

Point-defect-induced forbidden reflections in resonant X-ray scattering†

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Point defects in crystals cause displacements of neighbouring atoms and hence become the source of an additional anisotropy of the X-ray resonant scattering amplitude. This anisotropy can induce ‘forbidden’ Bragg reflections near absorption edges, called point-defect-induced (PDI) reflections, which are absent in non-resonant X-ray scattering and in resonant X-ray scattering by perfect crystals. The deformation of external electron shells is the physical reason for this phenomenon. Some examples of crystals are considered in which the PDI reflections could be observed.

Keywords: resonant X-ray diffraction; forbidden reflections; point defects.

1. Introduction

In resonant X-ray diffraction, forbidden Bragg reflections can occur near absorption edges owing to the anisotropy of X-ray susceptibility, induced by an asymmetric environment of resonant atoms (Templeton & Templeton, 1980; Dmitrienko, 1983, 1984). The asymmetric environment disturbs the valence electronic shells of atoms and causes the mentioned anisotropy. The asymmetry of a local atomic position can be an intrinsic property of a crystal, or it can be induced by different factors like magnetic interactions, thermal vibrations, point defects *etc.* Thus the forbidden reflections provide a tool for studying distortions in electronic states induced by different anisotropic factors.

The physical reason behind the forbidden reflections is that just near absorption edges the atomic scattering factor becomes a tensor f_{ij} , depending on the symmetry of the resonant atom site (Dmitrienko, 1983; Blume, 1994). Under non-resonant conditions, at X-ray wavelengths far from absorption edges, these reflections are strictly forbidden by the extinction rules corresponding to screw axes and glide planes (Hahn, 1996). Therefore synchrotron radiation is needed to observe them. The dipole transition E1 usually provides the main contribution to the resonant scattering [see the review by Hodeau *et al.* (2001)]. Sometimes, however, the dipole resonant transition does not violate the extinction rules. Then, forbidden reflections can appear owing to the dipole–quadrupole (Templeton & Templeton, 1994), quadrupole (Finkelstein *et al.*, 1992) transitions, thermal vibrations, point defects (Dmitrienko, Ovchinnikova & Ishida, 1999; Dmitrienko & Ovchinnikova, 2000) or by local chirality of atomic positions (Dmitrienko & Ovchinnikova, 2001).

Up to now, forbidden Bragg reflections, caused exclusively by the natural asymmetry of local atomic positions, have been studied in many crystals (see, for example, Templeton & Templeton, 1985; Finkelstein *et al.*, 1992; Templeton, 1994; Kirfel *et al.*, 1995; Nagano *et al.*, 1996; Kokubun *et al.*, 1998; Hagiwara *et al.*, 1999; Garcia *et al.*, 2000; Collins *et al.*, 2001).

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A survey of earlier works on the subject was given by Belyakov & Dmitrienko (1989). Magnetic reflections were also justified theoretically and observed experimentally (Blume, 1985; Hannon *et al.*, 1988; Gibbs *et al.*, 1985). Recently, forbidden reflections that appear due to thermal vibrations were observed in a wide temperature interval (Kokubun *et al.*, 2001; Kirfel *et al.*, 2002)

In the present paper we consider some details concerning point-defect-induced (PDI) reflections, which are absent in perfect crystals, and describe new structures suitable for experimental observation.

2. Resonant X-ray scattering by crystals with point defects

The influence of point defects on the X-ray diffraction pattern far from absorption edges was studied in detail a long time ago (Krivoglaz, 1983). Those defects, together with accompanying atomic displacements, cause the appearance of diffuse scattering and influence the position and intensity of the structural peaks.

Below we consider a special case of point defects: namely the impurities, which substitute the host atoms without violation of the local point symmetry. We also suppose that the concentration of defects is small, so that they do not influence each other. According to our evaluations (Dmitrienko & Ovchinnikova, 2000), minimal concentrations of the impurities necessary to provide sufficient intensities of the forbidden reflections should be about 0.01–0.001, depending on the atomic number considered.

The atomic displacements caused by defects violate the local symmetry of each neighbouring atom (Fig. 1). We see that if the defect appears in the closest neighbourhood of the *s*th resonant scattering atom it changes its local symmetry and influences the atomic factor f_{ij}^s (*s* enumerates atoms inside one crystallographic position). The resonant structure amplitude corresponding to the diffraction vector **H** is equal to

$$F_{ij}(\mathbf{H}) = \sum_s f_{ij}^s \exp(i\mathbf{H}\mathbf{r}^s). \quad (1)$$

In the absence of the defects, f_{ij}^s is invariant under the \hat{q}^l transformations, where \hat{q}^l is an element of the point group G^s describing the symmetry of the *s*th atomic site, $\hat{q}^l \mathbf{R}^{sl} = \mathbf{R}^{sl}$, $\mathbf{R}^{sl} = \mathbf{r}^l - \mathbf{r}^s$, $l = 1 \dots N$, enumerates atoms around the considered one. Hence we write $f_{ij}^s = \hat{q}^l f_{ij}^s (\hat{q}^l)^{-1}$.

In the presence of the defect we have $\mathbf{r}^{l\mu} = \mathbf{r}^l + \mathbf{u}^{l\mu}$, $\mathbf{r}^{s\mu} = \mathbf{r}^s + \mathbf{u}^{s\mu}$, $\mathbf{R}^{sl\mu} = \mathbf{R}^{sl} + \mathbf{u}^{l\mu} - \mathbf{u}^{s\mu}$, where $\mathbf{u}^{l\mu}$ is the displacement of the *l*th atom

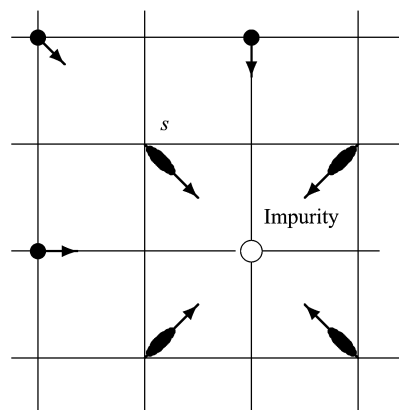


Figure 1 Displacements (arrows) and the atomic factor anisotropy (ellipses) of resonant atoms in the presence of a non-resonant impurity (the open circle). The anisotropy is assumed only for the closest neighbours of the impurity atom.

owing to the μ th impurity. The scattering amplitude of the s th resonant atom becomes equal to

$$f_{ij}^{s\mu} = f_{ij}^s + g_{ij}(\mathbf{R}^{s\mu}), \quad (2)$$

where the first term is invariant over the G_I group, and tensor $g_{ij}(\mathbf{R}^{s\mu})$ describes the additional contribution of the defect to the resonant scattering amplitude compared with the perfect crystal. Tensor $g_{ij}(\mathbf{R}^{s\mu})$ is invariant under the subgroup G^μ of the G^s point group, which corresponds to the direction between the resonant atom and the impurity $\mathbf{R}^{s\mu}$. Supposing that the displacements $\mathbf{u}^{s\mu}$ of all atoms is small, we can write the following expression for the tensor structure factor describing the PDI reflections (hence we suppose that the contribution of f_{ij}^s is zero),

$$F_{ij}(\mathbf{H}) \sum_{s,\mu} (g_{ij}^{s\mu} + g_{ijn}^{s\mu} u_n^{s\mu}) (1 + iH_k u_k^{s\mu}) \exp(i\mathbf{H}\mathbf{r}^s), \quad (3)$$

where $g_{ijn} = \partial g_{ij} / \partial R_n^s$. It is easy to see that the term $\sum_{\mu} g_{ij}^{s\mu}$ is invariant under the G_I symmetry group; hence it gives no contribution to the discussed reflections. The main contribution from the point defects to the forbidden reflection in the dipole resonant transition can be written as

$$F_{ij}(\mathbf{H}) = \sum_{\mu} \sum_s iH_k u_k^{s\mu} g_{ij}^{s\mu} \exp(i\mathbf{H}\mathbf{r}_s). \quad (4)$$

Below we shall consider several structures which allow the appearance of forbidden reflections of this type.

3. Crystals with $Fd\bar{3}m$ symmetry

Some examples of the structures with $Fd\bar{3}m$ space symmetry (impurities in Ge and intermetallides with C-15 structure RFe_2), which allow the existence of PDI reflections, were discussed previously (Dmitrienko & Ovchinnikova, 2000). Let us consider the forbidden reflections $0kl$, $k+l=4n+2$, in the Ge crystal where atoms with different orientations, 1 and 2, are in the (000) and $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ positions, respectively. The corresponding structure factor is equal to $F(0kl, k+l=4n+2) = 4(f^1 - f^2)$. Taking into account that these atoms are connected by inversion, we can write $f_0^1 = f_0^2$, $f_{ij}^1 = f_{ij}^2$, $f_{ijk}^1 = -f_{ijk}^2$, $\mathbf{u}^1 = -\mathbf{u}^2$. The impurity substitutes the Ge atoms and the neighbouring atoms are displaced along the $\langle 111 \rangle$ directions. In this case the g_{ij} tensors are invariant under the group $3m$ and they are characterized by two eigenvalues g_1 and g_2 . We obtain that the contribution, induced by the defects to the structure amplitude, is equal to

$$\hat{F}(0kl, k+l=4n+2) = 8i C_{\text{imp}} g_2 u \begin{pmatrix} 0 & l & k \\ l & 0 & 0 \\ k & 0 & 0 \end{pmatrix}, \quad (5)$$

where C_{imp} is the impurity concentration. This expression coincides with that given in our previous paper (Dmitrienko & Ovchinnikova, 2000) if the displacements are small.

4. Forbidden reflections in A-15 intermetallides

Intermetallides with A-15 structure are described by the space group $Pm\bar{3}n$ and correspond to the chemical formula A_3B (Nb_3Ge , V_3Co etc.). B -type atoms are in the 2(a) position with $m\bar{3}$ symmetry; A -type atoms occupy the 6(d) position with $\bar{4}2m$ symmetry.

No forbidden reflections appear in the dipole transition near the absorption edge of the B atom because its local symmetry is cubic, $f_{ij} \simeq \delta_{ij}$. Point defects cannot induce any reflection, because all tensors in equation (3) vanish after averaging over the point-defect

positions. Thus, in the considered approximation there are no PDI reflections near the absorption edge of the B atom.

Near the absorption edge of the A atom we can find the following forbidden reflections, induced by the dipole resonant transition: hkl with $h+k+l=2n+1$ excepting $h=2n+1, k=4n, l=4n+2$ (they are allowed) and $h=2n+1, k=2n'+1, l=2n''+1$. For these reflections the structure factor is equal to

$$F(h, k, l) = \exp[2\pi i(h/4 + k/2)(f_1 - f_2)] \\ + \exp[2\pi i(k/4 + l/2)(f_3 - f_4)] \\ + \exp[2\pi i(h/2 + l/4)(f_5 - f_6)], \quad (6)$$

where atoms are enumerated in correspondence with the *International Tables for Crystallography* (Hahn, 1996). Odd and even atoms are connected by inversion, hence for the dipole transition $f_{2n} = f_{2n+1}$ and the reflection vanishes.

Let us suppose that there are impurities in the B position. They provide a correction to the tensor scattering amplitudes and the displacements of the A atoms in the first coordination sphere. For example, the impurity at the (000) point causes the appearance of the tensor factor $g_{ij}^{3\mu}$ on the third atom in the $(0\frac{1}{4}\frac{1}{4})$ position and a corresponding displacement towards the point (000). Because these two atoms are in the mirror plane m_y , $\mathbf{u}^3 = (u_x, 0, u_z)$, $g_{ij}^{3\mu}$ is invariant over the group m_y . For each atom we must average the term $iH_k u_k^{s\mu} g_{ij}^{s\mu}$ over all possible positions of impurity around the s th atom (i.e. over the group $\bar{4}$). After the summation over all atoms inside the position 6(d), the tensor structure amplitude of the forbidden reflection hhl ($l \neq h$) is equal to

$$F(hhl) = 2i C_{\text{imp}} (h+l) \begin{pmatrix} g_{11}u_z & 0 & -2g_{xz}u_x \\ 0 & -g_{11}u_z & 2g_{xz}u_x \\ -2g_{xz}u_x & 2g_{xz}u_x & 0 \end{pmatrix}, \quad (7)$$

where $g_{11} = g_{yy} - g_{xx}$. This reflection is forbidden far from the absorption edge of an A element and in the dipole transition, but it is allowed for the dipole–quadrupole scattering. In the latter case, without any impurities, the tensor structure amplitude can be calculated as $F(\mathbf{H}) = \sum_s i(H_k f_{ijk}^s + l_k f_{ijk}^a)$, where f_{ijk}^s and f_{ijk}^a are the symmetric and antisymmetric parts of the third-rank tensor invariant over the $\bar{4}m2$ point group, $\mathbf{l} = \mathbf{k} + \mathbf{k}'$. According to the tables of Sirotn & Shaskolskaya (1975), f_{ijk}^s has two independent components and f_{ijk}^a has one component. Hence the dipole–quadrupole transition gives the following contribution to the considered reflections,

$$F_{ij}^{dq} = 2i(h+l) \begin{pmatrix} -f_{xxz}^s & 0 & -f_{xzx}^s \\ 0 & f_{xxz}^s & f_{xzx}^s \\ -f_{xzx}^s & f_{xzx}^s & 0 \end{pmatrix} + 2if_{yzx}^a \begin{pmatrix} 0 & 0 & l_y \\ 0 & 0 & -l_x \\ -l_y & l_x & 0 \end{pmatrix}. \quad (8)$$

We see that the tensor structure of the PDI contribution (7) takes the same form as the symmetric part of the dipole–quadrupole contribution (8). This is rather obvious, because the transformation properties of the production $u_k f_{ij}$ are similar to the properties of a third-rank tensor. To separate the PDI contribution we would have to measure the dependence of the PDI forbidden reflections on the impurities concentration.

5. Crystals with $la\bar{3}d$ symmetry

In this section we consider ferrites with the garnet structure, which are widely used in magnetic devices because of their useful magnetic properties. It is known that the substitution of Fe atoms or rare-earth atoms essentially influences the magnetic properties of these structures (Smit & Wijn, 1959). The study of forbidden reflections induced

by impurities provides information about the influence of defects on the valence electron states, which can be useful for the description of the magnetic properties.

Below we shall consider as an example the yttrium–iron garnet (YIG; $Y_3Fe_5O_{12}$). In the pure YIG, magnetic ions Fe^{3+} occupy two sites: octahedral, 16(a), with $\bar{3}$ local symmetry, and tetrahedral, 24(d), with $\bar{4}$ symmetry. Y^{3+} ions occupy the 24(c) position with 222 local symmetry. O atoms are in 96(e) positions.

In the dipole resonant transition near the K -edge of Fe (7.1 keV), forbidden reflections can occur, which are induced separately by the 16(a) and 24(d) positions of iron. Near the absorption edge of yttrium (the K -edge, 17.04 keV) we can find forbidden reflections induced by yttrium in the 24(c) position. The 16(a) position provides the following set of forbidden reflections: $h = 2n + 1, k = 2n' + 1, l = 0$ and $h = k = 2n + 1, l = 4n'$ (plus permutations), for example, 110. The 24(d) and 24(c) sites yield forbidden reflections with $h = k = 4n, l = 4n' + 2$ (for example, 002). We can also find reflections which are forbidden for one of the positions and allowed for another. For example, $h = 2n + 1, k = 2n' + 1, h + k + l = 4n$ reflections are allowed for the 24(d) position and forbidden for 16(a). The reflections $h = k = 4n + 2, l = 4n' + 2$ still remain forbidden for both positions.

All these reflections occur exclusively owing to anisotropy induced by asymmetric atomic environment. Purely magnetic reflections are absent, because the magnetic moments inside each position are parallel. Forbidden reflections similar to the considered ones have been studied theoretically and observed experimentally in Mössbauer nuclear diffraction (Winkler *et al.*, 1983; Ruffer *et al.*, 1989).

Let us suppose that Me^{3+} ions are substituted for Fe ions. They can both be in the 16(a) and 24(d) positions. Then the 110 and 200 reflections will appear near the absorption edges of both Fe and Me. In the garnets, where yttrium atoms are substituted by atoms of another element M, the 002 reflection can be observed near the absorption edges of yttrium and M, but the 110 reflection remains forbidden.

Let us consider the hkl reflections with $h = k = 4n + 2, l = 4n' + 2$ near the absorption edges of iron. For clarity we shall perform all the calculations for the 226 reflection. The 16(a) position of iron will not contribute to the forbidden reflection because its local symmetry $\bar{3}$ forbids the existence of both the symmetric and antisymmetric parts of a third-rank tensor. The symmetry $\bar{4}$ of the 24(d) position allows the symmetric third-rank tensor with four independent components. The calculation similar to that made above for the $Pm\bar{3}n$ group shows that Fe atoms of the 24(d) position give the following contribution to the forbidden reflection,

$$F(226) = -16iC_{\text{imp}} \begin{pmatrix} 0 & g_{xy} & g_{xz} \\ g_{xy} & 0 & -g_{yz} \\ g_{xz} & -g_{yz} & 0 \end{pmatrix}, \quad (9)$$

where $g_{xy} = g_{yz}u_y + g_{xz}u_x, g_{xz} = g_{xz}u_x + 3g_{yz}u_y, g_{yz} = 3g_{xz}u_x + g_{yz}u_y$. Similarly we can show that the 24(d) Fe position in the presence of defects will contribute to the reflections corresponding to the 16(a) position in the absence of defects, for example, into the 110 reflection. PDI forbidden reflections 110 can also appear near the absorption edge of yttrium. However, the term $iH_k u_k g_{ij}$ cannot explain the appearance of the PDI forbidden reflections from the 16(a) position to the reflections 002. Atoms of the 16(a) position also cannot induce forbidden reflections in a perfect crystal owing to the dipole–quadrupole resonant transition or the thermal vibrations. Nevertheless, the contribution from the 16(a) position was observed in the purely nuclear 002 reflection in the Mössbauer diffraction pattern (Labushkin *et al.*, 1995). To explain this we have to take into account

the magnetic structure of YIG. The experiment was carried out at room temperature, and the magnetic moments in the single-crystal film of YIG were aligned along the [001] direction. Because the magnetic moments are time-reversible but not space-reversible, they violate the local symmetry of atomic sites. In the case of the 16(a) position, the magnetic interaction violates the $\bar{3}$ local symmetry. As a result, effects induced by the third-rank tensors can appear.

It follows from the above consideration that the forbidden reflections near the absorption edges of Fe, Y, M and Me would allow the concentrations of M and Me atoms to be found in all crystallographic positions and the displacements and the distortions of electronic states of the atoms to be studied.

6. Conclusions

Point defects violate the local symmetry of atomic environments and provide an additional anisotropy of resonant scattering. This anisotropy, together with the defect-induced atomic displacements, causes the appearance of forbidden reflections, which are absent far from absorption edges and in perfect crystals. Of course, the discussed PDI reflections can, but not necessarily will, be observed and their experimental observation is a challenge for the future. To meet this challenge, the use of synchrotron radiation is certainly indispensable.

Various crystals, considered in the present paper, provide examples of structures which allow the appearance of forbidden reflections of this type. It was shown that such reflections are accompanied by the contributions from a dipole–quadrupole resonant transition and from thermal vibrations. These contributions can be separated because only the PDI forbidden reflections depend on the defect concentration. Note that point defects can also create some corrections to the vibration modes, because a local vibration mode can occur. This may be essential for the study of thermal-motion-induced reflections near the absorption edge of the impurity.

Sometimes the study of the PDI forbidden reflections can allow the concentration of impurities to be measured in different crystallographic positions. Such a situation exists in garnets with $Ia\bar{3}d$ symmetry, where different forbidden reflections originate from different iron positions.

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