Band Structure Approach to Resonant X-Ray Scattering

I. S. Elfimov,[1] N. A. Skorikov,[2] V. I. Anisimov,[2] and G. A. Sawatzky[1,3]

[1]*Laboratory of Applied and Solid State Physics, Materials Science Center, University of Groningen,*
Nijenborgh 4, 9747 AG Groningen, The Netherlands
[2]*Institute of Metal Physics, Russian Academy of Sciences, 620219 Ekaterinburg GSP-170, Russia*
[3]*Department of Physics and Astronomy, University of British Columbia, 6224 Agricultural Road,*
Vancouver, British Columbia, Canada V6T 1Z1

We study the resonance behavior of the forbidden 600 and 222 x-ray Bragg peaks in Ge. These peaks remain forbidden in the resonant dipole scattering approximation, even taking into account the nonlocal nature of the band states. However, they become allowed at resonance if the eigenstates of the unoccupied conduction band involve a hybridization of p-like and d-like atomic states. We show that the energy dependence of the resonant behavior, including the phase of the scattering, is a direct measure of this p-d hybridization and obtain quantitative agreement with experiment. We discuss the implications of this to other materials like V_2O_3 in which the resonating atom is not at a center of inversion symmetry.

In a recent paper Lee *et al.* [1] describe a detailed study of the energy dependence of the 600 reflection in the vicinity of the Ge K-edge. They demonstrate a strong 600 reflection close to the Ge K-edge with an energy dependence quite different from the absorption edge structure in that the 600 intensity drops rapidly at energies just beyond the edge. The intensity of this reflection at the edge corresponds to a structure factor of 0.475 electrons. The fact that one sees this reflection at all as well as the large intensity and the peculiar energy dependence is difficult to explain. This is because, even if we take into account the nonspherical nature of the charge distribution and put electron charge in the bonds between the atoms from which the x rays scatter, the 600 reflection remains forbidden. Also the usual dipole-dipole or quadrupole-quadrupole-like resonances as discussed for the manganites [2–5] and V_2O_3 [6–8] cannot contribute to this reflection as discussed below. Recently Templeton and Templeton [9] showed that the lowest order process which will allow such a reflection is one involving a product of a dipole and a quadrupolelike matrix element for the scattering and demonstrated that the azimuthal angular dependence of forbidden reflections in Ge could be described by their theory. In this Letter we start from the Templeton and Templeton proposal and show that band structure calculations provide a natural and detailed explanation for the observed behavior and that the resonance behavior is a direct measure of the energy dependence of the p-d hybridization in the conduction band of Ge. We describe here a detailed theory and predict the full energy dependence of the intensity and the phase of the scattering.

We also show that the 222 reflection becomes allowed in this fashion but this is not as spectacular since the 222 reflection is also weakly allowed by simple Thomson scattering of the charge situated in the bonds between the atoms [10–12]. Nonetheless the energy dependence of the phase

of this extra scattering channel causes a decrease in the net scattering close to the edge as observed and we predict an increase at energies about 30 eV above the edge because of a change in the phase of the p-d mixing at these energies. Although the case of Ge may, for some, not be that interesting, it serves as a demonstration of the effect and the success of theory to explain it. We suggest that this effect will play an important role in the resonant behavior of recently discussed controversial materials such as V_2O_3, Fe_3O_4, and many more vanadates, titanates, and manganites which often also lack inversion symmetry at the resonating ion. In fact, quite generally this effect could be very important in ferro- and antiferroelectric as well as piezoelectric materials. This may also provide a simple way to actually distinguish between materials with and without an inversion center which is an important problem in crystallography.

Ge has the diamond structure which contains eight atoms per unit cell as depicted in Fig. 1 showing also the location of these atoms in a simple cubic notation. Since the Ge atoms are so-called "crystallographically" equivalent we might expect the 600 and 222 reflections to be forbidden. Even if we take into account that the charge density around each atom is not spherical but somewhat enhanced along the bond directions, we still find zero intensity for the 600 reflection because of the space group symmetry. However, in this case the 222 reflection can become weakly allowed in a purely Thomson scattering mechanism. Looking at Fig. 1 more carefully, however, and at the Ge atoms connected by a bond it is easy to see that in fact Ge_1 and Ge_2 are not really equivalent in that the charge distribution around atom 1 is, by 180°, the rotated image of that around atom 2. In Thomson scattering this difference is not noticed, however. This difference between Ge_1 and Ge_2 is caused by a change in sign of the hybridization between s and p and the p and d wave functions forming the
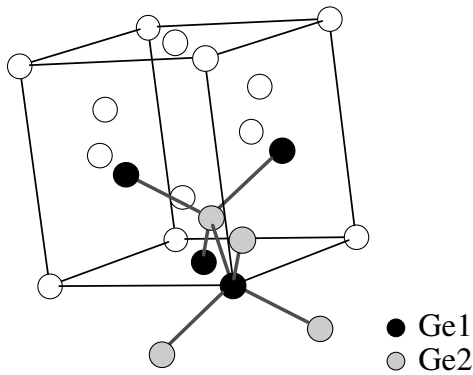
FIG. 1.   The diamond crystal structure.

eigenstates of the occupied valence and unoccupied conduction band states. For example, if we take the Ge_1-Ge_2 direction to be the z direction then a wave function such as $\alpha s + \beta p_z + \gamma d_{3z^2-r^2}$ on Ge_1 would have charge pileup in the Ge_1-Ge_2 bond but for Ge_2 this combination at the same energy would be $\alpha s - \beta p_z + \gamma d_{3z^2-r^2}$. Notice the sign change of the p contribution because of the ungerade character of its wave function. We note that s, p, d can mix in this structure because of the lack of inversion symmetry about the Ge atoms.

We do not see this difference in an experiment which is sensitive only to the charge density as in Thomson scattering. However, in a resonant scattering process the anomalous form factor is given by

$$A \sim \sum_b \frac{\langle a|\vec{\epsilon}' \cdot \vec{r} e^{-i\vec{K}'\cdot\vec{r}}|b\rangle \langle b|\vec{\epsilon} \cdot \vec{r} e^{i\vec{K}\cdot\vec{r}}|a\rangle}{E_a - E_b + \hbar\omega - i\Gamma/2}, \quad (1)$$

where ϵ' and ϵ are the polarization of the scattered radiation and the incident radiation, respectively, and K' and K are the respective wave vectors. For the K-edge studies a refers to a $1s$ orbital and b to a band eigenstate.

Following Templeton we expand the exponential as $1 + i\vec{K} \cdot \vec{r}$ resulting in three kinds of contributions: dipole-dipole, quadrupole-quadrupole, and the cross terms dipole-quadrupole. The dipole-dipole and quadrupole-quadrupole terms are the same for atoms 1 and 2 because they involve only the squares of the wave functions and therefore the sign difference in the p component for atoms 1 and 2 disappears. Therefore we concentrate only on the dipole-quadrupole cross terms which for each of the two atoms is given by

$$A_{dq} \sim i \sum_b \left(\frac{\langle a|\vec{\epsilon}' \cdot \vec{r}\vec{K}' \cdot \vec{r}|b\rangle\langle b|\vec{\epsilon} \cdot \vec{r}|a\rangle}{E_a - E_b + \hbar\omega - i\Gamma/2} \right.$$
$$\left. - \frac{\langle a|\vec{\epsilon}' \cdot \vec{r}|b\rangle\langle b|\vec{\epsilon} \cdot \vec{r}\vec{K} \cdot \vec{r}|a\rangle}{E_a - E_b + \hbar\omega - i\Gamma/2} \right).$$

The two terms are obviously not equal yielding a net result for each. For the K-edge we see that the r^2 terms get us from the ground state to the d component of the excited state eigenfunction and the dipole (r) term gets us back

from this eigenstate via the p component to the ground state or vice versa. Immediately we see that the phase of the p-d mixing in the eigenstate enters and therefore the two Ge atoms discussed above in fact scatter differently. Now one might say that this would also be the case for the s-p hybridization but a s-s transition is not quadrupole allowed because an s orbital has no quadrupole moment. This kind of hybridization could be observed only in a combination of a dipole and monopole transition.

Now that we understand which physical scattering mechanism can distinguish between these two Ge atoms we can check if there is such a difference seen in the electron structure of Ge. To do this we look at the conduction band part of the band structure in a local density approximation calculation (TBLMTO-47 computer code [13]), where we neglect the core hole potential. The $4p$ projected local density of states would correspond to the energy dependence of the K-edge x-ray absorption spectrum broadened by the core hole lifetime. This core hole lifetime is about 3 eV. The 600 and 222 reflection structure factors in this mechanism will be determined by the energy dependence of the product of the amplitude of the p and d component of the band eigenstate times a radial integral and is given by

$$A_{dq} \sim i \sum_n e^{-i\vec{G}\cdot\vec{R}_n} \sum_{m=-l}^{l} \sum_{m'=-l'}^{l'} \hat{\epsilon}' \bar{d}_m \hat{K}' T^n_{lm,l'm'} \hat{\epsilon} \vec{p}_{m'}$$
$$- \hat{\epsilon}' \vec{p}_{m'} T^n_{l'm',lm} \hat{\epsilon} \bar{d}_m \hat{K},$$

where $\vec{G} = \vec{K}' - \vec{K}$, m and m' are magnetic quantum numbers of the d and the p orbital, respectively,

$$T_{lm,l'm'} = \sum_j \int d\vec{k} \frac{C^j_{lm}(\vec{k})C^{j*}_{l'm'}(\vec{k})}{E_{1s} - E_j(\vec{k}) + \hbar\omega - i\Gamma/2},$$
$$p^i_m = \int dr \, R_{1s}(r)r^3 R_{4p}(r) \int d\Omega \, Y_{00}\hat{r}^i Y_{1m},$$
$$d^{ij}_m = \int dr \, R_{1s}(r)r^4 R_{4d}(r) \int d\Omega \, Y_{00}\hat{r}^i\hat{r}^j Y_{2m},$$

where j is a band index, $C^j_m(\vec{k})$ are components of the eigenvector projected on a particular orbital of site n with lattice vector $\vec{R}_n$, and Y_{lm} are cubic spherical harmonics.

In Fig. 2 we show the $4p$ projected partial density of states and this convoluted with a Lorentzian of width 3 eV. We note that we have not taken into account higher lying p bands than the $4p$ band to which dipole transitions are of course also allowed so the experimental absorption edge will fall off somewhat less rapidly than calculated here. To calculate the resonant amplitude we use the scattering geometry of Fig. 3 and the angles determined by the Bragg conditions for the given energies. At a photon energy equal to 11 107 eV the scattering angle is 36.35° for the 600 reflection and 20.01° for the 222 reflection. The resonant intensity is determined by the product of the p and d amplitude at a given energy in the band structure integrated over k space and summed over atoms 1 and 2 with the
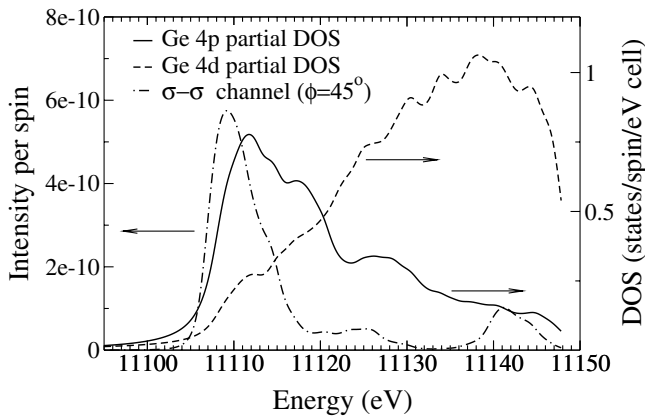
FIG. 2. Ge partial density of states and the intensity of 600 reflection. The DOS and structure factor are broadened by 3 eV Lorentzian.

appropriate phase factor $e^{-i\vec{G}\cdot\vec{R}_n}$. As discussed above the product of the p and d amplitude for atoms 1 and 2 has the opposite sign which in the sum is canceled by the opposite phase factor for the reciprocal wave vector 600 or 222.

In Fig. 2 we also show the $4d$ partial density of states and we see that in general the $4d$ states are as expected higher in energy than the $4p$ states. It is then easy to see that there is a phase change in the p-d mixing as we go from the edge to the high energy states at about 30 eV higher. The dot-dashed curve is then the resonant scattering intensity calculated for the scattering geometry of Fig. 3 which demonstrates the strong energy dependence of the p-d mixing resulting in a strong peak close to threshold and a weaker structure 16 to 18 eV higher in energy and another peak at 30 eV above threshold. In fact the energy scans done to date did not cover the high energy region, so this should be considered as a prediction which should be checked experimentally. The first strong peak at threshold agrees very well in intensity and width with the experimental data of Lee *et al.* [1].

We notice that the resonant intensity goes to zero at about 11 135 eV which is a strong indication that the phase
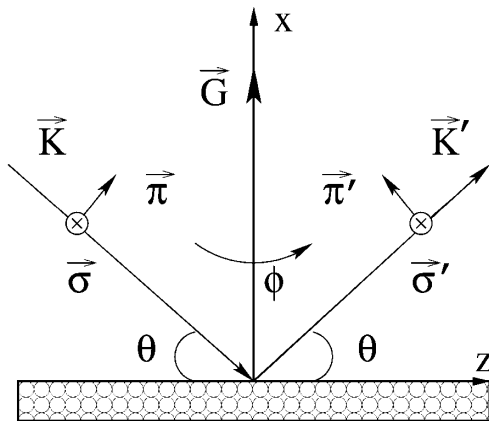
of the mixing changes sign. In order to study this we show in Fig. 4 which shows a strong energy dependence and a change of sign at about 18 eV above the edge and again at about 30 eV above the edge. In fact, we predict another resonance at higher energies and this should be looked for in the future. In addition to the prediction of the second resonance we also predict that the phase of the scattering changes by 3π. This change of phase should change the interference with the umweg scattering [14] dramatically and also this should be studied as a function of energy.

In agreement with the paper by Templeton and Templeton [9] our calculations show that only the dipole-quadrupole term contributes to the resonant intensity in the crystal structure of diamond. First of all, the pure dipole as well as the quadrupole term in Eq. (1) is essentially proportional to local partial p or d density of states projected on a particular site. Because of the fact that there is no difference in the correspondent partial densities of states of the eight germanium atoms in the unit cell and the reverse of signs in the structure factor the intensity of resonant scattering in dipole-dipole or quadrupole-quadrupole channels is zero. Second, as already mentioned, the mixed dipole-quadrupole term involving transition from $1s$ to $4p$ and from $4s$ to $1s$ orbitals of germanium also does not give any contribution to the resonant scattering because neither of these are quadrupole allowed. This means that $sp3$ hybridization does not contribute to this scattering.

The net tensor has then only two significant contributions which, in, for example, the p-d dipole-quadrupole transition has a symmetry:

$$\begin{pmatrix} 0 & 0 & 0 & C & 0 \\ C & 0 & 0 & 0 & 0 \\ 0 & C & 0 & 0 & 0 \end{pmatrix}.$$

Here C is some constant for each particular energy and independent on azimuthal angle ϕ. The rows and columns of this matrix are numerated according to quantum number
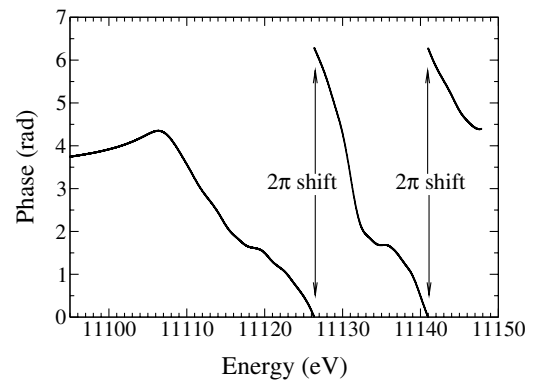

FIG. 3. The geometry of x-ray scattering.

FIG. 4. The energy dependence of the phase of the 600 reflection in σ-σ (π-π) channel with $0 < \phi < 90$ or $180 < \phi < 270$; σ-π with $-40 < \phi < 40$ or $140 < \phi < 220$; π-σ with $40 \lesssim \phi \lesssim 140$ or $220 \lesssim \phi \lesssim 320$. To obtain the phase for other ϕ angles one needs to shift these by 180°.
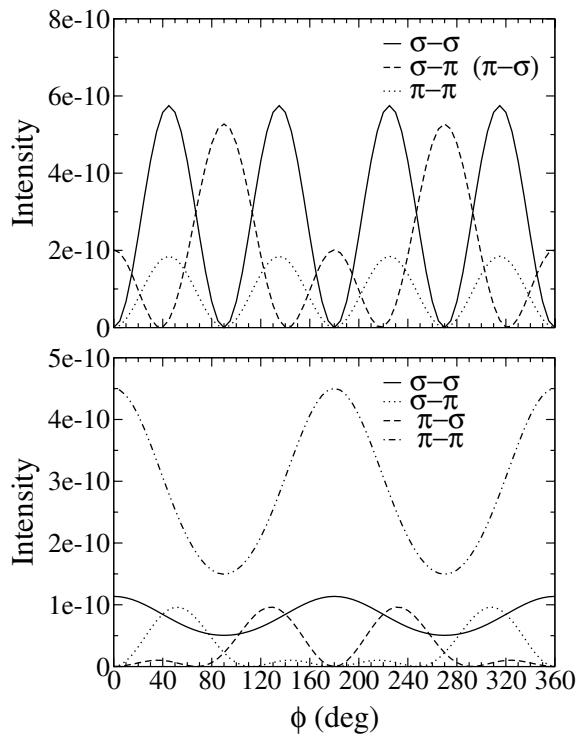
FIG. 5. The azimuthal angle dependence of resonance peak at energy 11 109.2 eV. The upper panel shows 600 reflection for scattering angle $\theta = 36.35°$. The lower panel shows 222 reflection at $\theta = 20.01°$.

order ($m = -l, \ldots, l$). The reverse transition has exactly the same symmetry and sign but both of them have opposite signs to the matrix elements related to the second type of germanium atoms in the unit cell. The latter is a direct consequence of wave function symmetry caused by the particular mixing of p and d orbitals in the diamond crystal structure.

Finally we present the calculated azimuthal angle dependence of the 600 and 222 reflections at K-edge. Figure 5 shows that the intensity of the 600 reflection follows a $(\sin\phi \cos\phi)^2$ behavior in σ-σ and π-π channels with ϕ equal to zero when the (001) axis is in the scattering plane and the incident beam is approximately parallel to this axis (Fig. 3). For the 222 reflection it changes to more like $\cos^2\phi$ behavior whereas the period in σ-π (π-σ) channel is changing from π to 2π.

For the 600 reflection we also calculate the absolute value of the structure factor following the paper by Colella and Merlini [11] where we choose the polarization factor and the Debye-Waller factors to be 1. To compare our calculations with experiment we define the integrated intensity I as $\sum_s I^s_{\pi\text{-}\pi} + I^s_{\sigma\text{-}\sigma}$, where s is a spin index. In that case for an azimuthal angle of 25° the integrated intensity is calculated to be 1.656×10^{-10} and the structure factor 0.44 which is in excellent agreement with 0.475 determined from the experimental data by Lee $et\ al.$ [1].

In conclusion, we have demonstrated that the quadrupolar-dipolar resonant scattering in Ge will indeed yield a 600 scattering intensity and that this is a direct measure of the p-d hybridization as a function of energy in the conduction band. Band theory does an excellent job of explaining both the magnitude and the energy dependence of the resonance. In addition we have made a number of predictions regarding more resonances at somewhat higher energies and we have predicted the phase. Future experiments related to these predictions should provide an even more critical test of the theory. Since such p-d mixing is allowed only if the atom is not at an inversion center, this mechanism could also be important for all such materials and may explain part of the structure seen at resonance for the transition metal oxides in general and V_2O_3 in particular.

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