

X-RAY SPECTROSCOPY OF THERMALLY DISTORTED ELECTRONIC STATES IN CRYSTALS

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We suggest a new type of X-ray spectroscopy which allows to detect the thermal-motion-induced distortions of atomic electronic states in crystals. We show that those distortions can cause extra Bragg reflections (so-called forbidden reflections) and their intensity should grow with temperature increasing. The reason is that the thermal displacements, changing the symmetry of atomic environment, can modify the tensor amplitude of X-ray resonant scattering. In the first approximation, the structure factor of extra reflections is proportional to the reflection vector \mathbf{H} and to the mean-square thermal displacement $\overline{u_j u_k}$ for optical phonons. We demonstrate that the forbidden resonant reflections, observed recently in Ge, could be caused by the thermal motion.

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X-ray resonant scattering is now widely used to study structural and magnetic properties of solids [1,2]. The resonant effects are especially important for additional reflections, which can appear in X-ray diffraction when the energy of the incident radiation approaches to the values required to excite an inner-shell electron to an empty state of outer shells. 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 [3-5]. It was shown that the anisotropy violates the extinction rules, tabulated for glide planes and/or screw axes, and new general extinction rules were found in the dipole approximation [4]. This anisotropy is local and therefore it is allowed even in cubic crystals and in icosahedral quasicrystals [5,6] 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 principle, if ATS reflections are forbidden in the dipole approximation they can be obtained in the dipole-quadrupole or higher approximations [7,8]. ATS reflections have been observed in many crystals and in liquid crystals, they demonstrate very unusual polarization properties (see [9,10] for reviews). From the practical point, the ATS reflections provide us with an instrument for X-ray spectroscopy of the atomic electronic states distorted by crystal fields.

The present paper explores some of the complications in coherent resonant scattering of X-rays that arise when thermal atomic motion is taken into account. Previously the forbidden reflections caused by the asphericity of thermal motion were observed far from absorption edges (a survey may be found in [11]). The latter effect does not violate the glide-planes and screw-axes extinction rules. In contrast, we show that the thermal motion

can change the anisotropy of the resonant scattering and can induce extra reflections violating the glide-planes and screw-axes extinction rules. Thus the spectroscopy of these thermal motion induced (TMI) reflections could provide information about thermally distorted electronic states.

Anisotropy of scattering and thermal atomic motion. In this section we demonstrate schematically how the anisotropy of resonant scattering and the tensor structure factor could be changed by thermal motion. To illustrate the principal idea we will use atomic scattering factors instead of a more rigorous approach based on X-ray susceptibility. The anomalous contribution to the scattering factor of an atom is described by a symmetric tensor, f_{jk} , which depends not only on the X-ray frequency ω but also on the environment of this atom. The resonant part of the tensor scattering factor of the s -th atom in the unit cell can be written in dipole approximation as [2]:

$$f_{jk}^s(\omega, \mathbf{r}^s) = \sum_{a,b} p_a \frac{(E_a - E_b)}{\hbar\omega m} \frac{\langle a | P_j^+ | b \rangle \langle b | P_k | a \rangle}{E_a - E_b + \hbar\omega - i\Gamma/2}, \quad (1)$$

where \mathbf{r}^s is a current atomic position, $|a\rangle$ describes the initial and final electronic states with energy E_a , p_a is a probability to find the atom in the $|a\rangle$ state, $|b\rangle$ describes an intermediate electronic state with energy E_b , $\mathbf{P} = -i\hbar \sum_n \nabla^{(n)}$, the last summation extends over all electrons in the atom.

Tensor f_{jk}^s is a function of \mathbf{r}^s because the intermediate states $|b\rangle$, corresponding to outer shells, depend on atom's environment and, in particular, on the current position \mathbf{r}^s of the s -th atom among other atoms. In fact, it is well known that even small *static* changes of the environment can noticeably change f_{jk}^s . For example, for octahedral symmetry f_{jk}^s should be isotropic. However, in the FeS₂ and Fe₂O₃ crystals, where each iron atom is contained inside a slightly distorted octahedron of sulfur or oxygen atoms, the pronounced anisotropy of f_{jk}^s is observed [12, 13]. The thermal motion produces *dynamic* changes of the environment. For them it is important that $f_{jk}^s(\omega, \mathbf{r}^s)$ is determined by electron subsystem of crystal which is much faster than nuclear motion – the so-called Born–Oppenheimer or adiabatic approximation. Therefore the outer electronic states follow the current atomic configurations. Another important approximation, used implicitly in (1), is that the typical time of X-ray resonant scattering, \hbar/Γ , is much smaller than the typical time of thermal motion. Just because of this we should take into account only the current atomic position \mathbf{r}^s in (1) as if it would be static position (i.e. the atomic position does not change during scattering).

We see that the value of the tensor $f_{jk}^s(\omega, \mathbf{r}^s)$ 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 thermal motion and the symmetry of the resonant scattering amplitude corresponds to the *average* symmetry of the atomic site. 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}^s are functions of \mathbf{r}^s only, i.e. we neglect the thermal motion of neighbouring atoms.

To obtain the tensor structure factor $F_{jk}(\mathbf{H})$ describing the coherent scattering for reflection \mathbf{H} , we should multiply $f_{jk}^s(\omega, \mathbf{r}^s)$ by $\exp(i\mathbf{H}\mathbf{r}^s)$, make a summation over all

atoms and then average over thermal vibrations:

$$F_{jk}(\mathbf{H}) = \sum_s \overline{f_{jk}^s(\omega, \mathbf{r}^s) \exp(i\mathbf{H}\mathbf{r}^s)}; \quad (2)$$

hereafter the bar means thermal averaging.

Actually, it is very difficult to compute $f_{jk}^s(\omega, \mathbf{r}^s)$, therefore we will use a phenomenological approach. We suppose the thermal displacement \mathbf{u}^s ($\mathbf{u}^s = \mathbf{r}^s - \mathbf{r}^{0s}$) from the average position \mathbf{r}^{0s} being small enough so that we can use a tensor expansion of f_{jk}^s and $\exp(i\mathbf{H}\mathbf{r}^s)$:

$$\exp(i\mathbf{H}\mathbf{r}^s) = (1 + i\mathbf{H}\mathbf{u}^s + \dots) \exp(i\mathbf{H}\mathbf{r}^{0s}), \quad (3)$$

$$f_{jk}^s(\omega, \mathbf{r}^s) = (f_{jk}^{0s} + f_{jkl}^{1s}u_l^s + f_{jklm}^{2s}u_l^s u_m^s + \dots). \quad (4)$$

In the right side of (4), all the tensors \hat{f}^{ps} of different ranks are invariant under the "average" symmetry group which coincides with the point group of the atom site. Substitution of (3) and (4) into (2) gives us 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 zero-order term, f_{jk}^{0s} , vanishes owing to symmetry reason. 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 (4). Thus the TMI contribution arises only from those cross terms in (2) which are proportional to $\mathbf{H}\mathbf{u}$ or to higher powers of $\mathbf{H}\mathbf{u}$. Generally, the first non-vanishing term is $i f_{jkl}^{1s} H_m \overline{u_l^s u_m^s}$.

The analysis of (2) provides the following simple recipe for TMI-ATS reflections: only those extinction rules and those restrictions on tensor structure factor, which are found for the general atomic sites [4], are valid. The additional restrictions, found for special sites [5], 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.

Examples. If the resonant atoms are at the sites with cubic point symmetry, then $f_{jkl}^{1s} = f^{1s} T_{jkl}$, 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. Tensor \hat{T} is non-zero only for the 23 and $\bar{4}3m$ cubic groups, where its non-zero components are $T_{xyz} = T_{yzx} = T_{zxy} = T_{zyx} = T_{yxz} = T_{xzy} = 1$. Taking into account that for cubic symmetry $\overline{u_j u_k} = \overline{u^2} \delta_{jk} / 3$, we have $f_{jkl}^{1s} = i f^{1s} T_{jkl} H_l \overline{u^2} / 3$.

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

$$F_{ij}(0kl, k+l = 4n+2) = \frac{8}{3} i f^{1s} \overline{u^2} \begin{pmatrix} 0 & H_z & H_y \\ H_z & 0 & 0 \\ H_y & 0 & 0 \end{pmatrix}. \quad (5)$$

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

If resonant atoms are at special sites of noncubic crystals, there is a variety of the cases when the conventional ATS contribution is absent but the TMI contribution is possible. Let us consider K_2CrO_4 where the resonant Cr atoms are in sites 4(c) of the space group $Pnma$ with the coordinates: (1) $x, 1/4, z$; (2) $-x, 3/4, -z$; (3) $1/2 - x, 3/4, 1/2 + z$; (4) $1/2 + x, 1/4, 1/2 - z$. 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 10 independent components and one of them, f_{xyy}^{1s} , contributes into the structure amplitude:

$$F_{jk}(0k0, k = 2n + 1) = 4iH_y \overline{u_y^2} f_{xyy}^{1s} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (6)$$

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

Discussion and conclusion. 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 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. In this case we should calculate $\overline{u_j u_k}$ taking into account only optical phonons. In Ge crystal, the frequency of optical modes ω_0 changes only slightly with the wave vector and for estimations we can put $\omega_0 = \text{const} = 5 \cdot 10^{13} \text{ s}^{-1}$. In this case,

$$\overline{u_i^2} \sim \frac{\hbar}{2M\omega} \coth \frac{\hbar\omega}{2k_B T}$$

where M is the Ge atomic mass. For high temperature $\overline{u_i^2} \sim k_B T / M\omega^2$, and therefore the structure amplitude of TMI-ATS reflections is proportional to T and to H (for 1000 K $\sqrt{\overline{u_i^2}} \approx 0.06 \text{ \AA}$). More exactly, instead of $iH_m \overline{u_i^s u_m^s}$ we should write

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

Thus, the tensor structure factor stops to grow with T and H and reaches its maximum when $H^2 \sim 1/\overline{u^2}$. The TMI anisotropy should be more pronounced when the amplitude of optical modes is large, for example near structural phase transitions of second order.

Notice, that the tensor form of (5) coincides with the tensor form of the dipole-quadrupole contribution to the structure amplitude [8] but in the latter case the structure amplitude should decrease with temperature growth because of the Debay-Waller factor. This allows 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 Ge¹) [8]. Those two contributions may be also distinguished owing to their different spectra corresponding to dipole-quadrupole and dipole-dipole transitions.

In conclusion, we have shown that the resonant spectroscopy of special "forbidden" reflections could provide a unique method to study those distortions of electronic states which appear owing to thermal deviation from average atomic positions. The considered effect is sensitive only to the thermal vibrations of resonant atoms, all other atoms give no contribution. From the other side, this effect may be used to study the temperature dependence of special phonon modes contributing to local symmetry distortions.

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