Temperature-dependent forbidden resonant x-ray scattering in zinc oxide

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We have measured the resonance spectrum of glide-plane forbidden x-ray diffraction in hexagonal ZnO as a function of temperature. This is the only method to observe deformations of the electronic states caused by thermal atomic motion. The results provide the first evidence for a complex line shape in the spectrum of thermal-motion-induced scattering and the first observation of a dramatic change in resonance spectrum with temperature. The measurements are in agreement with a phenomenological model, based on a combination of constant (most probably dipole-quadrupole) and temperature-dependent amplitudes. This model provides a means of separating the two components, including their relative phase.

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Resonant x-ray diffraction signals at the positions that are exactly forbidden by glide-plane or screw-axis selection rules have received a great deal of attention in recent years. Since such signals vanish in the case of a scalar scattering response, the technique has played a key role in identifying orbital anisotropy in, for example, manganites and other strongly correlated electron systems.¹ Most of these studies have exploited the coupling of the photon polarization to dipolar anisotropy (described by a second-rank tensor) in order to reduce the symmetry of the scattering system. For many materials, however, the crystal symmetry is such that even dipolar anisotropy cancels in the calculation of structure factors, and the lowest-order residual scattering is described by third- or fourth-rank tensors. These effects have been observed experimentally,²⁻⁴ and attributed to (electric) dipole-quadruplole (E1E2) and pure quadrupole (E2E2) resonances, respectively.

The study of resonant diffraction is important not only for orbital ordering but also for determination of atomic positions of resonant atoms and of their local environment. However, the most important application is a spectroscopy of excited electronic states in crystals, hybridization of different orbitals, etc. While the ground-state electronic structure can be quantitatively described by *ab initio* methods, the environment-induced distortions of the exited electronic states is still a difficult problem both for theory and experiment. The "forbidden" resonant diffraction is much more sensitive to tiny details of the distortions than absorption spectroscopy. This is because the latter is averaged over all the atoms in the unit cell, whereas the former is a differential method that is directly sensitive to the *change* in resonance response with atomic position.

Of special significance to this work is the series of studies of germanium,⁵⁻⁸ pioneered by Templeton and Templeton,² who observed a sharp resonance close to the Ge-K edge, which was found to be consistent with the symmetry properties of a third-rank scattering tensor. Interpretation was given in terms of a mixed dipole-quadrupole resonance, allowed due to the *p*-*d* hybridization in the conduction band.^{2,9} Recently, a second mechanism has been proposed,¹⁰ and observed in germanium,^{5,7,8} whereby a third-rank scattering tensor arises from small thermal displacements from the nominal sites of high symmetry. While the temperature dependence of the resonant scattering in germanium does indeed show convincing evidence for two competing processes, i.e., a temperature-independent (TI) part, probably dominated by E1E2 events, and a thermal-motion-induced (TMI) part, the spectra for each process are surprisingly similar, and there is very little variation in the spectral line shape.

Since TMI scattering arises from the relative displacement of adjacent atoms, its strength depends crucially on the thermal population of optical phonon modes. The search for suitable materials in which to study this effect is, therefore, governed by the requirements for: (1) a suitable space group, which includes glide-plane and/or screw-axis symmetry, (2) a site symmetry such that forbidden reflections have no contribution from anisotropic E1E1 scattering, (3) an absorption edge resonance at a wavelength suitable for crystal diffraction, (4) a low-lying optical phonon mode, and (5) a high quality single crystal sample. ZnO, which crystallizes with the wurtzite structure (space group $P6_3mc$, No. 186) and has an optical phonon mode of energy 12.4 meV at the Γ -point,¹¹ satisfies the above requirements. Moreover, it is of considerable interest as a material for optics and spin electronics, and is commercially available as a substrate crystal.

The study of electronic systems in perturbed or excited states is one of the great challenges for the coming decades, towards which thermal-motion-induced scattering can play a significant role. The combination of experimental and theoretical studies of forbidden reflections should shed light on a number of important aspects of electronic structure, including hybridization, the evolution of electronic states with nuclear position, and the validity of the Born-Oppenheimer approximation. The x-ray diffraction intensity for weak scattering can be written, for a fixed geometry, in terms of the electric field components of the incident ($\hat{\varepsilon}$) and scattered ($\hat{\varepsilon}'$) photon, and a scattering matrix *F*:

$$I \propto |\hat{\varepsilon}'^* F \hat{\varepsilon}|^2. \tag{1}$$

The matrix for TMI scattering is derived from the third-rank structure factor tensor by projecting onto the scattering vector.⁷

An important aspect of this work is that, for materials that crystallize with wurtzite structure (site symmetry 3m) the third-rank scattering tensors for E1E2 and TMI processes possess *precisely* the same elements, and are thus experimentally distinguishable only via their temperature dependence. While this is also true in germanium, it is not generally the case as the E1E2 tensor can contain terms that are antisymmetric with respect to the polarization vectors, while the TMI tensor is always symmetric. The 3m site symmetry also allows second-rank dipolar anisotropy, but this anisotropy is the same for all the equivalent atoms and, hence, it contributes only to the anisotropy of allowed reflections and the absorption coefficient.

For either atom type of the wurtzite structure, for the *hhl* (l=odd) glide-plane forbidden reflections, the resulting scattering matrix is of the form similar to that found for Ge:⁷

$$F(hhl) \propto h \left(\delta + \sum_{m=1}^{5} f_m u_m^2 \right) \left(\begin{array}{ccc} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{array} \right), \qquad (2)$$

where the *x*, *y*, and *z* axes are parallel to the crystal mirrorplane, glide-plane, and sixfold axes, respectively; δ and f_m are complex phenomenological coefficients corresponding to dipole-quadrupole² and TMI scattering channels; and u_m^2 are the correlations in atomic displacements of the closest Zn and O neighbors. According to the site symmetry, there are five correlation functions u_m^2 (two of which correspond to relative displacements parallel and perpendicular to the threefold Zn-O bond and remaining three correspond to the bonds in the equivalent mirror planes). From Eq. (2) it is clear that the reflections of interest will be of the form *hhl*, with *l*=odd and *h*≠0. One cannot infer that the scattering amplitude will simply scale with *h*, however, as there are a number of geometrical factors (the azimuthal angle, polarization, etc.).

The experiments reported here were carried out on the XMaS UK CRG beamline at the European Synchrotron Radiation Facility. The bending-magnet beamline utilizes a toroidal focusing mirror, and a Si 111 monochromator with energy resolution, for the present setup, of ~1.6 eV. The sample was a large $(10 \times 10 \times 1 \text{ mm})$ plate, supplied by MaTecK GmbH, which was attached to a 50–800 K cryofurnace, mounted on the Eulerian cradle of a large multiaxis diffractometer. Photon polarization was perpendicular to the scattering plane. The absorption spectrum was measured from a thin ZnO powder, in order to apply absorption corrections to the diffraction data. Anisotropy in the absorption was assumed to be negligible, based on preliminary dichro-



FIG. 1. (Color online) The ZnO 115 absorption-corrected resonance spectrum near the Zn K-edge, at temperatures of 59 and 800 K. Total absorption is shown by the solid line.

ism measurements on a thin crystal sample, and the absence of any obvious spectral variation with azimuthal angle.

One of the most severe complications with measurements of weak scattering with integer Miller indices is contamination by multiple scattering. Fortunately, the high quality of the sample (the rocking-curve widths were $\sim 0.01-0.02^{\circ}$) meant that the majority of such features were very sharp, and easily avoided by performing a modest azimuthal rotation. Azimuthal angles were kept close to 41° for most of the reported measurements (zero corresponds to the 001 vector lying within the scattering plane). This value was chosen to be roughly in the center of the accessible range (which was limited by the fact that the surface normal was along the 001 vector), to give a strong resonant intensity, and be relatively free from multiple scattering. For extended energy scans, it was necessary to combine data sets taken over an azimuthal range of around 6° in order to identify and eliminate contributions from multiple scattering.

Resonant diffraction signals were observed at the 113 and 115 glide-plane-forbidden positions, with the 115 studied in some detail. No clear diffraction intensity was observed at the 003 position, which would require a structure-factor tensor of at least fourth rank. In stark contrast to the results from Ge, we find resonance spectra at high and low temperatures that are complex, extend over more than 30 eV in energy, and are completely different in line shape (Fig. 1). Weaker resonance features extend well beyond the absorption edge (Fig. 2). The evolution of the resonance spectrum with temperature was determined from the measurements at 17 temperatures, ranging from 59 to 800 K. The resulting surface (Fig. 3, top) shows a remarkable array of features: at various photon energies, the intensities, with increasing temperature, are found to fall, to rise, to fall and rise, and to remain almost constant.

In the absence of a theoretical model for the resonant scattering, and in an attempt to separate the TI and TMI components, we have performed a least-squares fit of the measured intensities to a phenomenological two-process model,⁵ via the expression,



FIG. 2. (Color online) The ZnO 115 absorption-corrected resonance spectrum near the Zn K-edge, at temperatures of 59 and 800 K, showing the weak spectral features over an extended energy range.

$$I(E) = \left| A(E)e^{i\phi(E)} + B(E) \operatorname{coth}\left(\frac{\hbar\,\omega_o}{2kT}\right) \right|^2 e^{-2M},\qquad(3)$$

where A(E) and B(E) represent energy-dependent (scalar) amplitudes for the TI and TMI scattering components, and $\phi(E)$ is the relative phase angle between the two components. These quantities are assumed to be independent of temperature. The correlations u_m^2 scale with the thermal



FIG. 3. (Color online) ZnO 115 absorption-corrected resonant intensity vs energy and temperature. Top: measured intensities, bot-tom: intensities from a least-squares fit to the model outlined in the text [see Eq. (3)].



FIG. 4. (Color online) The results of the least-squares fit to the model outlined in the text. Errors in the fitted parameters are comparable to the symbol sizes.

population of the optical phonon modes as $\operatorname{coth}(\hbar\omega_m/2kT)$, if one assumes a simple model in which the phonon energy $\hbar\omega_m$ is independent of the wave vector. Obviously, it is impossible to separate the contributions of five correlation modes to the intensity, and in Eq. (3) all the contributions are described by the function $\operatorname{coth}(\hbar\omega_0/2kT)$ with some effective ω_0 . The total scattering intensity is further modified by the Debye-Waller factor e^{-2M} , where *M*, which is a function of momentum transfer, temperature, atomic mass and characteristic (Debye) temperature, is discussed in detail by James.¹² For the present work, we take the average atomic mass \overline{m} = 40.7, and a Debye temperature of 370 K, determined from a crystal structure refinement study.¹³

Equation (3) was found to give a remarkably good fit to the data (Fig. 3), with the maximum difference being only 3% of the peak value. The fit yielded three separate energydependent curves: the TI and TMI amplitudes, A(E) and B(E), and their relative phase, $\phi(E)$. These are shown in Fig. 4. The results for 300 K are shown in Fig. 5, in the form of the relative intensity contributions from pure TMI and TI scattering, and TMI-TI interference scattering. The quality of the fit was found to be relatively insensitive to the value chosen for the optical phonon energy, giving an error interval ranging from 0 to 35 meV. Equation (3) indicates that the low-temperature intensity ($T \sim \hbar \omega_o/2k \approx 72$ K) could be particularly sensitive to the phonon energy, but in this region the TMI contribution is relatively small and very careful measurements are needed. While this effectively rules out the possibility of using the TMI scattering technique to extract precise phonon energies, it does, at least, suggest that the known dispersion in the low-lying optical mode¹¹ and the presence of high energy modes should have only a modest effect on the above analysis, beyond an overall scaling of B(E). The influence of the choice of $\hbar \omega_o$ on the fitted temperature-independent amplitude spectrum A(E) and phase $\phi(E)$ is negligible for all but the highest values within the error interval. All fits were performed with $\hbar \omega_o$ fixed at 12.4 meV. Neglecting the Debye-Waller factor in Eq. (3) led to a significantly worse fit.



FIG. 5. (Color online) The results of the least-squares fit to the model outlined in the text, for T = 300 K, shown in the form of intensity contributions from pure TMI scattering, pure TI scattering, and the TMI-TI interference term. Also shown is the sum of the three terms, superimposed on the experimental values.

One of the most notable features of the data in Fig. 3 (top) is the tendency for the scattering intensity to drop, as the temperature increases from T=59 K, suggesting destructive interference between the TI and TMI amplitudes. This is confirmed quantitatively via the least-squares fit: the phases shown in Fig. 4 lie almost entirely between 90° and 180°. The only exception is a very narrow region around 9.674 keV, where the amplitudes are very slightly constructive. Figure 5 reflects this finding by showing a very strong and predominantly negative interference intensity. The results show that the peak in the measured spectrum at 9.674 keV

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(at T = 300 K) is not due to a peak in either the TMI or TI amplitudes, but results from the sharp drop in the phase angle at that point.

It is interesting that in both Ge and ZnO, the TI and TMI amplitudes are similar in magnitude. As there is no obvious connection between these two physical processes, this may be purely coincidental.

While recent theoretical work on Ge supports the interpretation of the temperature-independent scattering component as arising from E1E2 processes,⁹ one cannot rule out a contribution from pure dipolar scattering, if one takes into account the variation in the scattering tensor with the relative displacement of the scattering center from the nucleus. It is likely, however, that the limited extent of the 1*s* core level involved in the resonance will mean that this contribution is weak.

The results from ZnO are important in several respects. First, they represent convincing evidence for TMI scattering in a material other than Ge, suggesting that the phenomenon is more general than may have been inferred from previous work. Second, unlike Ge, we observe resonance spectra that are complex and change dramatically with temperature. A fuller appreciation of the physical implications of the reported results will require the development of a detailed microscopic theoretical model for both the TMI and E1E2 processes in ZnO. However, the phenomenological model has proved extremely useful in establishing that the intensities can be understood very well with the assumptions that two processes are required, one of which has an amplitude that follows closely the population of the low-lying optical phonon mode, and that the phase between the two amplitudes is independent of temperature.

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