Atomic displacement effects in near-edge resonant “forbidden” reflections

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Abstract

A survey of atomic displacement effects in the resonant scattering of synchrotron radiation is presented. It is shown that the dynamical displacements, associated with thermal vibrations, provide the thermal-motion-induced (TMI) “forbidden” reflections, while static displacements (e.g. induced by impurities) provide the point-defect-induced (PDI) “forbidden” reflections. Both kinds of reflections occur owing to perturbation of valent electrons wave functions by atomic displacements. The results of numerical calculations of TMI forbidden reflections in Ge and ZnO are compared with experimental data.

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1. Introduction

The tensor character of X-ray scattering provides a class of important phenomena, which includes the dichroism and excitation of
“forbidden” reflections (see recent reviews [1,2]). This anisotropy is caused by distortions of the valent electron wave functions by crystal fields and, because it has significant value only at X-ray energies just near the absorption edges of chemical elements, it is easily accessible with the synchrotron radiation but not with conventional X-ray sources. Atomic displacements, changing generally the symmetry of atomic environment, can induce an additional anisotropy of the atomic scattering factor and therefore give rise to extra Bragg reflections, otherwise forbidden. This effect could be caused by dynamic displacements (thermal vibrations or diffusion) [3] and/or by static displacements (e.g. displacements induced by impurities [4]). Its quantitative description would be very important for a better understanding of the interaction between phonons and electronic states in crystals. The most spectacular effect in this field is a very strong growth in the forbidden states in crystals. The most spectacular effect in this field is a very strong growth in the forbidden reflections intensity with growing temperature, which was experimentally observed in Ge [5,6] and ZnO [7] and the drastic change of the energy spectrum in ZnO. In this paper we present a survey of theoretical explanations and some numerical simulations of the phenomenon.

2. Scattering factor for near-edge “forbidden” Bragg reflections

To determine the properties of forbidden reflection, one needs to calculate the structure factor \( F_{ij}(H) \). In the present paper we discuss the case when a certain reflection is forbidden both in scalar and dipole–dipole approximations because of symmetry restrictions. However, this forbidden reflection can be excited owing to atomic displacements (violating site symmetry) and owing to the multipole contributions into the scattering amplitude (dipole–quadrupole, quadrupole–quadrupole, etc.). In general, the scattering factor taking into account all these contributions can be written as

\[
F_{ij}(H) = F_{ij}^{\text{TMI}}(H) + F_{ij}^{\text{PDI}}(H) + F_{ij}^{\text{diq}}(H) + F_{ij}^{\text{dq}}(H),
\]

where the first term occurs owing to thermal vibrations, the second appears if there are some impurities or vacancies, distorting the crystal structure, whereas the last two terms can appear even in a perfect lattice due to the dipole–quadrupole and quadrupole–quadrupole contributions. Three terms, \( F_{ij}^{\text{diq}}(H), F_{ij}^{\text{dq}}(H) \) and \( F_{ij}^{\text{PDI}}(H) \), depend slightly on temperature in correspondence with the Debye–Waller factor, but the TMI contribution can strongly grow with temperature in absolute value.

To study the TMI contribution one needs to calculate the structure factor \( \hat{F}_{ij}^{\text{TMI}}(H) \) averaged over thermal vibrations (i.e. over temporary configurations). Because the typical time of X-ray scattering (~10\(^{-17}\) s) is much less than the time of thermal vibrations (~10\(^{-13}\) s), temporary atomic configuration is fixed during the scattering process. Hence, it seems that there is no principal difference between the description of static and dynamic displacements. Nevertheless, the difference exists, because in the dynamical case all terms linear over atomic displacements \( \mathbf{u} \) vanish, while in a static case they can give a contribution to the scattering factor.

Because atomic displacements are small in comparison with interatomic distances, a linear dependence is supposed for the anisotropic part of the atomic scattering factors \( f_{ij} \) induced by atomic displacements from the equilibrium sites. This allows one to obtain the expression for the TMI structure factor as a sum over scattering atoms \( (s) \) and over neighbouring atoms \( (N) \):

\[
\hat{F}_{ij}^{\text{TMI}}(H) = \sum_s f_{ij}^s \exp[iHr(s)] = iH \sum_{s,N} f_{ij}^{sN} u_i(s)u_k(N)
\]

where \( u(s) = r(s) - r_0(s) \) is the displacement of the \( s \)th atom from its equilibrium position \( r_0(s) \), \( f_{ij}^{sN} = \delta f_{ij}/\delta u_k(N) \) is a partial derivative of the dipole–dipole atomic scattering factor of the scattering atom with respect to the \( k \)th component of the \( N \)th neighbouring atom displacement, \( u_k(s)u(N) \) means a correlation function, which describes the cooperative character of thermal movements in crystals (summation over repeated indices is
assumed). The terms with \( s = N \) describe the dependence of the scattering factor on the displacement of the resonant scatterer itself. The other terms in (2) appear owing to the displacements of neighbouring atoms. In principle, thermal dependence of different terms in (2) is also different. In some cases, it gives a possibility to obtain information about correlations of phonon displacements.

The intensity of the forbidden reflections can be represented as

\[
I(E) = |A(E)|^2 e^{i\varphi} + B(E, T)^2 e^{-2M}
\]

where \( A(E) \) is the amplitude of the thermal-independent contribution, corresponding to the multipole terms or PDI mechanism, \( B(E, T) \) describes the TMI amplitude, and \( \varphi \) is their relative phase. In principle, the energy spectrum of the forbidden reflection can be rather complicated owing to interference between all terms in (1). Changing temperature, one can separate \( A(E) \) and \( B(E, T) \), but only comparison of numerical calculations with experimental results allows to separate all the contributions. Below, we describe some numerical results concerning Ge and ZnO, where the thermal dependence of forbidden reflections was observed [5–7].

3. Forbidden reflections in Ge and ZnO

In the last years, great progress in the numerical calculation of atomic scattering factors was achieved. Different computer codes were developed, which allow one to calculate the atomic scattering factors both with the muffin-tin approximation (KXDQ [8], FEFF8 [9,10]) of crystal potentials and with full potentials (FDMNES [11] and PARATEC [12,13]). In the present paper the simulations were made with FDMNES code [11], which allows one to fulfill both kinds of calculations.

The numerical calculations of TMI reflections need a theoretical model, which allows one to simulate the thermal effect. The simplest model is the model of independent displacements randomly directed in space [14]. This model, however, does not take into account the correlation of atomic movements, which is essential for Ge [16]. It was shown in Ref. [6] that four first neighbours give essential contribution to the forbidden reflection intensity. Further it was shown that both the displacement of the resonant atom itself together and the displacements of its neighbours are essential for the adequate TMI reflection description. Taking into account both contributions, in Ge the structure factor can be written as

\[
F(006)_{xy} = -i8H_c[L + M(T)]u_z^2
\]

where \( L = f_{xyz}(0) = \delta f_{xy}/\delta u_z(0) \) does not depend on temperature, but \( M(T) = 4f_{xyz}(1)u_z(1)u_z(0) + 8f_{xxy}(1)u_x(1)u_y(0) \) is a thermal-dependent part. In the absence of atomic correlations only the term \( L \) remains in square brackets, which corresponds to a linear growth of \( F(600) \) at high temperatures. Correlations of atomic displacements correct this dependence, providing more slow growth of the scattering factor, because the sign of \( M \) is opposite to the sign of \( L \).

Numerical calculations have shown that the dipole–quadrupole term is small in Ge, so it practically does not influence the energy spectra at different temperatures. The tensor components \( f_{ik} \) were simulated with the help of the FDMNES code and then put into Eq. (4). The results for 30, 300 and 700 K are represented in Fig. 1. These
results better fit the experimental data than those obtained with the model of independent random displacements [14,15]. The calculations made with the help of XKDQ code have also shown that correlations of atomic movement in Ge essentially influence the thermal behaviour of forbidden Bragg reflection in Ge.

Contrary to Ge, in ZnO the dipole–quadrupole contribution to the 115 forbidden reflection is not so small. Moreover, it dominates at low temperatures. At room and higher temperature, it is compared with the TMI contribution. The quadrupole–quadrupole term, which is absent for the 006 reflection in Ge, also differs from zero in ZnO, and must be taken into account. So, the interference between three terms in Eq. (1) essentially affects the energy spectra, providing their change at various temperatures. Because in ZnO the phonon vibration modes participating if the formation of the \( hhl, l = 2n + 1 \) forbidden reflections are two-dimensional, the calculations have used the atomic displacements representation as a sum of phonon modes [17]. Fig. 2 shows the absolute value of the structure factor anisotropy for the 115 “forbidden” reflection induced by different modes in ZnO. The \( E_{2l} \) mode spectrum is different from the other two modes and this allows, in principal, to distinguish contributions of the different modes.

4. Conclusions

It is shown that synchrotron radiation is a unique tool to study the TMI/PDI “forbidden” reflections induced by distortions of electron states. Such reflections are weak and cannot be studied with conventional radiation sources. The existence of thermal-dependent and thermal-independent parts in the reflections intensity allows one to separate physically different contributions to forbidden reflections. The numerical simulation performed here for Ge and ZnO demonstrates quantitative coincidence with experimental data and allows one to obtain important physical information.

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References
