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Temperature-induced distortions of electronic states observed via forbidden Bragg reflections in germanium

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According to the adiabatic approximation, the electronic states of atoms in solids are bound up with thermal atomic motion. As a result, thermal-motion-induced (TMI) anisotropy of x-ray susceptibility can appear for atoms occupying positions with high symmetry. We report evidence for this effect found in the very strong temperature dependence of the 006 forbidden Bragg reflections from a germanium single crystal. The intensity of these reflections increases or decreases drastically as the temperature rises from 30 K to 300 K, in contrast with nonforbidden reflections. It is found that the TMI anisotropy of the structure amplitude scales with the temperature as the mean square of the atomic displacements. This observation is very important for understanding the intricate interplay between phonon and electronic properties of solids.

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Forbidden x-ray reflections, excited exclusively owing to anisotropy of the atomic susceptibility, can be observed in crystals near x-ray absorption edges. Such reflections are referred to as ATS (anisotropy of the tensor of susceptibility) reflections. The ATS can violate the glide-plane and screw-axis selection rules for forbidden reflections so that most of them become nonforbidden. The physical reason for this violation is that the anisotropic susceptibility is not invariant under rotations and mirror transformations. The ATS is related to electronic resonant transitions and is caused by distortions of the electronic states in an anisotropic environment. Therefore reflections of this type provide direct evidence for the distortions of electronic states in crystals.

Up to now much effort has been spent to study the *dynamic* changes of the electronic states during thermal motion, phase transitions, or chemical reactions in solids (there is no need to explain the evident importance of such studies). However, those changes are hardly accessible even with ultrafast optical techniques and the optical probes are often poor indicators of atomic structure. By contrast the x-ray technique developed here, based on ATS reflections, is an effective structural probe sensitive to dynamic changes of local atomic environments. Of course, the time evolution of the distortions cannot be measured in our experiments.

ATS reflections have been observed in a $NaBrO_3$ cubic crystal near the *K* edge of the Br atoms.[1] Then they were studied for many crystals: TiO_2,[2] Cu_2O,[2] Fe_2O_3,[3] etc., and even for liquid crystals.[4] The theory of these reflections was developed first in the dipole approximation[5] and then in higher approximations.[6] It was shown recently that ATS reflections can be excited owing to the orbital ordering in colossal magnetoresistance materials, manganites and vanadite.[7–9] Earlier we studied the ATS scattering from Fe atoms, in pyrite[10] (FeS_2) and magnetite[11] (Fe_3O_4), where the iron atoms are surrounded by slightly distorted octahedra of sulfur and oxygen atoms, respectively (see also a very recent study of magnetite.[12]) The polarization and azimuthal dependences of the measured ATS reflections are in good agreement with a calculation based on electric dipole transitions. In iron pyrite, however, the effects of quadrupole transitions are observed in the pre-edge region.[13] It is of great consequence for the present work that even small deviations from high (octahedral) symmetry produce enough anisotropy for reliable detection of the ATS reflections. This means that the ATS reflections provide a very sensitive tool for studying small distortions of the relevant electronic states.

The ATS reflections should be distinguished from other types of forbidden reflections excited owing to aspherical electron density (like the well-known 222 reflection in diamond-type crystals.[14]) This aspherical density can be caused by atomic bonding or anharmonic thermal motion. The corresponding forbidden reflections are not resonant and they never violate the glide-plane and screw-axis selection rules.

In the present work, we investigate the ATS reflections from a germanium crystal near the Ge *K* absorption edge. (Preliminary results were reported elsewhere[15]). Germanium crystal has the diamond structure and any atomic site has the symmetry of the regular tetrahedron, $\overline{4}3m$. In the dipole approximation, ATS scattering cannot be excited from the Ge atoms, because the second-rank atomic scattering tensor is isotropic under the symmetry. Therefore, the ATS reflections observed from a germanium crystal[16] were presumed to originate from a mixed dipole-quadrupole term in resonant scattering. However, if the thermal motions of the atoms or point defects are taken into account, ATS reflections are predicted to be possible even in the dipole approximation,[17,18] since displacements of the atoms from their average positions violate the site symmetry.

We report here experimental evidence for thermal-motion-induced (TMI) anisotropy in germanium at room temperature and, most surprisingly, even at low temperatures. This means that, in Ge, unlike other crystals, we observe the *dynamic* changes of the electronic states that follow the thermal atomic motion. The same effect was recently observed by other researchers.[19]

The synchrotron experiments were carried out using four-circle diffractometers installed at BL3A and BL4C of the KEK Photon Factory in Tsukuba. Low temperature measurements were carried out at BL4C using a He-cooled refrigerator. In order to avoid the higher harmonic components, the Si (111) double-crystal monochromators of the lines were detuned to produce about 60% of the maximum intensity. The energy resolution of the system was about 1 eV at BL3A and 3 eV at BL4C. The experimental arrangement was the same as that used in previous work.[11,13] The synchrotron radiation at both lines was polarized horizontally so that the incident x-ray beam was σ polarized. A [001] surface was prepared by cutting a single germanium crystal grown by the zone-level method.

In order to obtain the ATS spectrum, the integrated intensity of the $00l, l=4n+2$, forbidden reflections was measured by a θ-2θ scan at each point of incident energy. During the measurement, the azimuthal angle φ was kept constant: $\varphi=45.0°$ for the 002 reflection and $\varphi=44.5°$ for 006. The angles were chosen to avoid excitation of multiple-beam Renninger reflections.

There is no quantitative theory of x-ray anisotropy taking into account thermal atomic motion. However, we can use phenomenological and symmetry considerations of the observed phenomena which allow us to describe the main features and find a typical temperature dependence.[17] In the dipole approximation, the anisotropic x-ray scattering can be described by the anisotropic part of the tensor atomic factor f_{jk} depending on the x-ray energy E and on the atomic position symmetry. In germanium, the atomic position symmetry is $\bar{4}3m$ and therefore $f_{jk}=0$. However, when the resonant atom moves among neighboring atoms or the configuration of neighboring atoms is changed owing to their motion, the symmetry becomes lower, the electronic states of the resonant atoms are distorted asymmetrically, and anisotropy of f_{jk} can appear even in the dipole approximation. It is significant for this phenomenon that changes of the electronic states can follow the changes of atomic configurations (the well-known adiabatic approximation, widely used in the electronic theory of solids). It is also important that the x-ray scattering process is much faster than any changes of atomic configurations.

For the phenomenological description of TMI anisotropy let us suppose that for the sth atom in the unit cell the f^s_{jk} tensor depends only on displacement of this atom, $\boldsymbol{u}^s=\boldsymbol{r}^s-\boldsymbol{r}^s_0$, and not on displacements of neighboring atoms. For displacement of this general type, the symmetry of the atomic position also becomes of the general type, that is, no symmetry at all. Supposing that $\boldsymbol{u}^s$ is small, we can expand f^s_{jk}:

$$f^s_{jk}(E,\boldsymbol{u}^s)=f^{1s}_{jkl}(E)u^s_l+f^{2s}_{jklm}(E)u^s_l u^s_m+\cdots \tag{1}$$

where the tensors $f^{1s}_{jkl}, f^{2s}_{jklm}, \ldots$ should have $\bar{4}3m$ symmetry. For example, $f^{1s}_{jkl}=f^1(E)T_{jkl}$, where $f^1(E)$ is an unknown scalar function of E and the tensor T_{jkl} has the following nonzero components: $T_{xyz}=T_{yzx}=T_{zxy}=T_{xzy}=T_{zyx}=T_{yxz}=1$.

To obtain the resonant tensor structure factor $F_{jk}(E,\boldsymbol{H})$ of the Bragg reflection with the wave vector $\boldsymbol{H}$, we should multiply f^s_{jk} by the phase factor $\exp(i\boldsymbol{H}\cdot\boldsymbol{r}^s)$, make a summation over the unit cell, and average over thermal displacements:

$$F_{jk}(E,\boldsymbol{H})=\sum_s \overline{f_{jk}(E,\boldsymbol{r}^s)\exp(i\boldsymbol{H}\cdot\boldsymbol{r}^s)}; \tag{2}$$

hereafter the overbar means averaging over all possible displacements of atoms (as in the case of a Debye-Waller factor calculation). Because the displacements $\boldsymbol{u}^s$ are small we can expand $\exp(i\boldsymbol{H}\cdot\boldsymbol{r}^s)$:

$$\exp(i\boldsymbol{H}\cdot\boldsymbol{r}^s)=[1+i\boldsymbol{H}\cdot\boldsymbol{u}^s-\tfrac{1}{2}(\boldsymbol{H}\cdot\boldsymbol{u}^s)^2\cdots]\exp(i\boldsymbol{H}\cdot\boldsymbol{r}^s_0). \tag{3}$$

Substitution of Eqs. (3) and (1) into Eq. (2) gives terms like $\overline{u^s_l u^s_m\cdots u^s_n}$. For $\bar{4}3m$ symmetry the first nonvanishing term is obviously $\overline{u^s_l u^s_m}=\overline{\boldsymbol{u}^2}\delta_{lm}/3$ and hereafter we keep only its contribution to the tensor structure factor (the index s is omitted because $\overline{\boldsymbol{u}^2}$ has the same value for all the atoms). It is evident that the second-rank tensor $f^{2s}_{jkmm}\overline{\boldsymbol{u}^2}$ vanishes for $\bar{4}3m$ symmetry and the TMI contribution arises from the term proportional to $\boldsymbol{H}\cdot\boldsymbol{u}^s$. This means that not only the induced anisotropy but also the phase shifts $i\boldsymbol{H}\cdot\boldsymbol{u}^s$ are important. Higher powers of $\boldsymbol{H}\cdot\boldsymbol{u}^s$, which give contributions to the Debye-Waller factor, will not be considered here. Thus for the sth atom in Eq. (2) the first nonvanishing term is $i\overline{\boldsymbol{u}^2}\exp(i\boldsymbol{H}\cdot\boldsymbol{r}^s_0)f^{1s}_{jkl}H_l/3$.

Now let us find the structure amplitude (2) for the $0kl$ forbidden reflections where $k,l=2n; k+l=4n+2$. In the diamond unit cell of Ge, there are two basic atoms at the $\boldsymbol{r}^1_0=(000)$ and $\boldsymbol{r}^2_0=(\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4})$ sites related by inversion symmetry; all other sites can be obtained from one of those two by fcc translations. For conventional x-ray scattering the basic atoms give opposite contributions to the structure amplitude [owing to the phase factor $\exp(i\boldsymbol{H}\cdot\boldsymbol{r}^s_0)$] and the structure amplitude vanishes. However, for the TMI contribution, the tensors T_{jkl} of the basic atoms have opposite signs because any odd-rank tensor changes its sign after inversion. Therefore the scattering amplitude is not zero and has the following tensor form:

$$\hat{F}(E,\boldsymbol{H})=\frac{8}{3}if^1(E)\overline{\boldsymbol{u}^2}\begin{pmatrix}0 & H_z & H_y\\ H_z & 0 & 0\\ H_y & 0 & 0\end{pmatrix} \tag{4}$$

(the factor 8 appears because there are eight atoms per diamond unit cell). The structure factor has a tensor form as in dipole-quadrupole theory[16] but in our case it varies proportionally to $\overline{\boldsymbol{u}^2}$ and depends strongly on the temperature.

Figure 1 shows the energy spectra of the forbidden reflections 002 and 006 and the absorption curve. Both reflections are evidently resonant and their energy dependence is essentially of the same form, as expected both from the dipole-quadrupole theory[16] and from the TMI dipole contribution. These two theories predict the same azimuthal angle dependence, which agrees very well with our observation (Fig. 2), and the same polarization dependence (therefore we did not study the polarization properties). To separate these two contributions we measured the 006 reflection for different temperatures.

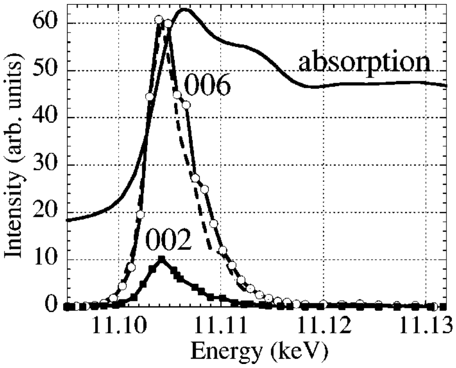

FIG. 1. Energy spectra measured for the 002 and 006 reflections in Ge at room temperature. The dashed line shows the 002 spectrum normalized to the same maximum value as the 006 spectrum. Both curves have essentially the same form. The absorption curve was measured simultaneously with fluorescent yield. Therefore, the relative energy scales of the absorption and ATS spectra are the same (the error in the nominal energy value is about 1 eV).

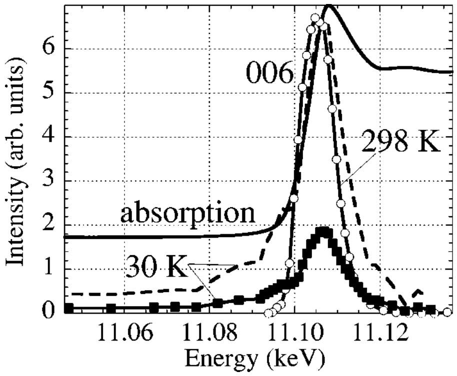

FIG. 3. Comparison of the 006 energy spectra observed at room temperature (circles) and at 30 K (squares). The dashed line shows the 30 K spectrum normalized to the same maximum value as the room temperature spectrum. The spectra are different both in the absolute value and in the shape. It should be noted that there is a long tail on the low energy side at the low temperature.

Figure 3 illustrates the essential difference of the energy spectra at room temperature and 30 K. Notice that here the 006 room temperature curve is measured with worse energy resolution than in Fig. 1; hence there is a small difference in the resonance widths. For more quantitative characterization, we measured the temperature dependence of the reflection intensity for two energies, one just at resonance (11.105 keV) and the other lower than the edge (11.087 keV). At resonance, the intensity increases four times as the temperature rises from 30 K to 300 K (Fig. 4). In contrast, at 11.087 keV, the intensity decreases ten times in the same temperature interval.

Remarkably, both the decrease and the increase of the intensity can be described with the same temperature dependence of TMI anisotropy. Indeed, the TMI anistropy of the structure amplitude is proportional to $\overline{\boldsymbol{u}^2}$ [see Eq. (4)]. Low momentum acoustical phonons should give no contribution to the TMI anisotropy because for these modes each unit cell moves as a whole and there is no change of the local atomic environment. Acoustic phonons with very high momentum could distort the environment but their contribution is expected to be small for low and room temperatures. Hence, for an estimation, only the relative atomic displacements resulting from optical phonon modes will be taken into account. In the Ge crystal, the frequency of the optical modes, ω_0, changes only slightly with the wave vector, and for estimations we can put $\omega_0 = \text{const}$ (the Einstein model). As a result, $\overline{\boldsymbol{u}^2}$ is proportional to $\coth(\hbar\omega_0/2kT)$. Therefore the temperature dependence of the intensity of the forbidden reflections is described by the following expression: $I = |A(E) + B(E)\coth(\hbar\omega_0/2kT)|^2$ where $A(E)$ and $B(E)$ are complex functions of the x-ray energy E, not of the temperature. The non-TMI part, $A(E)$, can include the dipole-quadrupole,[16] defect-induced,[18] and multiple-wave contributions. Notice that for a fixed energy we can fit the temperature dependence with three parameters because the common phase of $A(E)$ and $B(E)$ gives no contribution. Using $A(E)$ and $B(E)$ as fitting parameters and accepting the recently measured value[20] (3 THz) as an appropriate average for the Einstein frequency ω_0, we obtain a phenomenological description that

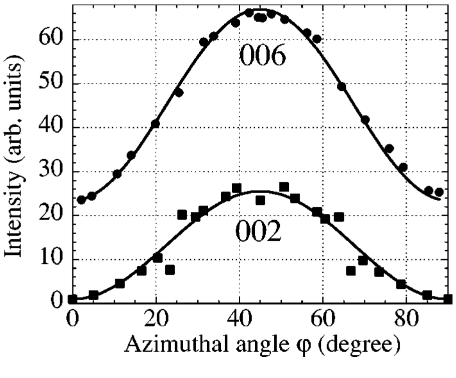

FIG. 2. The azimuthal dependence of the 002 and 006 reflections at room temperature for $E = 11.105$ keV. The lines show the predicted dependence proportional to $1 - \cos^2\theta_B \cos^2 2\varphi$. The deviations observed for the 002 reflection at 25° and 65° are due to multiple-wave Renninger reflections.

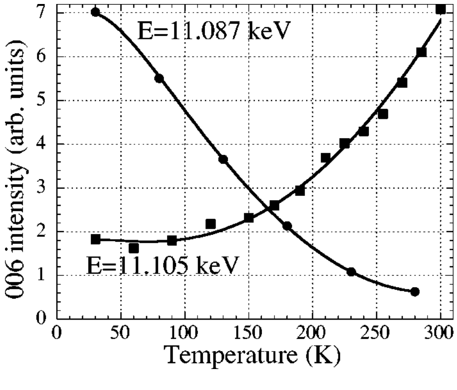

FIG. 4. The temperature dependence of the 006 reflection intensity at resonance ($E = 11.105$ keV, squares) and out of resonance ($E = 11.087$ keV, circles, intensity multiplied by 30). The curves are the best fits to the Einstein model for optical phonons as discussed in the text.

agrees with the experimental temperature dependence (Fig. 4). In our estimations we neglect another optical mode (7.55 THz) having much smaller relative atomic displacements.[20]

This result indicates that the TMI anisotropy scales with temperature as $\overline{\boldsymbol{u}^2}$ for optical phonon modes. The 11.087 keV reflection intensity decreases with increasing temperature because of *destructive* interference between the TMI and non-TMI parts of the structure amplitude. At room temperature, the TMI anisotropy is the main effect for the resonant energy whereas for 11.087 keV the nonthermal and thermal contributions are almost equal and have opposite signs. We expect that for 11.087 keV an increase of the 006 intensity will be observed for temperatures above 300 K because the thermal contribution becomes dominant.

In conclusion, we have found that the $00l, l=4n+2$, forbidden reflections, observed near the germanium *K* edge, are strongly temperature dependent. They are excited at least partly owing to the dynamic changes of electronic states bound up with thermal atomic motion. The temperature-dependent part of their structure amplitude scales as the mean square atomic displacement in optical phonon modes. This effect provides a tool for studying both phonon and electronic properties of crystals. The energy dependence of the TMI reflections is very sensitive to distortions of the electronic states and its quantitative interpretation is an evident challenge for solid state theory. Our observation of TMI reflections gives hope that defect-induced reflections in diamond-type semiconductors, which could be of great technological importance, will be observed in the not too distant future.

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