

# Resonant X-ray diffraction: 'forbidden' Bragg reflections induced by thermal vibrations and point defects

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In general, the local atomic environment becomes less symmetric owing to point defects and thermal vibrations of atoms in crystals. It is shown that, as a result of this phenomenon, an additional anisotropy of the resonant scattering factors can occur and the forbidden Bragg reflections can be excited near absorption edges. Examples of crystals are presented (Ge, K<sub>2</sub>CrO<sub>4</sub>, *C-15* type) where such thermal-motion-induced (TMI) and point-defect-induced (PDI) reflections can be observed. The tensor structure factors of both types of reflection are computed. Owing to their resonant character, the PDI reflections allow both impurity atoms and host atoms of different types to be studied separately. The considered phenomena can provide a very sensitive method to study point defects because only the atoms distorted by defects produce contributions to the PDI reflections.

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## 1. Introduction

X-ray resonant scattering is now developing to study structural and magnetic properties of solids (Templeton, 1994; Blume, 1994). It is also called anomalous scattering and observed when the energy of the incident radiation approaches the values required to excite an inner-shell electron into an empty state of outer shells or into a free-electron state. For structure investigations, the most informative portion is that part of the anomalous scattering that depends on the atomic environment. This dependence has been observed for many years in the XANES region (X-ray absorption near-edge structure) and about 10<sup>2</sup>–10<sup>3</sup> eV above absorption edges in the EXAFS region (extended X-ray absorption fine structure). In the latter case, it is referred to as DAFS (diffraction anomalous fine structure).

The resonant effects are especially important for additional reflections, which can appear in X-ray diffraction just through the environment-induced anisotropy of resonant scattering. These ATS (anisotropy of the tensor of susceptibility) reflections occur even in non-magnetic crystals because the outer shells are strongly affected by the local environment and therefore the atomic scattering amplitude becomes anisotropic (Templeton & Templeton, 1980; Dmitrienko, 1983, 1984). The anisotropy violates the extinction rules tabulated for glide planes and/or screw axes. New general extinction rules and structure factors of the ATS reflections were found in the dipole approximation (Dmitrienko, 1983). For the first time, these 'forbidden' reflections were observed by

Templeton & Templeton (1985, 1986) in NaBrO<sub>3</sub> near the bromine *K*-absorption edge. Later, the ATS reflections were observed in many crystals; they demonstrate very unusual polarization properties [see Belyakov & Dmitrienko (1989) and Kirfel & Petcov (1991) for reviews]. From the practical viewpoint, ATS reflections provide us with an instrument for X-ray spectroscopy of the atomic electronic states distorted by crystal fields.

The anisotropy of the atomic scattering factor corresponds to the symmetry of the local atomic environment. Therefore, it is allowed even in cubic crystals and icosahedral quasicrystals (Dmitrienko, 1984, 1989) if the resonant atoms are at sites with not too high symmetry. However, if the symmetry of the sites occupied by the resonant atoms is high (for instance cubic), the anisotropy is absent and no ATS reflections are expected (in the dipole approximation). In principle, if ATS reflections are forbidden in the dipole approximation, they can arise in the dipole–quadrupole or higher approximations (Finkelstein *et al.*, 1992; Templeton & Templeton, 1994).

In the present paper, we consider situations when the resonant atoms, occupying special positions with high symmetry, are shifted to positions with lower symmetry. For example, this happens due to thermal motion or point defects (impurity atoms or vacancies). We study the effect of these displacements on Bragg reflections, especially on forbidden reflections. It is well known that the forbidden reflections, caused by anharmonic and anisotropic thermal motion, are observed far from absorption edges (Dawson, 1975; Borie, 1974; Tischler & Batterman, 1984). The latter effect does not

violate the glide-plane and screw-axis extinction rules. In contrast, we show that, for example, the thermal motion can induce the anisotropy of atomic susceptibility and can excite extra reflections violating the glide-plane and screw-axis extinction rules. They will be referred to as thermal-motion-induced (TMI) reflections; some examples were discussed previously by Dmitrienko *et al.* (1999). In a similar way, we take into account the static atomic displacements owing to the point defects in a crystal. The same kind of consideration was made by Ovchinnikova & Dmitrienko (1999) for the case of incommensurate crystals with occupational modulations. Here, we consider the case when local anisotropy is induced by the static atomic displacements owing to *randomly* distributed point defects. The resonant atoms, occupying (in the absence of defects) special high-symmetry positions, can be displaced to low-symmetry positions. As a result, the local anisotropy and point-defect-induced (PDI) reflections can appear. We consider both the case when the symmetry of the point defect coincides with the symmetry of a special position and the case when the symmetry of the point defect becomes lower. Moreover, we show that in several cases PDI reflections can be observed not only near an absorption edge but even far from it, where the X-ray susceptibility is isotropic.

## 2. Anisotropy of X-ray scattering near absorption edges

The resonant anomalous contribution to the scattering factor of an atom is described by a tensor,  $f_{jk}$ , depending on the X-ray frequency  $\omega$ . For an isolated atom,  $f_{jk}$  is isotropic:  $f_{jk}(\omega) = (f' + if'')\delta_{jk}$ . This expression is used most frequently in X-ray structure analysis. However, in condensed matter, the scattering factor depends also on the environment of the scattering atom, *i.e.* on its position  $\mathbf{r}_s$ , on the type of neighbouring atoms, on their positions  $\mathbf{r}_{s1}, \mathbf{r}_{s2}, \dots$  *etc.* Correspondingly, the resonant structure factor, describing the scattering in the  $\mathbf{H} = 2\pi(h, k, l)$  Bragg reflection, is also a tensor depending on the environment of the atoms:

$$F_{jk}(\mathbf{H}) = \sum_s f_{jk}(\omega, \mathbf{r}_s, \mathbf{r}_{s1}, \dots) \exp(i\mathbf{H} \cdot \mathbf{r}_s), \quad (1)$$

where the summation extends over all the atoms in the unit cell. Hereafter, the Debye–Waller factor is omitted for the sake of simplicity.

In the dipole approximation,  $f_{jk}$  can be written as (Blume, 1994)

$$f_{jk}(\omega, \mathbf{r}_s, \mathbf{r}_{s1}, \dots) = -\frac{m}{\hbar\omega} \sum_{a,b} P_a \omega_{ba}^3 \frac{\langle a | R_j^s | b \rangle \langle b | R_k^s | a \rangle}{\omega - \omega_{ba} - i\Gamma/2\hbar}. \quad (2)$$

In this expression,  $|a\rangle$  describes the initial and final electronic states with energy  $E_a$ ,  $P_a$  is the probability of finding the atom in the  $|a\rangle$  state,  $|b\rangle$  describes an intermediate electronic state with energy  $E_b$ ,  $\omega_{ba} = (E_b - E_a)/\hbar$ ,  $\omega$  is a frequency of the incident radiation,  $\mathbf{R}^s = \sum_i \mathbf{r}_i^s$ , where the summation extends over all electrons in the atom.

For X-ray coherent scattering, the local atomic environment influences the structure factor through the intermediate

valence-electron state because the initial and final electronic states correspond to inner-electron shells inaccessible to external fields. Experimentally, it is well known that even small *static* changes of the environment can noticeably change  $f_{jk}$ . For example, in an octahedral environment,  $f_{jk}$  should be isotropic. However, in the  $\text{FeS}_2$  and  $\text{Fe}_2\text{O}_3$  crystals, where each Fe atom is contained inside a slightly distorted octahedron of S or O atoms, the pronounced anisotropy of  $f_{jk}$  was observed (Nagano *et al.*, 1996; Dräger *et al.*, 1988). Thus, point defects, producing local distortions, could drastically change  $f_{jk}$ .

The situation is more complicated with thermal motion because it produces *dynamic* changes of the environment. Nevertheless,  $f_{jk}$  is determined by the electron subsystem of a crystal, which is so fast that it can follow the atomic motion (the so-called Born–Oppenheimer or adiabatic approximation). Therefore,  $f_{jk}$  corresponds to current atomic configurations as if they were static. Another important approximation, used implicitly in (2), is that the typical time of X-ray resonant scattering,  $\hbar/\Gamma$ , is much smaller than the typical time of thermal motion. Because of this, we should take into account only the current atomic position  $\mathbf{r}^s$  in (2) as if it was a static position (*i.e.* the atomic position does not change during scattering). Finally, we see that the value of the tensor  $f_{jk}$  changes all the time in accordance with thermal motion and the current symmetry of this tensor corresponds to the current symmetry of atomic positions. This is in contrast, for example, with the Mössbauer resonant scattering, where the typical time is much longer than that of the thermal motion and the symmetry of the resonant scattering amplitude corresponds to the *average* symmetry of the atomic site.

It is extremely difficult to compute the valence-electron states distorted by the environment for any realistic situation. Therefore, below we will use symmetry analysis that allows us to find the general form of atomic and structure factors when the thermal motion or point defects are taken into account.

## 3. Forbidden reflections in resonant X-ray diffraction induced by thermal atomic vibrations

In this section, we find how the anisotropy of resonant scattering and the structure factor change owing to the thermal motion. For simplicity, we will suppose hereafter that the electronic wave functions for the  $s$ th atom,  $|b\rangle$ , their energy,  $E_b$ , and, hence,  $f_{jk}$  are functions of  $\mathbf{r}^s$  only, *i.e.* we neglect the thermal motion of neighbouring atoms. To obtain the tensor structure factor  $F_{jk}(\mathbf{H})$ , we should average equation (1) over thermal vibrations:

$$F_{jk}(\mathbf{H}) = \sum_s \overline{f_{jk}(\omega, \mathbf{r}^s) \exp(i\mathbf{H} \cdot \mathbf{r}^s)}. \quad (3)$$

Hereafter, the bar means thermal averaging. To avoid confusion, it should be emphasized that it is not a time averaging in (3) because the X-ray scattering is a very fast process. It is the averaging over all possible displacements of atoms in different unit cells (as in the case of the Debye–Waller factor).

Actually, it is very difficult to compute  $f_{jk}(\omega, \mathbf{r}^s)$ , therefore we will use a phenomenological approach. We suppose the

thermal displacement  $\mathbf{u}^s$  from the average position  $\mathbf{r}^{0s}$  is small enough ( $\mathbf{u}^s = \mathbf{r}^s - \mathbf{r}^{0s}$ ) that we can use a tensor expansion of  $f_{ik}(\omega, \mathbf{r}^s)$  and  $\exp(i\mathbf{H} \cdot \mathbf{r}^s)$ :

$$\exp(i\mathbf{H} \cdot \mathbf{r}^s) = [1 + i\mathbf{H} \cdot \mathbf{u}^s - (\mathbf{H} \cdot \mathbf{u}^s)^2/2 + \dots] \exp(i\mathbf{H} \cdot \mathbf{r}^{0s}) \quad (4)$$

$$f_{jk}(\omega, \mathbf{r}^s) = f_{jk}^{0s} + f_{jkl}^{1s} u_l^s + f_{jklm}^{2s} u_l^s u_m^s + \dots \quad (5)$$

All the tensors  $\hat{f}^{ps}$  of different ranks on the right side of (5) are invariant under the ‘average’ symmetry group, which coincides with the point group of the atom site. Substitution of (4) and (5) into (3) gives us after averaging over thermal displacements the terms  $\overline{u_l u_m \dots u_n}$ . Because we are interested in thermal effects, we will consider only those situations when the contribution from the zero-order term,  $f_{jk}^{0s}$ , vanishes for symmetry reasons. The first non-vanishing term is obviously  $\overline{u_l u_m}$  and hereafter we hold only its contribution to the tensor structure factor. It is evident that  $f_{jklm}^{2s} \overline{u_l^s u_m^s}$  has exactly the same symmetry as  $f_{jk}^{0s}$  and they vanish together; the same is valid for all the terms in (5). Thus, the TMI contribution arises only from those cross terms in (3) that are proportional to  $\mathbf{H} \cdot \mathbf{u}$  or to higher powers of  $\mathbf{H} \cdot \mathbf{u}$ . This means that both the atomic displacement and the induced anisotropy are important. Generally, the first non-vanishing term is  $i f_{jkl}^{1s} H_m \overline{u_l^s u_m^s}$ .

The analysis of (3) provides the following simple recipe for TMI ATS reflections: only those extinction rules and those restrictions on the tensor structure factor that were found for the general atomic sites (Dmitrienko, 1983) are valid. The additional restrictions, found for high-symmetry special sites (Dmitrienko, 1984), are violated by the thermal vibrations providing TMI ATS reflections. This is quite obvious from the physical point of view because vibrating atoms leave special sites and spend most of the time in general positions. Therefore, only the general extinction rules survive.

### 3.1. Examples

If the resonant atoms are at the sites with cubic point symmetry, then  $f_{jkl}^{1s} = f^1 T_{jkl}$ , where  $T_{jkl} = e_j^1 e_k^2 e_l^3$ ,  $\mathbf{e}^1, \mathbf{e}^2, \mathbf{e}^3$  is a right-hand triad of unit vectors directed along cubic axes,  $f^1$  is an unknown factor. Tensor  $\hat{T}$  is non-zero only for the 23 and  $\bar{4}3m$  cubic groups, where its non-zero components are

$$T_{xyz} = T_{yzx} = T_{xzy} = T_{xzy} = T_{zyx} = T_{yxz} = 1.$$

Taking into account that for cubic symmetry  $\overline{u_j u_k} = \delta_{jk} \overline{u^2}/3$ , we have

$$\overline{f_{jk}(\omega, \mathbf{r}^s) \exp(i\mathbf{H}\mathbf{r}^s)} = i f^1 T_{jkl} H_l \overline{u^2}/3.$$

Let us consider the  $0kl$  ( $k, l = 2n; k + l = 4n + 2$ ) forbidden reflections in a Ge crystal [symmetry group  $Fd\bar{3}m$ , atoms are in the special position  $8(a)$ ]. This extinction is induced by the atoms at  $(000)$  and  $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ , which scatter in antiphase making the conventional structure factor vanish. However, because these atoms are related by an inversion centre, the corresponding tensors  $f_{jkl}^{1s}$  have opposite signs. Hence, the TMI anisotropy provides the in-phase resonant scattering. Finally, we obtain from (3) for Ge crystals:

$$\hat{F}(0kl, k + l = 4n + 2) = \frac{16}{3} \pi i f^1 \overline{u^2} \begin{pmatrix} 0 & l & k \\ l & 0 & 0 \\ k & 0 & 0 \end{pmatrix}. \quad (6)$$

We see that the structure factor varies proportional to  $\overline{u^2}$  and  $H_j$ . The unknown phenomenological coefficient  $f^1$  is the same for all TMI reflections and does not depend on temperature. However, according to (2), it strongly depends on  $\omega$ .

If resonant atoms are at special sites of non-cubic crystals, there is a variety of cases when the conventional ATS contribution is absent but the TMI contribution is possible. Let us consider  $\text{K}_2\text{CrO}_4$ , where the resonant Cr atoms are on sites  $4(c)$  of the space group  $Pnma$  with the coordinates: (i)  $x, \frac{1}{4}, z$ ; (ii)  $-x, \frac{3}{4}, -z$ ; (iii)  $\frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z$ ; (iv)  $\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z$ . Because all the Cr atoms are on the mirror planes, the temperature-independent dipole–dipole terms vanish for  $0k0$ ,  $k = 2n + 1$ , reflections. However, for the group  $m_y$ , the third-rank tensor  $f_{jkl}^{1s}$  has ten independent components and one of them,  $f_{xyy}^{1s}$ , contributes to the structure amplitude:

$$\hat{F}(0k0, k = 2n + 1) = 8\pi i k \overline{u_y^2} f_{xyy}^{1s} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (7)$$

Again, we have only one phenomenological parameter,  $f_{xyy}^{1s}$ , for all  $0k0$ ,  $k = 2n + 1$ , reflections.

Now let us estimate the temperature effect. It is quite evident that acoustic phonons give no contribution to the TMI anisotropy because in the acoustic phonon modes each unit cell moves as a whole and no anisotropy appears. Thus, only relative atomic displacements should be taken into account. This is similar to the calculation of the temperature factor for the extended X-ray absorption fine structure (EXAFS), where also only relative positions of atoms are of importance. In the simplest approximation, we can suppose that each atom moves independently among the others occupying their average positions. In this case, we should calculate  $\overline{u_j u_k}$ , taking into account only optical phonons.

At high temperature,  $\overline{u_i^2} = 9h^2 T / 2Mk_B \theta_D^2$  (Reissland, 1973), where  $\theta_D = 300$  K is the Debye temperature for Ge. Therefore, the structure amplitude of TMI ATS reflections is proportional to  $T$  and to  $\mathbf{H}$  [at 1000 K,  $(\overline{u_i^2})^{1/2} \approx 0.19$  Å]. Taking into account higher-order contributions in (3), instead of  $iH_m \overline{u_l^s u_m^s}$ , we should write

$$\begin{aligned} \overline{u_l^s \exp(iH_m u_m^s)} &= -i \frac{d}{dH_l} \overline{\exp(iH_m u_m^s)} \\ &= -i \frac{d}{dH_l} \exp(-H_m H_n \overline{u_m^s u_n^s} / 2) \\ &= i H_m \overline{u_l^s u_m^s} \exp(-H_m H_n \overline{u_m^s u_n^s} / 2). \end{aligned}$$

Thus, the old expression is corrected by the Debye–Waller factor. As a result, the structure amplitude stops growing with  $T$  and  $\mathbf{H}$  and reaches its maximum when  $\mathbf{H}^2 \sim 1/\overline{u^2}$ .

#### 4. Forbidden reflections induced by point defects

A point defect like a vacancy, an interstitial or a substituted atom distorts the crystal structure. It causes displacements of the neighbouring atoms and changes their valence-electron states. Hence, defects influence the resonant susceptibility and can cause ATS reflections near absorption edges.

The influence of different defects on X-ray *non-resonant* scattering has been widely discussed in the scientific literature. It was shown that point defects lead to changes of intensity and position of main reflections and the appearance of the diffusion peaks (for example, see Krivoglaz, 1983). In the present paper, we will not touch upon these subjects. Below, we discuss only the extra reflections that appear near the absorption edges owing to point defects. We suppose random distribution and low density of the defects, hence any questions connected with superstructure and satellite reflections are omitted.

Atomic displacements induced by defects and corresponding electron states of the doped crystals are widely investigated both theoretically and experimentally (for reviews, see Stoneham, 1975; Maradudin, 1966; Kristofel, 1974). If an impurity is doped into a site with a certain symmetry, it can either preserve the symmetry or make it lower. The symmetry can be violated owing to the different physical reasons usually related with electronic interactions and the Jahn–Teller effect. The size, valency and charge of the impurity is essential for the lattice and electronic state distortions.

Below, we show that forbidden reflections can occur in resonant X-ray diffraction owing to the impurities, which cause atomic displacements as far as distortions of valence-electron states. We shall separately consider the cases when the symmetry of the defect position is violated and when this symmetry is conserved.

##### 4.1. A trivial case: impurity atoms in anisotropic positions

Let us suppose that impurity atoms substitute randomly some atomic position with non-cubic local symmetry in a crystal with glide planes and/or screw axes. If the impurity concentration is so small that they do not affect one another, then any impurity position is related to other positions of the same type by the symmetry operation as in the host crystal. Hence, the ATS reflections can appear near the absorption edge of the impurity and only the impurity gives the contribution to this ATS reflection (if a suitable absorption edge of the impurity is far from any absorption edges of the host atoms).

We consider here this trivial case just to make the following estimation for the possible sensitivity of this method. Typical values of the atomic factor anisotropy range from a few electrons for *K* edges of mid-*Z* elements up to several tens of electrons for *L* edges of high-*Z* elements. The structure factors of still observable reflections are about  $10^{-3}$  electrons (for example, for non-resonant magnetic reflections). Hence, the smallest impurity concentration accessible to observation with

this method is about 0.1% for mid-*Z* elements and 0.01% for high-*Z* elements.

##### 4.2. Point-defect-induced reflections in the case of high symmetry of defect positions

Let us suppose that the host atoms occupy special positions with such high symmetry that no ATS reflections are possible in the dipole approximation (examples were given by Dmitrienko, 1984). If we introduce some substitutional point defects of low concentration, then the defect sites also have the same symmetry and no ATS reflections are expected near the impurity resonances. However, owing to defect-induced structure distortions, some ATS reflections can be excited near the host-atom resonances. The reason is that the impurity causes both an anisotropy of susceptibility and some displacement of neighbouring atoms. This effect is quite similar to the case of TMI reflections considered above, but instead of TMI distortions we have now static PDI distortions of the initial perfect structure. It is important that, even after averaging over all equivalent positions of the impurity, the structure amplitude of the ATS reflections remains non-vanishing. To clarify this point, several examples are presented below.

**4.2.1. Defects in Ge crystals.** First we consider again a Ge crystal where atoms occupy the 8(*a*) position of the  $Fd\bar{3}m$  space group with (000) and  $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$  coordinates. As was pointed out above, the cubic local symmetry does not allow any ATS reflections in the dipole approximation.

Let us suppose that an impurity atom (or a vacancy) substitutes the Ge atom at the  $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$  site. It deforms locally the crystal structure inducing the displacements of the neighbouring atoms. From the symmetry, it is evident that four Ge atoms of the first coordination sphere, forming the tetrahedron  $(000; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2})$ , are shifted along the impurity–Ge bonds. Their coordinates become equal to  $(x_1, x_1, x_1; \frac{1}{2} - x_1, \frac{1}{2} - x_1, x_1; \frac{1}{2} - x_1, x_1, \frac{1}{2} - x_1; x_1, \frac{1}{2} - x_1, \frac{1}{2} - x_1)$ . If an impurity is at the (000) site, then the coordinates of neighbouring Ge atoms are equal to  $(\frac{1}{4} - x_1, \frac{1}{4} - x_1, \frac{1}{4} - x_1; -\frac{1}{4} + x_1, -\frac{1}{4} + x_1, \frac{1}{4} - x_1; -\frac{1}{4} + x_1, \frac{1}{4} - x_1, -\frac{1}{4} + x_1; \frac{1}{4} - x_1, -\frac{1}{4} + x_1, -\frac{1}{4} + x_1)$ . Obviously, all shifted atoms belong to the same 32(*e*) orbit of the  $Fd\bar{3}m$  space group. Below, for simplicity, the distortions of the next coordination shells are ignored because they are small.

The point defects reduce the initial  $\bar{4}3m$  symmetry of host atomic positions and induce the anisotropy of the atomic factors, which is especially strong for neighbouring atoms (the reduced symmetry of neighbouring atoms is  $3m$ ). Again, as in the trivial case considered above, the anisotropy of the atomic factor can reach a few electrons for the Ge atoms nearest to the point defect. Of course, the atomic displacements from the 8(*a*) to the 32(*e*) position also provide some anisotropy of resonant scattering but, contrary to the case of thermal motion, the impurities are the main source of the anisotropy. Notice that the symmetry of impurity positions is  $\bar{4}3m$  (if the impurity concentration is low enough) and hence no anisotropy and no ATS reflections are expected near the impurity absorption edge.

Taking the dipole transition for the  $K$  edge of Ge, we can write a general form of the tensor atomic factor  $\hat{f}^s$ , which corresponds to the reduced  $3m$  symmetry of the host Ge atoms at different sites:

$$\hat{f}^1 = \begin{pmatrix} f_1 & f_2 & f_2 \\ f_2 & f_1 & f_2 \\ f_2 & f_2 & f_1 \end{pmatrix} \quad (8)$$

for the sites  $(x_1, x_1, x_1)$  and  $(\frac{1}{4} - x_1, \frac{1}{4} - x_1, \frac{1}{4} - x_1)$ ;

$$\hat{f}^2 = \begin{pmatrix} f_1 & f_2 & -f_2 \\ f_2 & f_1 & -f_2 \\ -f_2 & -f_2 & f_1 \end{pmatrix} \quad (9)$$

for the sites  $(\frac{1}{2} - x_1, \frac{1}{2} - x_1, x_1)$  and  $(-\frac{1}{4} + x_1, -\frac{1}{4} + x_1, \frac{1}{4} - x_1)$ ;

$$\hat{f}^3 = \begin{pmatrix} f_1 & -f_2 & f_2 \\ -f_2 & f_1 & -f_2 \\ f_2 & -f_2 & f_1 \end{pmatrix} \quad (10)$$

for the sites  $(\frac{1}{2} - x_1, x_1, \frac{1}{2} - x_1)$  and  $(-\frac{1}{4} + x_1, \frac{1}{4} - x_1, -\frac{1}{4} + x_1)$ ;

$$\hat{f}^4 = \begin{pmatrix} f_1 & -f_2 & -f_2 \\ f_2 & f_1 & f_2 \\ -f_2 & -f_2 & f_1 \end{pmatrix} \quad (11)$$

for the sites  $(x_1, \frac{1}{2} - x_1, \frac{1}{2} - x_1)$  and  $(\frac{1}{4} - x_1, -\frac{1}{4} + x_1, -\frac{1}{4} + x_1)$ .  $f_1$  and  $f_2$  are two phenomenological parameters allowed by the symmetry of the  $32(e)$  positions.

After substitution of equations (8)–(11) into (1) and averaging over all possible positions of impurity, we obtain the following expression for the structure factor of forbidden reflections:

$$\begin{aligned} \hat{F}(hkl, h + k + l = 4n + 2) \\ = 8iC_i \left[ -s_h s_k s_l f_1 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + c_h c_k c_l f_2 \begin{pmatrix} 0 & t_l & t_k \\ t_l & 0 & t_h \\ t_k & t_h & 0 \end{pmatrix} \right], \end{aligned} \quad (12)$$

where  $C_i$  is the fraction of impurity atoms,  $s_h = \sin(2\pi h x_1)$ ,  $c_h = \cos(2\pi h x_1)$ ,  $t_h = \tan(2\pi h x_1)$  etc.

First, let us consider the isotropic part of equation (12), which is proportional to  $f_1$ . This part is non-vanishing if  $hkl \neq 0$  and it makes its contribution far from absorption edges where  $f_1$  becomes equal to  $f_0$ , that is to the conventional Thomson atomic factor. This is not unexpected because the  $hkl$  ( $h + k + l = 4n + 2$ ;  $hkl \neq 0$ ) reflections are not forbidden for  $32(e)$  positions. We see that there is the defect-induced contribution into the structure factor of the basis-forbidden reflections in diamond structure materials (the most famous of them is the 222 reflection). Surprisingly, to our knowledge, the defect-induced contribution has never been discussed either for the 222 or for other reflections of that type even in the most detailed papers where only the antisymmetric charge distributions and the anharmonic core vibrations were taken into account (Dawson, 1975; Borie, 1974; Tischler & Batterman, 1984). For low temperature (when the anharmonic effect vanishes) and for high  $h^2 + k^2 + l^2$  (when the effect of

the antisymmetric charge distribution becomes weak), the defect-induced contribution may be the most important. For the  $hhh$  ( $h = 4n + 2$ ) reflection, we have

$$\begin{aligned} \hat{F}(hhh, h = 4n + 2) \\ = 8iC_i \left[ -s_h^3 f_1 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + c_h^2 s_h f_2 \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \right]. \end{aligned} \quad (13)$$

Notice that the value and the sign of  $f_2$  can be measured from the interference of the first and second terms in equation (13).

Now let us consider true ATS reflections  $0kl$  ( $k, l = 2n$ ;  $k + l = 4n + 2$ ), which are impossible for the Thomson scattering. For them, there is only the defect-induced term:

$$\hat{F}(0kl, k + l = 4n + 2) = 8iC_i f_2 \begin{pmatrix} 0 & c_k s_l & c_l s_k \\ c_k s_l & 0 & 0 \\ c_l s_k & 0 & 0 \end{pmatrix}. \quad (14)$$

In particular, for the  $00l$  ( $l = 4n + 2$ ) reflections, the tensor structure factor is especially simple:

$$\hat{F}(00l, l = 4n + 2) = 8iC_i s_l f_2 \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (15)$$

For the unpolarized incident radiation, the following azimuthal dependence of intensity corresponds to these reflections:

$$I \sim C_i^2 \sin^2(2\pi l x) |f_2|^2 (2 \sin^2 \theta_B + \cos^4 \theta_B \sin^2 2\varphi), \quad (16)$$

where  $\varphi$  is the azimuthal angle,  $\theta_B$  is the Bragg angle.

**4.2.2. C-15 structures.** Intermetallic compounds of the  $A_2B$  (C-15) type have the same space group  $Fd\bar{3}m$  as Ge but their structure is more complicated. For the sake of definiteness, let us use  $ZrV_2$ , where Zr atoms occupy the  $8(a)$  position with cubic symmetry, V atoms are in the  $16(d)$  position with  $3m$  symmetry forming nearest neighbours to Zr. Let us study the influence of impurities in the V position on the resonant atomic factor of Zr near the absorption edge of Zr. There are 12 V atoms in the first coordination sphere of Zr and correspondingly there are 12 possible displacements of the Zr atom if we have a point defect (impurity or vacancy) instead of one of the V atoms. The defects in further shells are neglected and, because the concentration of defects is supposed to be small, the situations with two or more defects in the first shell are ignored. The defect in  $(-\frac{1}{8}, -\frac{1}{8}, -\frac{3}{8})$  causes the displacements of Zr from  $(0, 0, 0)$  to  $(x_1, x_1, z_1)$  and violates the symmetry of the Zr position providing the anisotropy described by a tensor  $\hat{f}^1$  invariant under  $m_{xy}$ :

$$\hat{f}^1 = \begin{pmatrix} f_1 & f_3 & f_4 \\ f_3 & f_1 & f_4 \\ f_4 & f_4 & f_2 \end{pmatrix}. \quad (17)$$

Correspondingly, the defect in  $(\frac{1}{8}, \frac{1}{8}, -\frac{3}{8})$  causes the displacements of Zr from  $(0, 0, 0)$  to  $(-x_1, -x_1, z_1)$  and the atomic factor  $\hat{f}^2$ :

$$\hat{f}^2 = \begin{pmatrix} f_1 & f_3 & -f_4 \\ f_3 & f_1 & -f_4 \\ -f_4 & -f_4 & f_2 \end{pmatrix}, \quad (18)$$

the defect in  $(\frac{1}{8}, -\frac{1}{8}, \frac{3}{8})$  displaces the Zr atom to  $(-x_1, x_1, -z_1)$ ,  $\hat{f}^3$  is described by

$$\hat{f}^3 = \begin{pmatrix} f_1 & -f_3 & f_4 \\ -f_3 & f_1 & -f_4 \\ f_4 & -f_4 & f_2 \end{pmatrix}, \quad (19)$$

and finally the defect in  $(-\frac{1}{8}, \frac{1}{8}, \frac{3}{8})$  displaces Zr to  $(x_1, -x_1, -z_1)$  and causes the atomic factor described by

$$\hat{f}^4 = \begin{pmatrix} f_1 & -f_3 & -f_4 \\ -f_3 & f_1 & f_4 \\ -f_4 & f_4 & f_2 \end{pmatrix}. \quad (20)$$

The displacements for the other eight atoms and related atomic factors  $\hat{f}^5, \dots, \hat{f}^{12}$  can be easily obtained from those listed above by circular permutations corresponding to the threefold rotations.

For the Zr atom in the  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  site, all the defect-induced displacements are related to the displacements of the (000) site by the inversion centre and the corresponding atomic factors are the same. Finally, the structure factor of the  $hkl$  ( $h = 4n + 2, k = 4n, l = 4n$ ) reflections near the absorption edge of Zr is given by the following:

$$\begin{aligned} & \hat{F}(hkl; h = 4n + 2; k, l = 4n) \\ &= i \frac{8C}{3} \left[ -(2f_1 + f_2)s_{hx}s_{kx}s_{lz} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right. \\ &+ (f_3c_{hx}c_{kx}s_{lz} + f_4c_{hz}c_{kx}s_{lx} + f_4c_{hx}c_{kz}s_{lx}) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ &+ (f_4s_{hx}c_{kx}c_{lz} + f_4s_{hz}c_{kx}c_{lx} + f_3s_{hx}c_{kz}c_{lx}) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ &\left. + (f_4c_{hx}s_{kx}c_{lz} + f_3c_{hz}s_{kx}c_{lx} + f_4s_{hx}c_{kz}c_{lx}) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \right], \quad (21) \end{aligned}$$

where  $s_{hx} = \sin 2\pi hx_1$ ,  $c_{hz} = \cos 2\pi hz_1$  etc. One can see that the  $hk0$  reflections are the ATS reflections excited owing to the off-diagonal elements. However, as in the case of Ge crystals, the defect-induced displacements of Zr can also cause the following forbidden reflections even for the conventional Thomson scattering:  $hkl$  ( $h = 4n + 2, k = 4n, l = 4n, kl \neq 0$ ) (the 222 reflection is not forbidden for the *C-15* structures).

### 4.3. PDI ATS reflections in the case of violated defect symmetry

Even if the impurity substitutes a host atom with a cubic environment, the symmetry of the final impurity site may be

lower owing to various physical reasons, such as the Jahn–Teller effect or other electronic interactions (see Stoneham, 1975). For example, in semiconductors, the impurity position is closely related to the electronic structure of the host atoms and the impurity. This question was widely discussed (see, for a review, Vavilov *et al.*, 1990) and a great number of impurities in semiconductors were studied both theoretically and experimentally

As an example, we consider here Ni in the Ge crystal. According to the results of Ludwig & Woodbury (1959) obtained with the help of the electronic spin resonance, the  $\text{Ni}^-$  ion, which substitutes Ge, is shifted along [001] by a distance of about 0.2 Å. Being displaced away from the 8(*a*) position with cubic symmetry,  $\text{Ni}^-$  occupies the 48(*f*) position with *mm2* symmetry. Far from the absorption edge, this position provides the same extinction rules as the initial 8(*a*) position, whereas in the resonant conditions the ATS reflections can appear. If an  $\text{Ni}^-$  ion is shifted from the (000) site to the  $(x_100)$  site, then near the *K*-absorption edge of Ni the tensor atomic factor is given by the following expression (in the dipole approximation):

$$\hat{f}^1 = \begin{pmatrix} f_1 & 0 & 0 \\ 0 & f_2 & f_3 \\ 0 & f_3 & f_2 \end{pmatrix}, \quad (22)$$

whereas for the ion shifted from (000) to  $(-x_100)$ , related to the first one by the  $2_z$  axis, we have

$$\hat{f}^2 = \begin{pmatrix} f_1 & 0 & 0 \\ 0 & f_2 & -f_3 \\ 0 & -f_3 & f_2 \end{pmatrix}. \quad (23)$$

Correspondingly, for the  $\text{Ni}^-$  ion displaced into  $(0x_10)$ ,  $(0 - x_10)$ ,  $(00x_1)$ ,  $(00 - x_1)$ , we have

$$\hat{f}^3 = \begin{pmatrix} f_2 & 0 & f_3 \\ 0 & f_1 & 0 \\ f_3 & 0 & f_2 \end{pmatrix}, \quad (24)$$

$$\hat{f}^4 = \begin{pmatrix} f_2 & 0 & -f_3 \\ 0 & f_1 & 0 \\ -f_3 & 0 & f_2 \end{pmatrix}, \quad (25)$$

$$\hat{f}^5 = \begin{pmatrix} f_2 & f_3 & 0 \\ f_3 & f_2 & 0 \\ 0 & 0 & f_1 \end{pmatrix}, \quad (26)$$

$$\hat{f}^6 = \begin{pmatrix} f_2 & -f_3 & 0 \\ -f_3 & f_2 & 0 \\ 0 & 0 & f_1 \end{pmatrix}. \quad (27)$$

For the  $\text{Ni}^-$  ion in the  $(\frac{1}{4} - x_1, \frac{1}{4}, \frac{1}{4})$  site, we have  $\hat{f}^7(\frac{1}{4} - x_1, \frac{1}{4}, \frac{1}{4}) = \hat{f}^1$  because the corresponding sites are connected by the centre of symmetry in  $(\frac{1}{8}\frac{1}{8}\frac{1}{8})$ . Similarly,  $\hat{f}^8(\frac{1}{4} + x_1, \frac{1}{4}, \frac{1}{4}) = \hat{f}^2$ ,  $\hat{f}^9(\frac{1}{4}, \frac{1}{4} - x_1, \frac{1}{4}) = \hat{f}^3$ ,  $\hat{f}^{10}(\frac{1}{4}, \frac{1}{4} + x_1, \frac{1}{4}) = \hat{f}^4$ ,  $\hat{f}^{11}(\frac{1}{4}, \frac{1}{4}, \frac{1}{4} - x_1) = \hat{f}^5$ ,  $\hat{f}^{12}(\frac{1}{4}, \frac{1}{4}, \frac{1}{4} + x_1) = \hat{f}^6$ . Experimentally,  $x_1 \approx 0.04$ .

The structure factor of the  $0kl$ ,  $k, l = 2n$ ;  $k + l = 4n + 2$ , reflections, averaged over the possible 48(*f*) sites is

$$\begin{aligned} & \hat{F}(0kl; k, l = 2n; k + l = 4n + 2) \\ & = i \frac{8C_l}{3} f_3 \left[ \sin(2\pi kx_1) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \right. \\ & \quad \left. + \sin(2\pi lx_1) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right]. \end{aligned} \quad (28)$$

We see that the forbidden PDI ATS reflections with  $0kl$ ,  $k, l = 2n; k + l = 4n + 2$ , can appear near the absorption edge of the impurity. Moreover, the  $00l$  reflections occur only owing to the atoms displaced along the  $z$  axis. Obviously, the host Ge atoms are also distorted in this case and the same PDI ATS reflections are possible near the absorption edge of Ge.

## 5. Conclusions

We have shown that the resonant spectroscopy of special ‘forbidden’ reflections could provide a unique method to study those distortions of electronic states that appear owing to thermal vibrations or point defects. The considered effects are very selective because they are sensitive only to the thermal vibrations or defect-induced displacements of resonant atoms; all other atoms give no contribution. The measurements of the scattered intensity of TMI-forbidden reflections may be used to study the temperature dependence of special phonon modes contributing to local symmetry distortions. PDI-forbidden reflections give information about the static displacements and the valence-electron states both of the impurity atoms and of the host atoms. In all the cases, the distorted electronic states are involved in the scattering. Therefore, the study of the energy spectra of forbidden reflections as far as their azimuthal and polarization properties will give information exclusively about the distorted electronic states.

It is crucial for the considered effects that *isolated* point defects occupy randomly a *finite* number of types of atomic sites and correspondingly produce the same number of fixed local distortions of the initial lattice (in this paper, we consider the case with one type of site occupied by impurity atoms). This is valid only for small impurity concentrations. For high defect concentrations, a huge number of types of differently distorted configurations can appear, demanding more sophisticated theoretical treatment; nevertheless, the PDI reflections should exist even in this case.

It is interesting to compare the suggested method with other methods used to study point defects. Different resonant methods like EPR, NMR and EXAFS are widely used to study the local properties of the doped crystals. However, for all of them, the information is averaged over all the orientations of atoms in crystals. In principle, non-forbidden reflections in the XANES region (Templeton & Templeton, 1980, 1985, and references therein) and in the DAFS region (Stragier *et al.*, 1992; Proetti *et al.*, 1999) give information about non-averaged local atomic configurations. However, all the atoms, affected

and not affected by impurities, give their contribution to the diffraction spectra. What we suggest here allows one to study exclusively the atoms affected by impurities and not only their positions but also their distorted electronic states.

Notice that there is a competition between the TMI/PDI contribution (obtained in the dipole approximation) and dipole–quadrupole or higher contributions to the scattering amplitude (for the latter there is no need of thermal motion or point defects). For example, the tensor form of (6) coincides with the tensor form of the dipole–quadrupole contribution to the structure amplitude (Templeton & Templeton, 1994) but in the latter case the structure amplitude should decrease with increasing temperature owing to the Debye–Waller factor. This allows one to distinguish the dipole–quadrupole and TMI contributions to the scattering factor. Therefore, high-temperature measurements are required to clarify the origin of  $0kl$ ,  $k + l = 4n + 2$ , reflections observed near the absorption edge of Ge (Templeton & Templeton, 1994; Colella, 1999). These two contributions may also be distinguished owing to their different energy spectra corresponding to dipole–quadrupole and dipole–dipole transitions. Additional information can be obtained from interference between the dipole–quadrupole, PDI and TMI contributions. The interference between all the contributions, depending on temperature and defect concentrations, can be useful for their separation and for solution of the phase problem.

Above, we have presented several examples to demonstrate how to deal theoretically with the TMI/PDI reflections. The results similar to the *C-15* structure may be obtained for crystals with spinel  $MgAl_2O_4$ -type structures described by the same space group  $Fd\bar{3}m$  with the same metal positions and with oxygen in  $32(e)$  position. Similar situations can be realized in crystals with many space groups, especially cubic. The suggested method may also be useful for more complicated problems. For example, if randomly distributed impurity atoms occupy tetrahedral positions in a crystal with diamond structure and their concentration is small, then there will be no ATS reflections at the impurity absorption edges because of the absence of local anisotropy. However, for larger impurity concentrations or if the impurity atoms tend to produce pairs, the local anisotropy and ATS reflections could appear for the impurity atoms.

In summary, the TMI and PDI reflections could be a useful tool to study the electronic states distorted by thermal vibrations and point defects. Of course, this method can be used only for non-symmorphic crystals with atoms in special positions. However, there are many crystals of suitable types and some of them, being impurity doped, have important technological applications.

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