquad (15)$$

This reflection is evidently forbidden for the potential X-ray scattering when $\chi_1 = \chi_2 = \chi_3 = \chi_4$.

Atoms (1) and (2) are connected by inversion at the centre, (1) and (4) by the glide plane perpendicular to the c axis with translation along the a axis. All the atoms lie in the mirror planes perpendicular to the b axis. Hence,

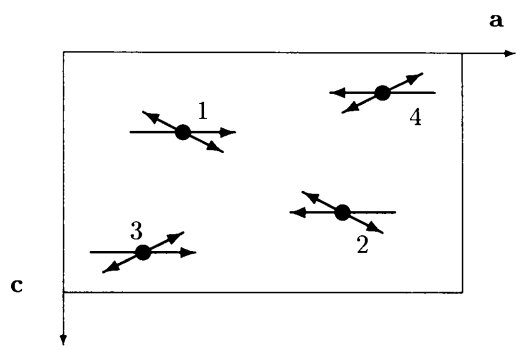

Fig. 2. The directions of the local crystal-field axes $\mathbf{n}_i$ (double-ended arrrows) and of the magnetic moments $\mathbf{m}_i$ (arrows) corresponding to the G_x structure on the atoms in the 4(c) position of the *Pnma* space group. All atoms lie on two mirror planes perpendicular to the b axis. The y coordinates for atoms 1 and 4 are equal to $b/4$, for 2 and 3, they are equal to $3b/4$.

the main axes of the local crystal fields can be directed either perpendicularly to a mirror plane or lie in the (010) plane. As a result of the symmetry constrains, the $\hat{\chi}$ tensors that describe a resonant scattering of X-rays in a paramagnetic region have the forms

$$\hat{\chi}_1 = \hat{\chi}_2 = \begin{pmatrix} \chi^{xx} & 0 & \chi^{xz} \\ 0 & \chi^{yy} & 0 \\ \chi^{xz} & 0 & \chi^{zz} \end{pmatrix},$$
$$\hat{\chi}_3 = \hat{\chi}_4 = \begin{pmatrix} \chi^{xx} & 0 & -\chi^{xz} \\ 0 & \chi^{yy} & 0 \\ -\chi^{xz} & 0 & \chi^{zz} \end{pmatrix}. \qquad (16)$$

After the substitution of (16) into (14), one can see that the $0k0$ ($k = 2n + 1$) reflection remains forbidden in anomalous X-ray scattering if only the local crystal-field anisotropy is taken into account (for instance, above a Néel temperature).

Let us now consider possible magnetic structures of crystals with *Pnma* symmetry. This space group is typical for rare-earth orthoferrites. Possible antiferromagnetic structures are classified as $F(+++-)$, $G(+--+)$, $C(++--)$ and $A(+---)$ (Bertaut, 1963; Turov, 1963). Plus and minus denote that the magnetic moments are coupled ferromagnetically or antiferromagnetically to each other. The G structure is the most interesting for us because it gives the extinction of the $0k0$ ($k = 2n + 1$) reflection below the Néel temperature. The noncollinear structure $F_\alpha G_\beta$, $(\alpha, \beta) = x, y, z$, also satisfies the extinction condition. For A and C structures and their mixing, the corresponding $\hat{\chi}(\mathbf{H})$ tensor should not be equal to zero and the magnetic reflection is not forbidden.

The question is whether the $0k0$ ($k = 2n+1$) reflection can appear in the X-ray resonant diffraction pattern if both the G-type magnetic moment ordering and the crystal-field anisotropy exist simultaneously. Let us consider the pure G_x magnetic structure. From the general properties of the polarizability tensor in the presence of a magnetic field, $\chi^{\alpha\beta}(\omega, \mathbf{k}, \mathbf{B}) = \chi^{\beta\alpha}(\omega, -\mathbf{k}, -\mathbf{B})$ (Landau & Lifschitz, 1952), we can write for the dipole transition (when the k dependence is absent) $\chi_1^{\alpha\beta} = \chi_2^{\beta\alpha}$, $\chi_3^{\alpha\beta} = \chi_4^{\beta\alpha}$. Taking into account the invariance of the polarizability in the absence of the magnetic field under the inversion of the coordinate sign, we can approximate the local axes transformation from atom 1 to atom 3 by the rotation around the a crystal axis by an angle equal to π. Then we can find the following expression for $\hat{\chi}(0k0)$ ($k = 2n + 1$):

$$\hat{\chi}(0k0) = a_2 \begin{pmatrix} 0 & 2(\chi^{xy} - \chi^{yx}) & 2(\chi^{xz} - \chi^{zx}) \\ 2(\chi^{yx} - \chi^{xy}) & 0 & 0 \\ 2(\chi^{zx} - \chi^{xz}) & 0 & 0 \end{pmatrix}$$
$$= a_2 \begin{pmatrix} 0 & 4\chi_-^{xy} & 4\chi_-^{xz} \\ -4\chi_-^{xy} & 0 & 0 \\ -4\chi_-^{xz} & 0 & 0 \end{pmatrix}, \qquad (17)$$

Table 1. *The orthorhombic space groups where the combined reflections are possible*

Symmetry group	Wyckoff positions	Combined reflections	Magnetic type
Pnnn	4(*g*), 4(*h*)	0*kl*, $k + l = 2n + 1$	*A*
	4(*i*), 4(*j*)	*h*0*l*, $h + l = 2n + 1$	*A*
	4(*k*), 4(*l*)	*hk*0, $h + k = 2n + 1$	*A*
Pccm	4(*i*)	0*kl*, $l = 2n + 1$	*G*
	4(*j*), 4(*k*), 4(*l*)	*h*0*l*, $l = 2n + 1$	*G*
Pban	4(*g*), 4(*h*)	0*kl*, $k = 2n + 1$	*G*
	4(*e*), 4(*j*)	*h*0*l*, $h = 2n = 1$	*G*
	4(*k*), 4(*l*)	*hk*0, $h + k = 2n + 1$	*G*
Pmma	4(*k*)	*h*00, $h = 2n + 1$	*A*
Pnna	4(*c*)	*hk*0, $h = 2n + 1$	*G* for $k = 2n$ *A* for $k = 2n + 1$
	4(*d*)	0*kl*, $k + l = 2n + 1$	*A* for $l = 2n$ *G* for $l = 2n + 1$
Pmna	4(*g*)	*h*0*l*, $h + l = 2n + 1$	*A* for $h = 2n$ *G* for $h = 2n + 1$
Pcca	4(*c*)	*h*0*l*, $l = 2n + 1$	*G* for $h = 2n$ *A* for $h = 2n + 1$
	4(*d*), 4(*e*)	*hk*0, $h = 2n + 1$	*A*
Pccn	4(*c*), 4(*d*)	*hk*0, $h + k = 2n + 1$	*A*
Pbcm	4(*c*)	0*kl*, $k = 2n + 1$	*A* for $l = 2n$ *G* for $l = 2n + 1$
	4(*d*)	00*l*, $l = 2n + 1$	*A*
Pmmn	4(*c*)	*h*00, $h = 2n + 1$	*A*
	4(*d*)	0*k*0, $k = 2n + 1$	*A*
Pbcn	4(*g*)	*h*0*l*, $l = 2n + 1$	*A* for $h = 2n$ *G* for $h = 2n + 1$
Pnma	4(*c*)	0*k*0, $k = 2n + 1$	*G*

which is generally different from zero. Notice that this expression is valid even for the biaxial local symmetry of the atomic positions 4(*c*), which is just the considered case.

An inspection of magnetic structures, which were experimentally investigated by neutron diffraction, has shown that *G*-type structures are typical for metamagnetics $R\mathrm{MeO}_3$ (*R* = rare earths, Me = metal atoms). For example, the pure magnetic structure of G_x type (we use *Pnma* instead of *Pbnm*) was observed for Gd atoms in GdAlO_3 at 3.95 K (Kappatsch, Quezel-Ambrunaz & Sivardière, 1970). It satisfies all the necessary symmetry conditions for the observation of the additional 0*k*0 ($k = 2n + 1$) reflections. In the rare earths, the splitting of an excited state Δ is more than a linewidth Γ for M_4 and M_5 edges; it is a good condition for the discussed phenomenon. Slightly worse is that the spin–orbital splitting is much greater than the crystal-field effects; however, this condition can be changed by a temperature variation. Indeed, owing to the temperature dependence of magnetic moments, the splittings can be made comparable slightly below the Néel temperature.

Pnma is not the only group suitable for the combined reflections appearance. All necessary symmetry conditions are fulfilled for several hexagonal perovskites $R\mathrm{MnO}_3$. They are described by the space group $P6_3cm$ and their magnetic structures were considered for example by Andreev & Marchenko (1980). The polarizabilty construction shows that the 00*l* ($l = 6n + 3$) reflections are similar to those considered above for *Pnma*. This hexagonal structure provides a more general example because the 00*l* ($l = 6n + 3$) extinctions above the Néel temperature occur due to the screw axis 6_3 unlike the 0*k*0 ($k = 2n + 1$) extinctions in *Pnma*, which correspond only to the 4(*c*) special position.

In Table 1, we list the special positions of space groups that belong to the rhombic dipyramidal symmetry type and allow the existence of the combined reflections. Only primitive groups are considered because the translations do not change the orientations of the local crystal fields but magnetic structures need additional discussion. The atomic enumeration inside the position corresponds to that in *International Tables for X-ray Crystallography* (1965).

The following approach was used in Table 1 for the enumeration of groups and atomic positions. Inversion is the only symmetry operation that does not change the components of the $\hat{\chi}$ tensor in the absence of magnetic moments. Thus, the inversion centre must exist in the group. Taking into account the equality of the

polarization tensors corresponding to atoms linked by inversion, we can calculate $\hat{\chi}(\mathbf{H})$ and find the extinction conditions in the presence of local crystal anisotropy and the kind of magnetic structure that gives the extinction too. Using this principle, one can construct similar tables for other space groups.

4. Conclusions

The investigations of many authors have shown that anomalous X-ray scattering near the absorption edges leads to the appearance of extra reflections in diffraction patterns owing to the anisotropy, caused (i) by magnetic moments and/or (ii) by the local atomic environments. We have characterized these two cases of anisotropy by the Laue groups L_m and L_q, which can differ from L_p, typical for the usual potential X-ray scattering. In the present paper, we have compared these Laue groups and found the situations when the same extinctions can be present in both of them. The existence of these two anisotropies together can violate the extinction rules associated with L_q and L_m. As a result, the combined group, L_c, corresponding to the simultaneous existence of two anisotropic fields, may contain the extra reflections that are absent in L_q and L_m. It means that the magnetic ordering after a phase transition can lead to the appearance of the additional reflections in the diffraction pattern near absorption edges. We have also considered the case when extra reflections with the indices, typical for the L_q group and forbidden for L_m, occur below the magnetic ordering temperature. The examples of crystal structures suitable for the discussed effects were studied from the symmetry point of view.

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