Resonant X-ray diffraction in incommensurately modulated crystals. Symmetry consideration of anisotropic anomalous scattering

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Abstract

Symmetry restrictions on the intensities and polarization properties of main reflections and their satellites are found for incommensurately modulated crystals in the case of anisotropic anomalous X-ray diffraction near absorption edges. It is shown that the modulation becomes a source of additional anisotropy for each resonant scatterer and induces a modulated behaviour of the susceptibility tensor. The four-dimensional approach is used to calculate the set of possible reflections. It is found that additional ('forbidden') reflections may appear both in the system of main reflections and in the system of satellites. The anisotropy also results in complex azimuthal and polarization properties of each reflection. The displacive modulation is discussed in detail. The ATS reflections corresponding to the resonant X-ray diffraction near the *K*-edge of iron in pyrrhotite-5.5*C* are considered.

1. Introduction

It is in the basics of conventional X-ray diffraction analysis that definite extinction rules correspond to the various spatial symmetry of crystals. The conditions limiting possible X-ray reflections are listed by Hahn (1987) providing the susceptibility to be a scalar function invariant under the space-group transformations. If this is not so, then 'forbidden' reflections can occur for various reasons, such as the asphericity of atomic electron density, anisotropic and unharmonic thermal motion (Renninger, 1937; Dawson, 1967), the spin-dependent scattering amplitude (de Bergevin & Brunel, 1981) *etc.* Special attention should be paid to the case where the wavelength of the incident radiation is close to the absorption edge of an element contained in a crystal. Then 'forbidden' reflections may occur due to the anisotropy of X-ray susceptibility. The following types of such reflections have been studied: the ATS or Templeton reflections caused by the local anisotropy of the tensor of susceptibility (ATS) (Templeton & Templeton, 1980; Dmitrienko, 1983), magnetic reflections (Gibbs *et al.*, 1988) and reflections due to the simultaneous existence of the magnetic and local crystal anisotropy (Ovchinnikova & Dmitrienko, 1997).

Any spatial modulation changes the crystal symmetry and hence changes the conventional X-ray diffraction pattern (it can even change the extinction rules). For example, additional 'satellites', *i.e.* reflections with non-integer indices, may appear. The following types of modulations have been studied in detail: magnetic, occupational (or substitutional) waves and displacive modulation. The theory of supersymmetry groups was developed for the description of incommensurate structures and composite crystals, which had allowed the extinction rules and intensities both for the integer 'main' reflections and for their satellites to be found (de Wollf, 1974; Janner & Janssen, 1977).

In the present paper, we are only concerned with non-magnetic crystals, so that the latter two types of modulation will be taken into account. We suppose that the X-ray frequency is near an absorption edge, hence the anisotropy of the local susceptibility can be essential when the symmetry of the corresponding atomic position is lower than cubic. A displacive-type modulation or an occupation wave can change the local symmetry of the atomic positions. Hence an additional anisotropy can appear compared with that existing in the fundamental structure. As a result, the anisotropic properties of X-ray resonant scattering can also be modulated. This leads to the question of whether the modulation can lead to the appearance of any additional reflections near the absorption edges compared with conventional X-ray diffraction. This is the main topic considered in the present paper. To resolve this problem, we use the symmetry properties of the susceptibility near the absorption edges. First we consider the changes of the local atomic environments caused by the modulation in a crystal. Then we apply both the three- and four-dimensional approaches to find the main ATS reflections and ATS satellites, which may occur just as a result of anisotropic X-ray scattering. We conclude with estimations of the considered effects and with several realistic examples.

2. Susceptibility of a modulated crystal near the absorption edge

Two types of modulation are widely studied in crystals – displacive and occupational (or substitutional) modula-

tions. Usually the latter is accompanied by the former; however, it is possible to find cases where they exist separately. For example, the polytype SiC can be regarded as a modulated structure with purely occupational modulation, where the displacive modulation can be ignored (Yamamoto, 1981; Yamamoto & Inoue, 1982). Of course, the occupational modulation essentially changes the local environments of the resonant atoms and hence can change the anisotropic properties of resonant scattering. For example, let us suppose that in the fundamental structure the resonant atom is at a position with cubic symmetry. Then its tensor of susceptibility is isotropic. The appearance of vacancies nearby violates the cubic symmetry, and anisotropy of the susceptibility will generally occur. This example can be explained using Fig. 1. It shows the environments of the atoms on the boundary of antiphase domains in Cu–Au alloy (see Yamamoto, 1982a). The occupational modulation may be the important source of anisotropy, which becomes essential near the absorption edge. A special paper will be devoted to its consideration. In the present paper, we neglect the occupational and temperature-factor modulations and consider mainly the atomic displacements. Before a description of a modulated crystal, we briefly discuss the symmetry properties of the susceptibility tensor in crystals.

2.1. Susceptibility of a fundamental structure near the absorption edge

To describe the diffraction of X-rays in crystals, we need the susceptibility tensor $\hat{\chi}(\mathbf{r})$ or its Fourier components $\hat{\chi}(\mathbf{h})$ (see James, 1982; Kolpakov et al., 1978); hereafter, the hat above a letter means a tensor.

Furthermore, we use the Fourier components of $\hat{\chi}(\mathbf{r})$, which can be represented as

$$\hat{\chi}(\mathbf{h}) = \sum_{\mu,s}[f^{\mu}(\mathbf{h})\hat{E} + \hat{\chi}_{\mathrm{res},s}^{\mu}]\exp(i\mathbf{h}\mathbf{r}_s^{\mu}), \qquad (1)$$

where the index μ characterizes the crystallographically unequal atoms, s enumerates crystallographically equivalent resonant atoms, $\hat{E}$ is a unit tensor, $f^{\mu}(\mathbf{h})$ corresponds to the potential (Thomson) scattering of X-rays and $\hat{\chi}_{\mathrm{res},s}^{\mu}$ describes the resonant scattering of X-rays (which is equal to zero for non-resonant atoms). Furthermore, we shall consider only the resonant part of the susceptibility tensor and omit the index 'res'. If the sth resonant atom is at a position with some special symmetry, then

$$\hat{\chi}_s = \hat{R}_l\hat{\chi}_s\hat{R}_l^{-1}, \qquad (2)$$

where R_l is the rotation part of the operator $\hat{g}_l \in G_l$; G_l is the point group of the local crystal position, which corresponds to the symmetry of the atomic configuration around the resonant (or probe) atom.

The properties of $\hat{\chi}_s$ strongly depend on the type of resonant transition in the atom. 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 (Hannon et al., 1988; Blume, 1994). For the dipole transition considered below, $\hat{\chi}_s$ is the second-rank tensor, which can be subdivided into the following parts,

$$\chi_s^{\alpha\beta} = \chi_{s0}\delta^{\alpha\beta} + \chi_{s-}^{\alpha\beta} + \chi_{s+}^{\alpha\beta}, \qquad (3)$$

where $\chi_{s0} = \mathrm{tr}(\hat{\chi}_s)/3$, $\chi_{s-}^{\alpha\beta} = (\chi_s^{\alpha\beta} - \chi_s^{\beta\alpha})/2$, $\chi_{s+}^{\alpha\beta} = (\chi_s^{\alpha\beta} + \chi_s^{\alpha\beta})/2 - \chi_{s0}\delta^{\alpha\beta}$. In (3), χ_0 is the scalar (isotropic) part; it provides nothing new for extinction rules in comparison with the potential scattering of X-rays. The antisymmetric part, $\hat{\chi}_-$, is absent for non-magnetic crystals. The properties of the symmetrical anisotropic part, $\hat{\chi}_+$, were considered by Dmitrienko (1983). There are strong symmetry restrictions on the tensor form of $\hat{\chi}(\mathbf{r})$ and $\hat{\chi}(\mathbf{h})$ in crystals (Dmitrienko, 1983; Belyakov & Dmitrienko, 1989) and quasicrystals (Dmitrienko, 1989). They arise because of the invariance of $\hat{\chi}(\mathbf{r})$ under the space-group transformations, i.e.

$$\hat{\chi}(\mathbf{r}) = \hat{R}_g\hat{\chi}(\mathbf{r}')\hat{R}_g^{-1}, \qquad (4)$$

where $\mathbf{r}' = \hat{R}_g^{-1}(\mathbf{r} - \mathbf{a}_g)$, $\hat{R}_g$ is the matrix of the rotation and $\mathbf{a}_g$ is the translation vector. It was shown that $\hat{\chi}_+$ causes the general-type ATS reflections corresponding to the glide planes and screw axes, but does not violate the general extinctions related to centring of the lattice. Let us now find the restrictions on the susceptibility of modulated crystals.

2.2. Susceptibility of a displacively modulated crystal

According to the well known formulae (de Wolff, 1974; Janner & Janssen, 1977), the atomic positions in the displacive wave are equal to

$$\mathbf{r}_{\mathbf{n}}^{\mu} = \mathbf{r}_{0\mathbf{n}}^{\mu} + \mathbf{u}_{\mathbf{n}}^{\mu}, \qquad (5)$$

where $\mathbf{u}_{\mathbf{n}}^{\mu}$ are the displacements of atoms from their positions in the fundamental (unmodulated) structure,
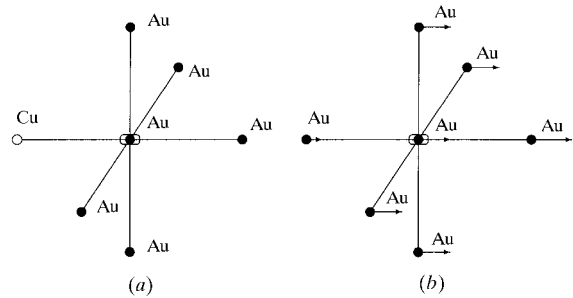

Fig. 1. The change of the octahedral local environment, which causes the appearance of the susceptibility anisotropy: (a) example of the substitutional modulation of the Au atom environment at the boundary of the antiphase domain in CuAu; (b) the displacive modulation, which deforms the cubic environment. The oval in the centre, where the resonant atom is located, characterizes the anisotropy of X-ray scattering near the absorption edge.

$\mathbf{r}_{0\mathbf{n}}^{\mu}$, and the index $\mathbf{n}$ describes the translation under the vector $\mathbf{n} = n\mathbf{a}$, where $\mathbf{a}$ is a lattice period. The displacements $\mathbf{u}_{\mathbf{n}}^{\mu}$ may be written as

$$\mathbf{u}_{\mathbf{n}}^{\mu} = \sum_{\mathbf{q} \in D_d^*} \mathbf{U}^{\mu}(\mathbf{q}) \exp(i\mathbf{q}\mathbf{n}), \qquad (6)$$

where D_d^* is a d-dimensional lattice ($d \leq 3$) and $\mathbf{q}$ is restricted to the first Brillouin zone (Janner & Janssen, 1977). The modulation leads to the appearance of satellites apart from the main reflections; their positions and intensities have been studied in detail.

In the modulated crystal, both the resonant atom and the neighbouring atoms displace from the average positions according to (5). Thus the local symmetry of the atomic positions may be violated by the modulation wave. If the symmetry transformations given by (4) are not true in the modulated crystal, then the anisotropic properties of the susceptibility tensor differ from those in the fundamental structure. For example, if the symmetry of a resonant atom position in the fundamental crystal corresponds to one of the cubic point groups, the susceptibility is isotropic (in this case no forbidden reflections may appear). However, the modulation can violate the cubic symmetry and an anisotropy can occur [see Fig. 1(b)]. Because the atomic displacements (in an incommensurately modulated crystal) also depend on the translation vectors, the susceptibility tensors depend on n as well, i.e. we must write $\hat{\chi}_{ns}$.

Thus, the displacive modulation influences the susceptibility tensor in two ways: (a) it can violate the symmetry of the local environment of a resonant atom and hence provides the additional anisotropy compared with that in the fundamental structure; and (b) it makes the susceptibility spatially modulated, i.e. not invariant under translations contrary to the fundamental structure. Therefore, we can expect that near absorption edges additional ATS main reflections and satellites may appear, which are forbidden in conventional diffraction of X-rays by a modulated crystal.

Different approaches can be used to consider the susceptibility tensor of an incommensurately modulated crystal near the absorption edge. The first one is to calculate the susceptibility tensors using the information on the atomic displacements in several coordination spheres. It is possible that a limited number of spheres should be taken into account, depending on the physical properties of the crystal. For example, in experiments with polarized XANES and EXAFS near the Cu K edge of high-T_c systems, the local cluster within a radius of about 5 Å from the central Cu atom is essential (see Saini et al., 1997). Using the preliminary information, we have to calculate the resonant part of the susceptibility with the help of known theoretical methods (see Carra & Thole, 1994, and references therein).

In the present paper, we will use another approach which is based only on the symmetry consideration. We shall see that it allows the general properties of diffraction patterns near absorption edges to be described. Furthermore, we shall apply the four-dimensional approach to consider the set of possible reflections, which can appear under the resonant conditions among the main reflections and satellites. The main idea is that the tensorial function $\hat{\chi}_{ns}$, which is not invariant under the space-group transformation in three-dimensional space R_3, should be invariant under the transformation in a superspace. Similar considerations were used by Dmitrienko (1989) to study the local anisotropy of icosahedral quasicrystals.

To describe the susceptibility tensor in an incommensurately modulated crystal, we shall use the superspace groups. It was proposed by de Wolff (1974) that the symmetry of the modulated structure can be successfully described with the help of the four-dimensional groups. The conception of superspace groups was successfully developed by de Wolff et al. (1981) for two- and three-dimensional modulations.

Let us introduce the four-dimensional second-rank tensor $\hat{\chi}'(\mathbf{h})$, which is equal to [$\mathbf{h} = (h_1, h_2, h_3, h_4)$]

$$\hat{\chi}'(\mathbf{h}) = \sum_{\mu} a_{\mu} \int_0^1 d\bar{x}_4 \hat{\bar{\chi}}^{\mu}(\mathbf{h}, x_4) P^{\mu}(\bar{x}_4^{\mu}) \exp[-B^{\mu}(\bar{x}_4^{\mu})h^2],$$

$$(7)$$

$$\hat{\bar{\chi}}^{\mu}(\mathbf{h}, x_4^{\mu}) = \sum_{(R_s|\tau)} \hat{\bar{\chi}}_s^{\mu}(\bar{x}_4^{\mu})$$

$$\times \exp\left(2\pi i \sum_j \{h_j[\hat{R}_s x^{\mu}(\bar{x}_4^{\mu})]_j + h_j \tau_j\}\right), \quad (8)$$

where P^{μ} is the occupation probability, B^{μ} is the isotropic temperature factor, $\bar{x}_4^{\mu}$ is the positional vector in the fundamental structure, a_{μ} is a multiplicity factor and $\hat{\bar{\chi}}_s^{\mu}(\bar{x}_4^{\mu})$ are the four-dimensional second-rank tensors corresponding to the different points of the (μ, s)th string in R_4. $\hat{R}$ and τ are the parts of the symmetry operators in R_4; they transform the coordinates as follows:

$$x_i' = (R \mid \tau)x_i = \sum_{j=1}^4 R_{ij}x_j + \tau_i, \qquad (9)$$

where τ_i are the components of the translation vector τ, $i = 1, 2, 3, 4$. The first 3×3 part of $\hat{R}$ is the same as the matrix representation of the rotation operator in R_3, $R_{4i} = R_{i4} = 0$ for $i = 1, 2, 3$ and $R_{44} = \pm 1$ (de Wolff, 1974).

The four-dimensional tensor $\hat{\chi}'(\mathbf{h})$ of the modulated crystal is invariant under the symmetry transformations in R_4; thus we can write

$$\hat{\chi}'(\mathbf{h}') = \hat{R}\hat{\chi}'(\mathbf{h})\hat{R}^{-1} \exp(i\mathbf{h}\tau). \qquad (10)$$

In (7), the four-dimensional susceptibility tensor is denoted as $\hat{\chi}'(\mathbf{h})$ to indicate its difference from $\hat{\chi}(\mathbf{h})$ in

R_3. Using $\hat{\chi}(\mathbf{h})$, we can calculate the scattering amplitude $F(\mathbf{h}) = \mathbf{e}_f^* \hat{\chi}(\mathbf{h})\mathbf{e}_i$, where $\mathbf{e}_f$ and $\mathbf{e}_i$ are the polarization vectors of the incident and scattered radiation. To obtain the susceptibility tensor $\hat{\chi}(\mathbf{h})$ from $\hat{\chi}'(\mathbf{h})$ we must find its projection onto R_3. Note that the symmetry of $\hat{\chi}'(\mathbf{h})$ is not lower than that of $\tilde{\hat{\chi}}(\mathbf{h}, x_4)$. Using (10), we can find the set of possible reflections and those tensor components that differ from zero.

If the resonant atoms occupy special positions in the fundamental structure, then the additional restrictions on the tensor components may appear. In this case the form of the modulation function is constrained owing to the site symmetry (see Yamamoto, 1982*b*). Thus the coordinates of an atom in a special position must satisfy the following equation:

$$x_i^\mu(\bar{x}_4^\mu) = \sum_{j=1}^4 R_{ij} x_j^\mu [R_{44}^{-1}(\bar{x}_4^\mu - \tau_4)] + \tau_i. \quad (11)$$

This restricts the possible values of the atomic displacements. For example, the possible displacements of Fe atoms in wustite were listed by Yamamoto (1982*c*). In §3.2, we discuss how the restrictions on the displacements are connected with the restrictions on the tensor components in R_3.

3. ATS reflections owing to the modulation of the susceptibility tensor

3.1. *The four-dimensional approach*

Let us again suppose the modulation to be one-dimensional. If tensor $\hat{\chi}'(\mathbf{h})$ is invariant under the operations $(R \mid \tau)$ of the four-dimensional space group, the relation (10) determines the restrictions on its possible components and then the forbidden reflections. Consider the possibility of additional reflections in the presence of a glide plane perpendicular to the x axis, with the accompanying translation. In the case of a one-dimensional modulation along the b or c axes, we have $(m_x 1 \mid 0, \tau_2, \tau_3, \tau_4)$; if $\mathbf{q} \parallel \mathbf{a}$ then we have $(m_x - 1 \mid 0, \tau_2, \tau_3, \tau_4)$. This symmetry element connects the resonant atoms with the coordinates (i) x_1, x_2, x_3, x_4 and (ii) $-x_1, x_2 + \tau_2, x_3 + \tau_3, \pm x_4 + \tau_4$. If the wavevector of the modulation is directed along the b or c axes, then the $+$ sign is realised for the fourth coordinate $(R_{44} = 1)$ and the $-$ sign is realised if $\mathbf{q} \parallel \mathbf{a}$ $(R_{44} = -1)$. The extinction rule for $0h_2h_3h_4$ reflections in conventional X-ray diffraction has the form $h_2\tau_2 + h_3\tau_3 + h_4\tau_4 = n + \frac{1}{2}$. For these reflections, the four-dimensional second-rank tensor $\tilde{\hat{\chi}}(\mathbf{h}, x_4)$, defined by (8), has the form, for $R_{44} = 1$ [$\mu = 1$, and it will be omitted; $\mathbf{h} = (h_1h_2h_3h_4)$],

$$\tilde{\hat{\chi}}(0h_2h_3h_4, x_4) = \exp[2\pi i(h_2 x_2 + h_3 x_3 + h_4 x_4)]$$

$$\times \left\{ \begin{pmatrix} \tilde{\chi}_{11} & \tilde{\chi}_{12} & \tilde{\chi}_{13} & \tilde{\chi}_{14} \\ \tilde{\chi}_{12} & \tilde{\chi}_{22} & \tilde{\chi}_{23} & \tilde{\chi}_{24} \\ \tilde{\chi}_{13} & \tilde{\chi}_{23} & \tilde{\chi}_{33} & \tilde{\chi}_{34} \\ \tilde{\chi}_{14} & \tilde{\chi}_{24} & \tilde{\chi}_{34} & \tilde{\chi}_{44} \end{pmatrix} \right.$$

$$+ \exp[2\pi i(h_2\tau_2 + h_3\tau_3 + h_4\tau_4)]$$

$$\times \left. \begin{pmatrix} \tilde{\chi}_{11} & -\tilde{\chi}_{12} & -\tilde{\chi}_{13} & -\tilde{\chi}_{14} \\ -\tilde{\chi}_{12} & \tilde{\chi}_{22} & \tilde{\chi}_{23} & \tilde{\chi}_{23} \\ -\tilde{\chi}_{13} & \tilde{\chi}_{23} & \tilde{\chi}_{33} & \tilde{\chi}_{34} \\ -\tilde{\chi}_{14} & \tilde{\chi}_{24} & \tilde{\chi}_{34} & \tilde{\chi}_{44} \end{pmatrix} \right\}$$

$$= \exp[2\pi i(h_2 x_2 + h_3 x_3 + h_4 x_4)]$$

$$\times \begin{pmatrix} 0 & 2\tilde{\chi}_{12} & 2\tilde{\chi}_{13} & 2\tilde{\chi}_{14} \\ 2\tilde{\chi}_{12} & 0 & 0 & 0 \\ 2\tilde{\chi}_{13} & 0 & 0 & 0 \\ 2\tilde{\chi}_{14} & 0 & 0 & 0 \end{pmatrix}, \quad (12)$$

and, for $R_{44} = -1$,

$$\tilde{\hat{\chi}}(0h_2h_30, x_4) = \exp[2\pi i(h_2 x_2 + h_3 x_3)]$$

$$\times \begin{pmatrix} 0 & 2\tilde{\chi}_{12} & 2\tilde{\chi}_{13} & 0 \\ 2\tilde{\chi}_{12} & 0 & 0 & 2\tilde{\chi}_{24} \\ 2\tilde{\chi}_{13} & 0 & 0 & 2\tilde{\chi}_{34} \\ 0 & 2\tilde{\chi}_{24} & 2\tilde{\chi}_{34} & 0 \end{pmatrix}. \quad (13)$$

Then, using (7), we can calculate $\hat{\chi}'(\mathbf{h})$. We will suppose that the symmetry of $\hat{\chi}'(\mathbf{h})$ coincides with that of $\tilde{\hat{\chi}}(\mathbf{h}, x_4)$ (which means the same positions of the zeroth and non-zeroth tensor components). Perhaps in special cases the integral under $\mathrm{d}\bar{x}_4$ can transform those components of $\tilde{\hat{\chi}}(\mathbf{h}, x_4)$ which differ from zero into the zeroth components of $\hat{\chi}'(\mathbf{h})$. We shall see in the following section that this is not true even in the case of a simple sinusoidal modulation.

To obtain the susceptibility tensor $\hat{\chi}(\mathbf{h})$, we have to find the projection of $\hat{\chi}'(\mathbf{h})$ onto R_3. For this purpose, we shall calculate the convolution of the type

$$\chi_{\alpha\beta} = n_i^\alpha \chi_{ij}' n_j^\beta. \quad (14)$$

Let us mention that in the case of modulation along the c axis the coordinate axes in R_4 are chosen in the following way: $a_1 = \mathbf{a}$, $a_2 = \mathbf{b}$, $a_3 = \mathbf{c} - q\mathbf{d}$, $a_4 = \mathbf{d}$, where $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are the unit vectors of the fundamental structure, and $\mathbf{d}$ is a vector perpendicular to R_3. Then we have $n^1 = (1, 0, 0, 0)$, $n^2 = (0, 1, 0, 0)$, $n^3 = (0, 0, 1, q)$, according to the chosen basic vectors in R_4. The projection onto R_3 of $\hat{\chi}'(\mathbf{h})$ with tensor structure corresponding to (12) gives $(R_{44} = 1)$

$$\hat{\chi}(0h_2h_3h_4) \simeq \begin{pmatrix} 0 & 2\chi'_{12} & 2\chi'_{13}+2q\chi'_{14} \\ 2\chi'_{12} & 0 & 0 \\ 2\chi'_{13}+2q'\chi_{14} & 0 & 0 \end{pmatrix}$$

$$(15)$$

instead of zero in conventional X-ray diffraction. For $\mathbf{q} \parallel \mathbf{a}$, we have $(R_{44} = -1)$

$$\hat{\chi}(0h_2h_30)$$
$$\simeq \begin{pmatrix} 0 & 2\chi'_{12}+2q\chi'_{24} & 2\chi'_{13}+2q\chi'_{34} \\ 2\chi'_{12}+2q\chi'_{24} & 0 & 0 \\ 2\chi'_{13}+2q\chi'_{34} & 0 & 0 \end{pmatrix}.$$

$$(16)$$

We can see that in the last case only the main ATS reflections can appear, but their susceptibility in R_3 depends on the modulation.

These expressions show that the anisotropy of the susceptibility in a modulated crystal can give the ATS reflections in both a system of main reflections and satellites. The intensity and polarization of the ATS reflections corresponding to the similar form of the susceptibility tensor was calculated by Dmitrienko (1983). This is the case when σ-polarization transforms into π-polarization and *vice versa*. Thus we have found the well known polarization properties. However, if we apply the expressions for the intensity of the scattered polarized radiation, given by Dmitrienko (1983), we can see that the functions, which describe the azimuthal dependences, are different for different kinds of modulation.

Note that this approach is based only on the symmetry consideration and does not take into account the nature of the modulation. Hence it is also correct for occupational modulation.

The considered approach allows the possibility of the appearance of forbidden reflections to be shown but does not allow the scattering amplitude to be calculated explicitly. It is a special problem to find the tensorial components $\tilde{\chi}_{j4}$. It would be better to find a model which allows the intensity of the reflections in the presence of modulation to be compared with those for the fundamental structure. Hence we shall apply another approach, using the model of the susceptibility tensor variation in R_3.

3.2. *The model of harmonic displacive modulation*

The expression for calculating the scattering amplitude for a modulated crystal has been given by de Wolff (1974) and Yamamoto (1982b). A similar expression can be written for the susceptibility tensor in R_3. It is the projection of (7) onto R_3,

$$\hat{\chi}(h_1h_2h_3h_4) = \sum_\mu \sum_{(R_s|\tau)} a_\mu \int_0^1 d\bar{x}_4^\mu [f^\mu(\mathbf{h})\hat{E} + \hat{\chi}_s^\mu(\bar{x}_4^\mu)]$$
$$\times P^\mu(\bar{x}_4^\mu) \exp\left(- B^\mu(\bar{x}_4^\mu)h^2 \right.$$
$$\left. + 2\pi i \sum_j \{h_j[R_s x^\mu(\bar{x}_4^\mu)]_j + h_j\tau_j\}\right). \quad (17)$$

The notations coincide with those used by Yamamoto (1982b). Here we include the potential scattering, described by the scattering amplitude $f^\mu(\mathbf{h})$. The difference between (17) and the expression given by Yamamoto (1982b) is that the scalar scattering amplitude, f^μ, depends only on the chemical type of the atoms (index μ), but the susceptibility tensor in a modulated crystal depends on μ, on the position of the resonant atom in a unit cell (*i.e.* on the rotational part R_s of the symmetry operator) and on the position in the displacive wave (coordinate $\bar{x}_4$). Note that in the presence of occupational modulation the product $f^\mu P^\mu(\bar{x}_4)$ may be represented as the modulated scattering amplitude. However, the modulated susceptibility occurs even in the case of the purely displacive modulation and it possesses essentially anisotropic tensor properties.

To calculate the susceptibility using this expression, we need a model for the displacements and a model for the change of the susceptibility under modulation. Let us suppose that the susceptibility tensor in the presence of small incommensurate modulation can be represented as

$$\hat{\chi}_s(\bar{x}_4^\mu) = \hat{\chi}_s^{0\mu} + \Delta\hat{\chi}_s^\mu(\bar{x}_4^\mu), \quad (18)$$

where $\hat{\chi}_s^{0\mu}$ is the susceptibility tensor corresponding to the sth resonant atom in a unit cell of the fundamental structure, and $\Delta\hat{\chi}_s(\bar{x}_4^\mu)$ is the correction which occurs due to the modulation. The most clear example is the case when the resonant atom is located in the point with cubic symmetry. Then $\hat{\chi}^0 \simeq \delta_{ij}$, but the one-dimensional modulation produces $\Delta\hat{\chi}(x_4) \neq k\delta_{ij}$ [see Fig. 1(b)]. Both $\Delta\hat{\chi}_s^\mu$ and $\hat{\chi}_s^\mu$ are spatially modulated and depend on $\bar{x}_4$. See the illustration of this statement in Fig. 2.

If the resonant atom occupies the general position in the fundamental structure, then all components of both tensors differ from zero. In the case of the special
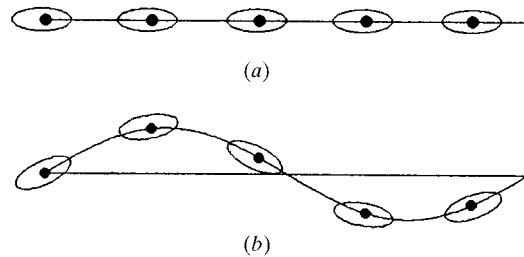

(a)

(b)

Fig. 2. Illustration of the susceptibility tensor modulation: (*a*) in the one-dimensional fundamental structure, (*b*) in the displacive wave.

position of resonant atoms, $\Delta\hat{\chi}_s^\mu(\bar{x}_4^\mu)$ may contain additional non-zero components compared with $\hat{\chi}_s^{0\mu}$. Let us consider an example. If the resonant atom lies on the mirror plane m_y in R_3, then $\hat{\chi}_s^{0\mu}$ has the form

$$\hat{\chi}_s^{0\mu} = \begin{pmatrix} \chi_{11}^{0\mu} & 0 & \chi_{13}^{0\mu} \\ 0 & \chi_{22}^{0\mu} & 0 \\ \chi_{13}^{0\mu} & 0 & \chi_{33}^{0\mu} \end{pmatrix}. \qquad (19)$$

If the superspace group contains $(m_y1 \mid 0000)$, it does not change the local symmetry in R_3. From (11), we have $u_1(\bar{x}_4^\mu) = u_1(\bar{x}_4^\mu)$, $u_2(\bar{x}_4^\mu) = -u_2(\bar{x}_4^\mu)$, $u_3(\bar{x}_4^\mu) = u_3(\bar{x}_4^\mu)$. Then $u_2 = 0$ and the mirror plane in R_3 still remains. If we have $(m_y1 \mid 000\frac{1}{2})$, then $u_1(\bar{x}_4^\mu) = u_1(\bar{x}_4^\mu + \frac{1}{2})$, $u_2(\bar{x}_4^\mu) = -u_2(\bar{x}_4^\mu + \frac{1}{2})$, $u_3(\bar{\bar{x}}_4^\mu) = u_3(\bar{x}_4^\mu + \frac{1}{2})$. u_2 can differ from zero, and then the symmetry group of the local position in R_3 is $G_l = 1$ instead of m_y for the fundamental structure. Then all components of the tensor $\Delta\hat{\chi}_s(\bar{x}_4^\mu)$ can differ from zero.

To calculate the integral in (17), we must consider the law of $\hat{\chi}_s^\mu(\bar{x}_4^\mu)$ variation. For simplicity, we shall consider the models of the displacive modulation and the susceptibility modulation to be harmonic. First, let us suggest the simplest sinusoidal law of modulation, $\mathbf{u}_s(\bar{x}_4^\mu) = U_0\sin(2\pi\bar{x}_4^\mu - \alpha_s^\mu)$, and the following form of $\hat{\chi}_s^\mu(\bar{x}_4^\mu)$,

$$\hat{\chi}_s(\bar{x}_4^\mu) = \hat{\chi}_s^{0\mu} + \Delta\hat{\chi}_s^{1\mu}\sin(2\pi\bar{x}_4^\mu - \alpha_s^\mu), \qquad (20)$$

where the elements of $\Delta\hat{\chi}_s^{1\mu}$ are proportional to U_0^μ.

Note that the susceptibility near the absorption edge is similar to the nuclear resonant susceptibility in Mössbauer diffraction in the presence of a quadrupole hyperfine interaction. The form of the susceptibility tensor is similar to the electrical field gradient (EFG) on nuclei. Using the simplest point charge theory for the EFG calculation, we can show that the above law of the tensor modulation can be realised for several cases (Ovchinnikova, 1997). For example, such a case is observed when the EFGs on the resonant nuclei are created by the neighbouring non-resonant atoms, which are not moved from their positions in the fundamental structure, but the resonant nuclei are displaced by the sinusoidal wave. A similar law of EFG modulation was experimentally observed with the help of NMR for the crystal Rb_2ZnCl_4, where Rb nuclei are located in the positions with m symmetry of a space group $Pnma$ (Aleksandrova et al., 1983). It was shown that those tensor components of $\Delta\chi^1$, which correspond to zero components of $\hat{\chi}^0$, differ from zero and depend on U_0, but the others depend on U_0^2.

Using this approach for the susceptibility variation, we obtain (neglecting the occupation modulation and temperature factor)

$$\begin{aligned} \hat{\chi}(h_1h_2h_3h_4) \simeq &\sum_\mu\sum_s \exp[2\pi i(h_1x_{1s}^\mu + h_2x_{2s}^\mu + h_3x_{3s}^\mu) \\ &+ ih_4(\alpha_s^\mu + \pi)] \\ &\times ([f^\mu(\mathbf{h})\hat{E} + \hat{\chi}_s^{0\mu}]J_m[2\pi(h_3 + h_4q)U_0^\mu] \\ &+ (i/2)\Delta\hat{\chi}_s^{1\mu}\{J_{m+1}[2\pi(h_3 + h_4q)U_0^\mu] \\ &- J_{m-1}[2\pi(h_3 + h_4q)U_0^\mu]\}). \end{aligned} \qquad (21)$$

For the main reflections, we obtain

$$\begin{aligned} \hat{\chi}(h_1h_2h_30) \simeq &\sum_\mu\sum_s \exp[2\pi i(h_1x_{1s}^\mu + h_2x_{2s}^\mu + h_3x_{3s}^\mu)] \\ &\times \{[f^\mu(\mathbf{h})\hat{E} + \chi_s^{0\mu}]J_0(2\pi h_3U_0^\mu) \\ &+ (i/2)\Delta\hat{\chi}_s^{1\mu}[J_1(2\pi h_3U_0^\mu) \\ &- J_{-1}(2\pi h_3U_0^\mu)]\}. \end{aligned} \qquad (22)$$

We can see that the correction to the susceptibility in the main reflections, which occur owing to the modulation, is proportional to the square of the modulation amplitude. For the first-order satellites, we have (neglecting U_0^3)

$$\begin{aligned} \hat{\chi}(h_1h_2h_31) \simeq &\sum_\mu\sum_s \exp[2\pi i(h_1x_{1s}^\mu + h_2x_{2s}^\mu + h_3x_{3s}^\mu) \\ &+ i(\alpha_s^\mu + \pi)]\{[f^\mu(\mathbf{h})\hat{E} + \hat{\chi}_s^{0\mu}] \\ &\times J_1[2\pi(h_3 + q)U_0^\mu] \\ &- (i/2)\Delta\hat{\chi}_s^{1\mu}J_0[2\pi(h_3 + q)U_0^\mu]\}. \end{aligned} \qquad (23)$$

Taking into account that $J_1 \simeq U_0^\mu$ and $\Delta\hat{\chi}^1J_0 \simeq U_0^\mu$, we find that the susceptibility is proportional to the amplitude of modulation. The considered case is similar to those known for conventional X-ray diffraction by the solid solutions with the modulation of concentration together with lattice parameter (Iveronova & Revkevitch, 1978). It is essential that the polarization of the resonant scattering corresponding to the main reflections and to the satellites may differ from each other. If both the potential and anisotropic scattering take place, we must take into account the interference effects.

Let us use these expressions to calculate the susceptibility of a modulated crystal with the sinusoidal modulation law, which contains two resonant atoms in a unit cell of the fundamental structure ($\mu = 1$ is omitted further, $s = 2$). If the superspace group contains the glide plane $(m_x1 \mid 0\frac{1}{2}0\beta)$, then the amplitudes of the displacements in two strings coincide, but their wave phases differ from each other: $\alpha_1 - \alpha_2 = \beta$. We find that in conventional X-ray diffraction the reflections $0kl0$ are absent for $k = 2n + 1$. For the main reflections near the absorption edge, we have (neglecting all the values proportional to the square of U_0 and higher), for $k = 2n + 1$ (hereafter the exponential multipliers are omitted),

$$\hat{\chi}(0h_2h_30) \simeq J_0(2\pi h_3 U_0)(\hat{\chi}_1^0 - \hat{\chi}_2^0)$$

$$= J_0(2\pi h_3 U_0)\begin{pmatrix} 0 & 2\chi_{12}^0 & 2\chi_{13}^0 \\ 2\chi_{12}^0 & 0 & 0 \\ 2\chi_{13}^0 & 0 & 0 \end{pmatrix}, \quad (24)$$

i.e. their susceptibility slightly differs from those of ATS reflections corresponding to the fundamental structure. For the first-order satellite, we have

$$\hat{\chi}(0h_2h_31) \simeq \exp[2\pi i(h_2x_2 + h_3x_3) + i(\alpha + \pi)]$$
$$\times \left[\left(f(\mathbf{h})\hat{E}\{1 + \exp[2\pi i(h_2/2 + \beta)]\} + \chi_1^0 \right. \right.$$
$$+ \chi_2^0 \exp[2\pi i(h_2/2 + \beta)])J_1[2\pi(h_3 + q)U_0]$$
$$- i/2\{\Delta\hat{\chi}_1^1 + \Delta\hat{\chi}_2^1 \exp[2\pi i(h_2/2 + \beta)]\}$$
$$\left. \times J_0[2\pi(h_3 + q)U_0] \right]. \quad (25)$$

The variants $\beta = 0$, $h_2 = 2n + 1$ and $\beta = 1/2$, $h_2 = 2n$ give the absence of the first-order satellites in conventional X-ray diffraction, but near the absorption edge the ATS satellite can be observed, where the susceptibility tensor is proportional to

$$\hat{\chi}(0kl1) \simeq (\hat{\chi}_1^0 - \hat{\chi}_2^0)J_1[2\pi(h_3 + q)U_0]$$
$$- (i/2)(\Delta\hat{\chi}_1^1 - \Delta\hat{\chi}_2^1)J_0[2\pi(h_3 + q)U_0]. \quad (26)$$

It was shown by Dmitrienko (1983) that the similar structure of the susceptibility tensor produces the ATS reflections with the scattering of σ-polarization into π-polarization and *vice versa*. The azimuthal dependence of their intensity is determined by the values of the non-zero tensor components. Hence the different kinds of azimuthal dependences will correspond to the main reflection (24) and first-order satellite (26). Their comparison in principle allows the correction of the susceptibility which appears due to modulation to be studied.

As discussed above in the case of special resonant atom positions, the tensors $\hat{\chi}^0$ and $\Delta\hat{\chi}^1$ may contain different elements. For example, if in the above example the resonant atoms are on the mirror plane $(m_y1 \mid 000\frac{1}{2})$, then

$$(\hat{\chi}_1^0 - \hat{\chi}_2^0) \simeq \begin{pmatrix} 0 & 0 & 2\chi_{13}^0 \\ 0 & 0 & 0 \\ 2\chi_{13}^0 & 0 & 0 \end{pmatrix}, \quad (27)$$

instead of a tensor similar to that obtained in (24). However, the difference $(\Delta\hat{\chi}_1^1 - \Delta\hat{\chi}_2^2)$ may contain the elements $\Delta\chi_{12}^1$ and $\Delta\chi_{21}^1$.

For the non-forbidden reflections, we have

$$\hat{\chi}(0kl1)$$
$$\simeq \begin{pmatrix} 2\chi_{11}^0 + f & 0 & 0 \\ 0 & 2\chi_{22}^0 + f & 2\chi_{23}^0 \\ 0 & 2\chi_{23}0 & 2\chi_{33}^0 + f \end{pmatrix} J_1[2\pi(l + q)U_0]$$
$$- \frac{i}{2}\begin{pmatrix} 2\Delta\chi_{11}^1 & 0 & 0 \\ 0 & 2\Delta\chi_{22}^1 & 2\Delta\chi_{23}^1 \\ 0 & 2\Delta\chi_{23}^1 & 2\Delta\chi_{33}^1 \end{pmatrix} J_0[2\pi(l + q)U_0],$$
$$\quad (28)$$

i.e. such reflections will possess completely different polarization and azimuthal properties.

If the transition with higher orders (quadrupole and higher) is taken into account, we should consider the tensor of fourth and higher orders. In this case, we can expect the appearance of additional reflections compared with the case of the dipole transition, which occur due to the high-rank anisotropy in a modulated crystal.

3.3. ATS reflections in pyrrhotite

As an example let us consider the diffraction near the K edge of iron in the modulated structure of pyrrhotite. Comprehensive studies of the modulation in pyrrhotite have been discussed by many authors (Bertaut, 1953; Tokonami *et al.*, 1972; Nakazawa & Morimoto, 1971; Koto & Kitamura, 1981; Yamamoto & Nakazawa, 1982). The fundamental structure of pyrrhotite is described by the space group *Ccmm*, where the Fe atoms occupy the position 4(*a*) with symmetry $2_y/m_y$ and the S atoms are in position 4(*c*) with symmetry m_ym_z.

Pyrrhotites are magnetic materials; their magnetic phases have been studied by Schwarz & Vaughan (1972). Both the incommensurate and magnetic structures of pyrrhotites depend on the composition and on the temperature. The phase diagram and magnetic phase diagram have been described by Nakazawa & Morimoto (1971) and Schwarz & Vaughan (1972). To avoid the problems connected with the magnetism, we will separate this part of the susceptibility, which is connected only with local anisotropy. The susceptibility of a magnetic crystal with local crystal anisotropy can be represented as

$$\hat{\chi}(\mathbf{h}) = \hat{\chi}_l^+(\mathbf{h}) + \hat{\chi}_m^+(\mathbf{h}) + \hat{\chi}_m^-(\mathbf{h}) + \hat{\chi}_c^+(\mathbf{h}) + \hat{\chi}_c^-(\mathbf{h}), \quad (29)$$

where $\hat{\chi}_l^+(\mathbf{h})$ is the part corresponding only to the local anisotropy, $\hat{\chi}_m^\pm(\mathbf{h})$ are the symmetric and antisymmetric parts, corresponding to the magnetic structure, and $\hat{\chi}_c^\pm(\mathbf{h})$ are the parts responsible for the combined effects (see Ovchinnikova & Dmitrienko, 1997). In the special case, an expression for the combined part was proposed by Blume (1994). Above we have considered the ATS reflections, corresponding only to $\hat{\chi}_l^+(\mathbf{h})$. Let us use these results for pyrrhotite, neglecting all other parts of the susceptibility. We should like to study the appearance of

the forbidden reflections only, hence we restrict our consideration to $\hat{\chi}_l^+(\mathbf{h})$. If the other parts of the susceptibility are taken into account, they can add something new and change the polarization properties of the scattering, but the ATS reflections still remain.

Hence we suppose that the susceptibility tensors $\hat{\chi}_s$ near the iron K edge in the fundamental structure for the atoms with coordinates $\mathbf{r}_1 = (000)$, $\mathbf{r}_2 = (\frac{1}{2}\frac{1}{2}0)$, $\mathbf{r}_3 = (00\frac{1}{2})$, $\mathbf{r}_4 = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ are equal to

$$\hat{\chi}_1^0 = \hat{\chi}_2^0 = \begin{pmatrix} \chi_{11}^0 & 0 & \chi_{13}^0 \\ 0 & \chi_{22}^0 & 0 \\ \chi_{13}^0 & 0 & \chi_{33}^0 \end{pmatrix}, \qquad (30)$$

$$\hat{\chi}_3^0 = \hat{\chi}_4^0 = \begin{pmatrix} \chi_{11}^0 & 0 & -\chi_{13}^0 \\ 0 & \chi_{22}^0 & 0 \\ -\chi_{13}^0 & 0 & \chi_{33}^0 \end{pmatrix}. \qquad (31)$$

For all S atoms, we have

$$\hat{\chi}_s^0 = \begin{pmatrix} \chi_{11}^0 & 0 & 0 \\ 0 & \chi_{22}^0 & 0 \\ 0 & 0 & \chi_{33}^0 \end{pmatrix}. \qquad (32)$$

The conventional X-ray diffraction pattern corresponding to the fundamental structure contains the extinctions, listed by Hahn (1987). The anisotropy of the scattering violates the extinction rules and the ATS reflection can appear near the absorption K edge of iron. The following tensor describes the ATS reflection $00l$ ($l = 2n + 1$) for the fundamental structure,

$$\hat{\chi}^0(hkl) = [1 + (-1)^{h+k}]\begin{pmatrix} 0 & 0 & 2\chi_{13}^0 \\ 0 & 0 & 0 \\ 2\chi_{13}^0 & 0 & 0 \end{pmatrix}. \qquad (33)$$

However, no ATS reflections occur near the absorption edge of S.

The modulation in pyrrhotite-5.5C was studied by Yamamoto & Nakazawa (1982) using the four-dimensional approach. It includes both occupational and displacive modulation. The interatomic distances between the atoms (Fe—Fe, Fe—S and S—S) were determined and represented as functions of the parameter $t = \bar{x}_4 - q\bar{x}_3$. It was shown that the four-dimensional symmetry group is generated by the following elements: $(E1 \mid 0, 0, 0, 0)$, $(m_x1 \mid \frac{1}{4}, \frac{1}{4}, \frac{1}{2}, \frac{1}{4})$, $(m_y1 \mid \frac{1}{4}, \frac{1}{4}, 0, \frac{1}{4})$, $(2_z1 \mid 0, 0, \frac{1}{2}, 0)$. The following extinction rules correspond to these symmetry elements: $h_1h_2h_3h_4$ ($h_1 + h_2 = 2n$, $h_2 + h_4 = 2n$, $h_1 + h_4 = 2n$); $0h_2h_3h_4$ ($h_2 + 2h_3 + h_4 = 4n$); $h_10h_3h_4$ ($h_1 + h_4 = 4n$); $00h_3h_4$ ($h_3 = 2n$).

To consider the diffraction pattern near the K edge of iron, we will use the four-dimensional symmetry approach suggested in §3.1, which does not depend on the type of modulation. As far as the distances between the atoms vary under t, the components of the susceptibility tensors depend on x_4. To obtain the susceptibility tensor in R_3, we shall calculate $\hat{\chi}'(\mathbf{h})$, but first we calculate $\hat{\tilde{\chi}}(\mathbf{h})$. For pyrrhotite, it can be represented as

$$\hat{\tilde{\chi}}(h_1h_2h_3h_4, x_4)$$

$$= \left\{ \begin{pmatrix} \tilde{\chi}_{11} & \tilde{\chi}_{12} & \tilde{\chi}_{13} & \tilde{\chi}_{14} \\ \tilde{\chi}_{12} & \tilde{\chi}_{22} & \tilde{\chi}_{23} & \tilde{\chi}_{23} \\ \tilde{\chi}_{13} & \tilde{\chi}_{23} & \tilde{\chi}_{33} & \tilde{\chi}_{34} \\ \tilde{\chi}_{14} & \tilde{\chi}_{24} & \tilde{\chi}_{34} & \tilde{\chi}_{44} \end{pmatrix} \exp[2\pi i(h_1x_1 + h_2x_2)] \right.$$

$$+ \begin{pmatrix} \tilde{\chi}_{11} & -\tilde{\chi}_{12} & -\tilde{\chi}_{13} & -\tilde{\chi}_{14} \\ -\tilde{\chi}_{12} & \tilde{\chi}_{22} & \tilde{\chi}_{23} & \tilde{\chi}_{23} \\ -\tilde{\chi}_{13} & \tilde{\chi}_{23} & \tilde{\chi}_{33} & \tilde{\chi}_{34} \\ -\tilde{\chi}_{14} & \tilde{\chi}_{24} & \tilde{\chi}_{34} & \tilde{\chi}_{44} \end{pmatrix}$$

$$\times \exp\{2\pi i[-h_1x_1 + h_2x_2 + (h_1 + h_2 + 2h_3 + h_4)/4]\}$$

$$+ \begin{pmatrix} \tilde{\chi}_{11} & -\tilde{\chi}_{12} & \tilde{\chi}_{13} & \tilde{\chi}_{14} \\ -\tilde{\chi}_{12} & \tilde{\chi}_{22} & -\tilde{\chi}_{23} & -\tilde{\chi}_{23} \\ \tilde{\chi}_{13} & -\tilde{\chi}_{23} & \tilde{\chi}_{33} & \tilde{\chi}_{34} \\ \tilde{\chi}_{14} & -\tilde{\chi}_{24} & \tilde{\chi}_{34} & \tilde{\chi}_{44} \end{pmatrix}$$

$$\times \exp\{2\pi i[h_1x_1 - h_2x_2 + (h_1 + h_2 + h_4)/4]\}$$

$$+ \begin{pmatrix} \tilde{\chi}_{11} & \tilde{\chi}_{12} & -\tilde{\chi}_{13} & -\tilde{\chi}_{14} \\ \tilde{\chi}_{12} & \tilde{\chi}_{22} & -\tilde{\chi}_{23} & -\tilde{\chi}_{23} \\ -\tilde{\chi}_{13} & -\tilde{\chi}_{23} & \tilde{\chi}_{33} & \tilde{\chi}_{34} \\ -\tilde{\chi}_{14} & -\tilde{\chi}_{24} & \tilde{\chi}_{34} & \tilde{\chi}_{44} \end{pmatrix}$$

$$\left. \times \exp[2\pi i(-h_1x_1 - h_2x_2 + l/2)] \right\}$$

$$\times [1 + (-1)^h + k][1 + (-1)^h + m]$$

$$\times \exp[2\pi i(h_3x_3 + h_4x_4)]. \qquad (34)$$

We can see that the extinctions of the general reflections corresponding to the centring translations still remain, *i.e.* near the absorption edge no additional reflections corresponding to the centring translations will occur compared with conventional diffraction.

Let us consider the reflections $00h_3h_4$, corresponding to the screw axis. Using (34), we shall obtain the form of the four-dimensional tensor, corresponding to the reflection with $00h_3h_4$ ($h_3 = 2n + 1$, $h_4 \neq 4n + 2$),

$$\hat{\tilde{\chi}}(00h_3h_4, x_4) \simeq \begin{pmatrix} 0 & 0 & 2\tilde{\chi}_{13} & 2\tilde{\chi}_{14} \\ 0 & 0 & 2\tilde{\chi}_{23} & 2\tilde{\chi}_{24} \\ 2\tilde{\chi}_{13} & 2\tilde{\chi}_{23} & 0 & 0 \\ 2\tilde{\chi}_{14} & 2\tilde{\chi}_{24} & 0 & 0 \end{pmatrix}. \qquad (35)$$

The projection onto R_3 of $\hat{\chi}'(\mathbf{h})$ corresponding to (35) gives the following form of $\hat{\chi}(00h_3h_4)$,

$\hat{\chi}(00h_3h_4)$

$$\simeq \begin{pmatrix} 0 & 0 & 2\chi'_{13} + 2\chi'_{14}q \\ 0 & 0 & 2\chi'_{23} + 2\chi'_{24}q \\ 2\chi'_{13} + 2\chi'_{14}q & 2\chi'_{23} + 2\chi'_{24}q & 0 \end{pmatrix}.$$

(36)

This shows that the ATS main reflections and $00h_3h_4$-type ($h_3 = 2n + 1$, $h_4 \neq 4n + 2$) satellites can appear near the absorption edge. They are absent in conventional diffraction patterns of pyrrhotite. The susceptibility tensor and hence the intensity and polarization properties of the reflections will depend on the tensorial components in four-dimensional space, *i.e.* on the type of modulation.

Let us consider the extinction rule corresponding to the glide plane $(m_x 1 \mid \frac{1}{4}, \frac{1}{4}, \frac{1}{2}, \frac{1}{4})$. For the reflection with $0h_2h_3h_4$ ($h_2 + 2h_3 + h_4 \neq 4n$), we have

$$\hat{\tilde{\chi}}(0h_2h_3h_4, x_4) \simeq \begin{pmatrix} 0 & 2\tilde{\chi}_{12} & 2\tilde{\chi}_{13} & 2\tilde{\chi}_{14} \\ 2\tilde{\chi}_{12} & 0 & 0 & 0 \\ 2\tilde{\chi}_{13} & 0 & 0 & 0 \\ 2\tilde{\chi}_{14} & 0 & 0 & 0 \end{pmatrix}.$$

(37)

We can see that this tensor differs from zero, and thus the ATS reflections can appear. The projection of (37) onto R_3 is equal to

$$\hat{\chi}(0h_2h_3h_4) \simeq \begin{pmatrix} 0 & 2\chi'_{12} & 2\chi'_{13} + 2\chi'_{14}q \\ 2\chi'_{12} & 0 & 0 \\ 2\chi'_{13} + 2\chi'_{14}q & 0 & 0 \end{pmatrix}.$$

(38)

Similarly, we can find that for the $h_1 0h_3h_4$ ($h_1 + h_4 = 4n + 2$) reflections the susceptibility can differ from zero,

$$\hat{\tilde{\chi}}(h_1 0h_3h_4) \simeq \begin{pmatrix} 0 & 2\tilde{\chi}_{12} & 0 & 0 \\ 2\tilde{\chi}_{12} & 0 & 2\tilde{\chi}_{23} & 2\tilde{\chi}_{24} \\ 0 & 2\tilde{\chi}_{23} & 0 & 0 \\ 0 & 2\tilde{\chi}_{24} & 0 & 0 \end{pmatrix}.$$

(39)

The projection onto R_3 is equal to

$$\hat{\chi}(0h_2h_3h_4) \simeq \begin{pmatrix} 0 & 2\chi'_{12} & 0 \\ 2\chi'_{12} & 0 & 2\chi'_{23} + 2\chi'_{14}q \\ 0 & 2\chi'_{23} + 2\chi'_{14}q & 0 \end{pmatrix}.$$

(40)

These calculations show the possibility of the ATS reflections corresponding to glide planes and screw axes, which can appear near the K edge of iron in pyrrhotite in the main reflections and satellite systems.

4. Conclusions

If the wavelength of the incident X-radiation is close to the absorption edge of one of the chemical elements in an incommensurate crystal, ATS reflections may appear owing to the anisotropic properties of the susceptibility tensor. These properties are caused by the local symmetry of the resonant atom positions in a crystal as well as by the type of resonant transition. In the fundamental structure, the ATS reflections can appear in those points of the reciprocal space where the extinctions, induced by glide planes and/or screw axes, exist in conventional X-ray diffraction. The displacive modulation changes the local crystal anisotropy and also modulates the susceptibility tensor. As a result, the following effects have been found in the present paper:

(i) the ATS reflections can appear both in the systems of main reflections and satellites;

(ii) the ATS reflections can correspond to glide planes and screw axes in four-dimensional space;

(iii) the ATS reflections can appear even in those cases when the resonant atoms in the fundamental structure are located in a position with cubic local symmetry;

(iv) all the ATS reflections, both the main and the satellites, possess the complex azimuthal and polarization properties;

(v) the properties of main ATS reflections and ATS satellites can differ from each other. They depend on the modulation type in a crystal. Therefore a comparison of the azimuthal dependences of the main reflections and satellites would allow the correction to the susceptibility to be calculated, which appears due to the modulation.

The anisotropy of the susceptibility near the absorption edge depends essentially on the electronic wave functions in the ground and excited states. The calculation of the correction to $\hat{\chi}(\mathbf{h})$ in a modulated crystal would allow the change of the valence electron wave functions under modulation to be studied. Hence the resonant diffraction near absorption edges provides the possibility of studying the modulated local environments of the resonant atoms and the chemical bonds in incommensurate crystals. The ATS reflections, first observed by Templeton & Templeton (1985), have since been found in many crystals (Kirfel & Petcov, 1991; Nagano *et al.*, 1996) and we can expect that they will be successfully observed in incommensurate structures.

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