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# Numerical simulation of the forbidden Bragg reflection spectra observed in ZnO

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#### Abstract

Thermal motion induced (TMI) scattering is a unique probe of changes in electronic states with atomic displacements in crystals. We show that it provides a novel approach to extract atomic correlation functions. Using numerical calculations, we are able to reproduce the temperature-dependent energy spectrum of the 115 'forbidden' Bragg reflection in ZnO. Our previous experimental studies showed that the intensity growth of such reflections over a wide range of temperatures is accompanied by a dramatic change in the resonant spectral lineshape. This is the result of the interplay between the temperature-independent (TI) and temperature-dependent TMI contributions. Here, we confirm that the TI part of the resonant structure factor can be associated with the dipole–quadrupole contribution to the structure factor and show that the temperature-dependent dipole–dipole tensor components to the structure factor. By fitting the experimental data at various temperatures we have determined the temperature dependences of autocorrelation  $\langle u_x^2(\text{Zn}) \rangle$  and correlation  $\langle u_x(\text{O})u_x(\text{Zn}) \rangle$  functions.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Modern synchrotron radiation sources allow the study of a wide range of interesting and often complex phenomena related to the anisotropic absorption, scattering, and diffraction of x-rays near absorption edges. Resonant x-ray scattering (RXS) [1-5] has become, in the last two decades, a popular method for studying local properties of crystals. 'Forbidden' reflections in RXS are extremely sensitive both to the state of the scattering atom and to surrounding atoms, and are very selective because they occur only near element-specific Such reflections were first described absorption edges. theoretically in [6, 7] and observed by Templeton and Templeton [8]. To date, 'forbidden' reflections have been studied experimentally in many crystals. They can be considered as a powerful tool for determining important crystal properties like environment-induced distortions of excited

electronic states or details of charge, magnetic, and orbital ordering in solids [1, 9, 10].

The sensitivity of RXS to local anisotropy arises from multipole electronic transitions and is hence described in terms of scattering tensors of various rank. The strongest contributions to pure resonant reflections are provided by dipole-dipole scattering (the electric dipole approximation). Beyond this, there are numerous physical phenomena contributing to the resonant reflections. Higher order contributions, such as dipole-quadrupole [11-13] or quadruple-quadrupole [9, 14] become important when the dipole-dipole contribution vanishes due to symmetry. Contributions associated with thermal vibrations (thermal motion induced, or TMI effect) and point defects were predicted in [15, 16]. The TMI effect can be observed when the dipole-dipole contribution to the forbidden reflections associated with the average crystal structure vanishes, but in fact the symmetry of the resonant atomic sites is violated owing to the atomic thermal displacements. Forbidden reflections

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arising from TMI effect have been observed in Ge [21–23], ZnO [24] and GaN [25].

The possibility of forbidden reflections caused either by TMI or dipole-quadrupole scattering were first predicted by phenomenological considerations, which were based on the symmetry properties of the atomic scattering tensor and rather simple models of atomic vibrations. Despite its simplicity, this approach allowed for a qualitative description of not only the azimuthal dependence of forbidden reflections (the variation in intensity with rotation about the scattering vector) but also of their thermal behavior. The remarkable increase with temperature of the h00, h = 4n + 2 forbidden reflections in Ge and the hhl, l = 2n + 1 forbidden reflections in ZnO, contrary to the usual decrease of 'allowed' (normal) reflections, show that the TMI mechanism plays the dominant role in the excitation of such reflections. This phenomenological approach, as used in [21, 22, 24], explains the main features of the reflections and considers interference between dipolequadrupole and TMI contributions to the structure factor tensor.

The phenomenological approach to anisotropic resonant diffraction is surprisingly robust; however, a quantitative interpretation of the experimental spectra requires numerical simulation of the various resonant scattering mechanisms. It is very important that, unlike the traditional x-ray optics, the atomic x-ray scattering factor near absorption edges depends on its environment, which is taken into account in the theory by considering multiple electron scattering by surrounding atoms. The construction of a microscopic theory of resonant anisotropic scattering encounters a number of difficulties associated mainly with the necessity of introducing into consideration electronic states and potentials that describe the excited state of the system.

While some attempts have been undertaken to make quantitative calculations of the TMI contribution to forbidden reflections at various temperatures using the tensor coefficients calculations [42, 43] and molecular dynamics simulation of the transient atomic configurations [30], they have not completely explained the observed changes in energy spectra with temperature. The aim of the present paper is to clarify the role of zinc and oxygen atomic displacements in the forbidden reflection energy spectra observed in ZnO crystals.

### 2. Theoretical

In the kinematic diffraction theory, which is usually applied to forbidden reflections, the energy dependence of intensity  $I_H(E)$  is determined by the energy dependences of tensor structure factor  $\hat{F}_H(E)$  and absorption coefficient  $\mu(E)$  [26]:

$$I_{H}(E) \sim e^{-2M} |e'^{*} \hat{F}_{H}(E, k, k') e|^{2} / \mu(E)$$
(1)

where H is reciprocal lattice vector of the forbidden reflection, e, k and e', k' are polarization and wavevectors of respectively the incident and diffracted beams (Bragg geometry, with the crystal surface normal to H, was assumed), and  $e^{-2M}$  is the Debye–Waller factor. The absorption coefficient  $\mu(E)$  can be written as a sum of the nonresonant, dipole and quadrupole terms [20]. The last two terms depend on beam polarizations; their anisotropic part usually weaker than their isotropic part (see, for example, discussion in [27]). Although strong linear dichroism has been observed in ZnO [28], we shall ignore this anisotropic part and use the absorption spectrum determined from a powder absorption experiment.

The tensor structure factor  $\hat{F}_{H}(E, k, k')$  depends not only on the energy but also, for dipole–quadrupole and quadrupole– quadrupole scattering, on the wavevectors of the incident and diffracted waves. It is given by the sum over the atomic scattering factors  $\hat{f}(E, k, k')$  of all resonant atoms in the unit cell, taking into account the different orientations of those atoms, and the phase factors corresponding to their positions. The tensor properties of atomic scattering factors near absorption edges have been considered in many studies, using either the Cartesian approach [17, 18] or (equivalently), spherical tensors [3, 9, 19, 20]. In the present paper we shall adopt the Cartesian formalism. Within this framework, the resonant scattering can be written as a sum of the main contributing multipoles, leading to a superposition of tensors of various rank,

$$f'_{jk} + if''_{jk} = \left[ D_{jk} - \frac{i}{2} (k_m I_{jkm} - k'_m I^*_{kjm}) + \frac{1}{4} k'_m k_n Q_{jkmn} \right]$$
(2)

where the summation over repeated indices is implied. Thus, in non-magnetic ZnO crystal, the resonant scattering tensor consists only of the second rank dipole–dipole tensor D, the third rank dipole–quadrupole (interference) tensor I, and the fourth rank quadrupole–quadrupole tensor Q, all of them possessing tensor elements that are sensitive to the incident radiation energy. In most cases, the intensity of forbidden reflections is dominated by the dipole–dipole contribution. However, when this contribution vanishes, e.g. due to crystal symmetry, higher order terms play an essential role. It was shown earlier that the symmetric part of the time-even dipole– quadrupole tensor gives rise to forbidden reflections in Ge and ZnO [11, 21, 22, 24].

It is well known that aspherical charge density and anisotropy of atomic thermal vibrations, give rise to the formation of 'quasi'-forbidden reflections, e.g., the corresponding contributions to the 222-type reflections were recorded in the diamond structure [31, 32]. These phenomena do not change the extinction rules due to glide planes and screw axes. Thermal motion of atoms, however, can give rise to the anisotropy of the resonant atomic factor and thus invalid these extinction rules [15, 16]. The atomic scattering tensor  $f_{ik}$  is determined by the atomic electrons, which follows the nuclear motion (so-called adiabatic approximation). Owing to thermal and zero-point motion, each atom is displaced from its average high symmetry position to positions with generally no symmetry. Because the typical time of resonant x-ray scattering is much less than the time of thermal vibrations, the transient atomic configuration is fixed during the scattering process.

To calculate the resonant structure factor we need to carry out the calculations for each transient atomic configuration and then to average over all configurations:

$$F_{ij} = \sum_{s} \langle f_{ij}^{s} \exp i\mathbf{H}\mathbf{r}^{s} \rangle.$$
(3)



Figure 1. ZnO unit cell.

where the sum is over all resonant atoms in the unit cell. In the presence of small atomic displacements the transient atomic scattering tensor can be written as follows:

$$f_{ij} = f_{ij}^0 + \sum_{p=0}^N f_{ijk}^p u_k^p,$$
(4)

where  $f_{ij}^0$  is an atomic scattering tensor corresponding to the average atomic position,  $f_{ijk}^p$  is a correction to the average atomic tensor provided by the *p*th atom displacement, p = 0 corresponds to the resonant atom itself, and *N* is a number of neighboring atoms, whose displacements influence significantly the resonant atomic tensor. This model was successfully used to describe the thermal growth of the 006 reflection in Ge [30, 33]. One can insert (4) into (3), and taking into account that  $\mathbf{u}^p = \mathbf{r}^p - \mathbf{r}_0^p$ , we obtain the dipole–dipole contribution to the atomic tensor which (remarkably) does not vanish after averaging and is responsible for TMI effect.

#### 3. Pure resonant reflections in zinc oxide

Zinc oxide has a wurtzite structure described by the space group  $P6_3mc$ . Zn and O atoms lie on 2(b) positions with 3msymmetry (figure 1). Each Zn atom is surrounded by an oxygen tetrahedron, whose apical length (1.985 Å) differs slightly from other distances (1.973 Å). The temperature behavior of ZnO, such as its thermal expansion and its Debye–Waller factor  $e^{-2M}$ , was studied both experimentally [34] and using *ab initio* calculations [35]. For the calculations below, we shall use the structural parameters reported in [34]. At room temperature they are:  $\mathbf{a} = 3.2499$  Å,  $\mathbf{c} = 5.2065$  Å, u = 0.3819 (*u* is the apical length of the Zn–O tetrahedra, i.e. the *z* coordinate of oxygen atoms, in crystallographic cell units). Phonon spectra in wurtzite have also been well studied [36–40]. Below we shall use these data for the simulation of resonant forbidden reflections.

The 115 forbidden reflection in ZnO was studied at various temperatures in [24]. It was found, that its energy spectrum varies strongly with temperature. Not only does its intensity increase, but also the shape of the spectrum changes dramatically. A simple theoretical model was used in [24]

to describe the phenomenon, with structure factor that can be written:

$$I(\mathbf{H}) = \left| A(E) \mathrm{e}^{\mathrm{i}\Phi(E)} + B(E) \coth\left(\frac{\hbar\omega_0}{2kT}\right) \right|^2 \mathrm{e}^{-2M}, \quad (5)$$

where A(E) and B(E) represent energy-dependent scalar amplitudes for the temperature-independent (TI) and TMI scattering components.  $\Phi(E)$  is the relative phase angle between the two components. All these quantities are assumed to be independent of temperature. A single low-lying optical phonon mode of energy  $\hbar\omega_0 = 12.4$  meV was assumed at the  $\Gamma$ -point and it was pointed out that a change in the  $\hbar\omega_0$  value is strongly correlated with the scaling of *B*. This model describes the experimental results well, but the phase factor  $\Phi(E)$  looks nontrivial. Below we shall use numerical calculations to fit the energy spectra and establish the thermal growth of the TI and TMI contributions. Both contributions provide the same azimuthal dependence of the reflection intensity  $I_H$ , therefore we shall compare the energy spectra of zinc oxide at various temperatures for fixed azimuthal angle.

Below all tensors are written in the Cartesian framework [29] with z along the **c**-axis, x along the **a**-axis and y in the mirror plane. The 3m symmetry of the Zn site provides the diagonal uniaxial form of the dipole–dipole tensor atomic factor, which cancels out at the forbidden reflections. In [24] it was shown that the structure factor of the *hhl* forbidden reflection contains only one nonzero component and can be written as:

$$F_{ij}(hhl) \sim h(\delta + \Sigma_{m=1}^5 f_m u_m^2) \begin{pmatrix} 0 & 1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 0 \end{pmatrix}$$
(6)

where *m* corresponds to the optical phonon modes at the  $\Gamma$  point of the Brillouin zone,  $\delta$  and  $f_m$  are complex phenomenal coefficients, and  $u_m^2$  are the correlation functions.

It is important to note that, not only displacements of the resonant atom itself influence the resonant atomic factor of Zn, but also displacements of neighboring atoms give significant contributions. Among the five optical modes at the  $\Gamma$  point, two of them describe atomic vibrations along the *c*-axis, and the three others in the *ab*-plane. The vibration modes along the c-axis respect the 3m symmetry and hence do not enable the dipole-dipole contribution. Atomic displacements in the mirror plane do not contribute to TMI either and thus only displacements along a are relevant [43]. When we displace either Zn atom itself or the neighboring atoms along the aaxis, the tensor component  $f_{xy}^{dd}$  appears. We have calculated its contribution numerically using the FDMNES code [41] which is well suited to RXS studies. The FDMNES code does not allow direct calculation of the TMI effect, because it is necessary to provide explicitly the transient atomic displacements. These displacements can be obtained using *ab* initio codes for molecular dynamics. First calculations using this approach were recently made [30] and gave satisfactory results up to room temperature. Nevertheless it is not clear in such approach which vibration modes dominate the TMI effect. In the present paper we shall analyze the forbidden



**Figure 2.** Real and imaginary parts of  $f_{xy}^{dd}$ , which appear owing to the Zn and O displacements along *x*-axis equal to 0.001 of the lattice parameter *a*. The dipole–quadrupole component  $f_{xyx}^{dq}$ , calculated for equilibrium atomic position, is also shown.

reflection spectra reconstruction using the calculation of the tensor structure factor components.

We have calculated those contributions to the tensor components  $f_{xy}^{dd}$ , which appear owing to small displacements along the *x*-axis ( $u_x = 0.001a$ ) of the resonant atom itself, the four surrounding oxygens and the twelve zinc atoms at the second coordination sphere. This way we have calculated the derivatives  $\frac{\partial f_{xy}^{dd}}{\partial u_x^2}$  needed for the TMI effect. The real and imaginary parts of these contributions are shown in figure 2. In the same figure we show the real and imaginary parts of the dipole–quadrupole (TI) contribution to the atomic scattering tensor, which provides non-vanishing components to the F(hhl).

The FDMNES code at first calculates the matrix elements describing the electron transition from the ground to the excited state, which is then convoluted with the energy denominator depending on the excited state width  $\Gamma(E)$ . To determine  $\Gamma(E)$  for ZnO we have fitted the absorption energy spectrum (see figure 3).

To compare the calculations with the experimental spectra of 115 reflection, it is necessary to take into account the absorption (see (1)). For simplicity the experimental value of  $e^{2M}I(\mathbf{H})\mu(E)$  was compared with  $|F(\mathbf{H})|^2$ , which was calculated using the FDMNES code. Figure 4 shows experimental data of the variation of  $e^{2M}I(\mathbf{H})\mu(E)$  for the 115 reflection with temperature. We aim to reproduce not only the thermal growth, but also the strong modification of the lineshape with temperature.

# 4. Fitting the 115 reflection energy spectrum at various temperatures

In [42] it was assumed that the displacement of Zn can be represented as the sum over various optical modes. However, the resonant atomic tensor is affected not only by displacements of the resonant atom itself, but also by displacements of the surrounding atoms. In [42] an attempt



Figure 3. Absorption: experiment versus FDMNES calculation.



**Figure 4.** Temperature dependence of  $e^{2M} \mu I (hkl) \sim |F(\mathbf{H})|^2$  for the 115 reflection obtained from the experimental data.

to take into account oxygen displacements was made. It was shown that three optical vibration modes mainly influence the forbidden reflection spectrum. Their contributions to the structure tensor factor component at various temperatures were in agreement with the mode frequencies. Nevertheless, this approach took into account only the  $\Gamma$  point, while other points of reciprocal space can also give a contribution to the autocorrelation and correlation functions. Below we shall not suppose any definite model for atomic vibrations, but try to determine the correlation function behavior with temperature using the experimental results.

We have carried out computer simulations using FDMNES in which we have displaced Zn itself, the four surrounding oxygen atoms and the next Zn atoms. FDMNES calculations confirm the linear dependence of the resonant atomic tensor on atomic displacements given by (4). We discovered that most of the contribution to the TMI amplitude comes from the displacements of the absorbing atom itself and from the three surrounding oxygen atoms in the basal plane of the tetrahedron. The fourth oxygen atom, which lies on



**Figure 5.** The correlation functions  $\langle u_x^2(\text{Zn}) \rangle$  and  $\langle u_x^2(\text{O}) \rangle$  obtained in [35] and [34] and the thermal growth of the mean square displacement corresponding to the low optical mode.

the same threefold axis as the resonant atoms, gives a very small contribution to the vibration-induced anisotropy. The next-shell Zn atoms were found to have little effect too. So, there is a very limited number of atoms, whose displacements essentially influence the resonant atomic tensor. Next, we calculate the non-vanishing component of the tensor structure factor as follows:

$$F_{xy}(115) = 2e^{-M} \left[ f_{xyx}^{dq} + \langle u_x^2(\mathbf{Zn}) \rangle \frac{\partial f_{xy}}{\partial u_x(\mathbf{Zn})} + \Sigma_{p=1}^3 \langle u_x(\mathbf{Zn}) u_x^p(\mathbf{O}) \rangle \frac{\partial f_{xy}}{\partial u_x^p(\mathbf{O})} \right].$$
(7)

The autocorrelation functions  $\langle u_i^2 \rangle$  were studied in many papers [34, 35]. In figure 5 the autocorrelation functions  $\langle u_x^2(Zn) \rangle$  and  $\langle u_x^2(O) \rangle$  calculated in [35] and measured experimentally [34] are shown. The thermal growth corresponding to the low-energy phonon mode is also given for comparison.

It is difficult to separate those parts of the correlation functions which correspond to optical vibrations alone. It is known, that in the low-energy  $E_{21}$  vibration mode the amplitude of Zn vibrations is larger than the oxygen vibration while for  $E_1$  and  $E_{2h}$  the situation is opposite. Because the ratio of these amplitudes is known, the correlation functions  $\langle u_x(O)u_x(Zn)\rangle$  can be determined. Nevertheless, there is an uncertainty in the decomposition of the mean square displacements into the parts corresponding to each mode at various temperatures, leading to difficulties in using for direct calculations. Consequently, to fit the experimental data we assume the following expression for the structure factor component:

$$F_{xy}(115) = 2e^{-M} \left[ f_{xyx}^{dq}(E) + V_{ZnZn}(T) \frac{\partial f_{xy}(E)}{\partial u_x(Zn)} + V_{OZn}(T) \Sigma_{p=1}^3 \frac{\partial f_{xy}(E)}{\partial u_x^p(O)} \right]$$
(8)

where  $V_{ZnZn}(T)$  and  $V_{OZn}(T)$  do not depend on *E*, but vary with temperature. The dipole–quadrupole term is associated with thermally independent part. In fact, it is not completely

independent of temperature. Calculations using the molecular dynamics simulation of the displaced atomic sites have shown that the dipole–quadrupole term slightly decreases with temperature (more strongly than it would be expected from the Debye–Waller factor). In simulations, we assume that it decreases linearly, so that  $f_{xyx}^{dq}(800 \text{ K}) = 0.9 f_{xyx}^{dq}(20 \text{ K})$ . Calculations also show that the sum over three oxygen atoms does not depend significantly on the displacement direction and can be described by only one energy-dependent function.

Taking into account all known coefficients in equation (5) we can find the ratio between the correlation functions and the fitting coefficients:  $V_{ZnZn}(T) = 780\langle u_x^2(Zn) \rangle$ ,  $V_{OZn}(T) = 780\langle u_x(O)u_x(Zn) \rangle$ . The Debye–Waller factor was fitted in accordance with [34]. In [24], there were three energy-dependent parameters, which may be varied to fit the 115 reflection energy spectra at various temperatures. There are only two fitting parameters,  $V_{ZnZn}(T)$  and  $V_{OZn}(T)$ , in our present analysis and they are physically quite well determined. The ratio  $V_{ZnZn}(T)/V_{OZn}(T)$  is mainly responsible for the spectral shape, while their absolute values determine the peaks intensity. Figure 6 shows the spectral fits of the 115 reflection for various temperatures in a wide range.

Figure 7 shows the TMI contribution to the 115 reflection intensity versus temperature together with the dipole-quadrupole (temperature-independent) term. It follows from this picture that the TMI contribution not only grows with temperature, but its shape also changes, only slightly. Let us note that the phenomenological parameters A(E) and B(E) from [24] look very similar to the absolute values of respectively the dipole-quadrupole and the TMI terms from (8). Nevertheless, in the present paper these values were calculated using the FDMNES code and possess a specific physical meaning. The TMI contribution can be divided into two parts, one corresponding to the displacements of the resonant Zn atom and the other to the correlated movement of Zn and surrounding oxygen atoms. This allows us to obtain the correlation functions by fitting the measured diffraction intensities.

Figure 8 shows the correlation functions  $\langle u_x^2(\mathbf{Zn}) \rangle$  and  $\langle u_x(O)u_x(Zn)\rangle$  corresponding to the best values  $V_{ZnZn}(T)$ and  $V_{OZn}(T)$  obtained from fit to the 115 intensity fitting at various temperatures. We can compare the correlation function  $\langle u_r^2(\text{Zn}) \rangle$  with the literature [35] and experimental results [34]. Naturally, the values of the correlation functions are less than given in [34, 35], because the TMI mechanism involves mainly the optical phonon vibrations and they are less sensitive to the acoustic modes. We see that the correlation function  $\langle u_x^2(\mathbf{Zn})\rangle$  is in good agreement with the coth $(\frac{E_{21}}{2kT})$  model which corresponds to the low-energy phonon mode. This supports our earlier model describing the temperature dependence of the 115 reflection [24]. Nevertheless, the oxygen vibration must clearly be taken into account. Between 200 and 400 K the growth of the contribution from oxygen vibrations is not monotonic. There is an interplay between the contributions to the TMI part of the scattering factor corresponding to the zinc and oxygen vibrations, allowing a good fit to the energy spectrum in this temperature interval.



Figure 6. Integrated intensity of the 115 reflection at various temperatures: experiment versus calculation. From top to bottom and from left to right: 50, 100, 200, 300, 500, 600, 800 K.

From figures 3 and 6 we see that our calculations provide a good description of the main features of the energy spectrum and its temperature dependence, but finer details of the spectral shape are not reproduced. The calculated curves look smoother than the measured ones. There are several possible reasons for this discrepancy, including: (1) neglect of the second neighbor displacements, which contribute to the resonant scattering tensor; (2) the application of the multiple scattering technique and muffin-tin approximation for crystal potential, which are more convenient to use. The FDM approach using full potential can in principle improve the results, but the model is very sophisticated and CPU-intensive; (3) the uncertainty in the determination of the excited state parameters, like  $\Gamma(E)$ . In the FDMNES code, the excited state energy levels are convoluted with an arctangent function. It is a reasonable approximation, but it smoothes sharp features drastically, and it is impossible to optimize, simultaneously, the general shape and detailed features. The convolution parameters we used were obtained from absorption spectra. It may be possible to find better parameters to reproduce the fine features, but it would not change significantly the conclusions relating to the correlation functions. The fits we present here describe satisfactorily the main features of the energy spectra of the 115 forbidden reflection and their temperature dependence,



**Figure 7.** Thermal motion induced contribution to the 115 reflection intensity growing with temperature and temperature independent (dipole–quadrupole) term.



**Figure 8.** Correlation functions obtained from the 115 reflection intensity fitting in comparison with the results of the paper [34] and with the growth corresponding to the low-energy vibration mode.

allowing us to make conclusions about the TMI contribution to the resonant atomic tensor and to extract correlation functions.

#### 5. Conclusions

Resonant x-ray diffraction in ZnO was studied over a wide range of temperatures. Owing to the change of the atomic scattering tensor during thermal vibrations the energy spectrum of the 115 forbidden reflection varies strongly with temperature. The resulting spectral lineshape arises from the complex interplay between several contributions to the structure factor, one being thermally independent and others thermally dependent. Theoretical calculations using the FDMNES code allow us to conclude that the temperature-independent term can be classified as dipole–quadrupole while the thermal-dependent terms are provided by the additional contributions to the resonant atomic factor induced by displacements of Zn and its three nearest oxygen ions.

The fits of the experimental spectra permit the separation of each of these contributions and therefore the determination of the autocorrelation function  $\langle u_x^2(\text{Zn})\rangle$  and correlation function  $\langle u_x(\text{O})u_x(\text{Zn})\rangle$ . The results are in good agreement with the data known from the scientific literature. We have therefore demonstrated that the temperature dependence of forbidden Bragg reflections can give valuable information about the optical phonon vibrations in crystals, and that the phenomenological description of TMI has a sound physical basis.

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