Band structure approach to the resonant x-ray scattering

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We study the resonance behaviour of the forbidden 600 and 222 x-ray Bragg peaks in Ge using LDA band structure methods. These Bragg peaks remain forbidden in the resonant dipole scattering approximation even taking into account the non local 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 behaviour, including the phase of the scattering, is a direct measure of this $p$-$d$ hybridization and obtain quantitative agreement with experiment. A simple physical picture involving a product of dipole and quadrupole transition matrix elements explains this behaviour and shows that it should be generally true for cases where the resonating atom is not at an inversion center. This has strong implications for the description of the resonance behavior of x-ray scattering in materials where the resonant atom is not at an inversion center such as V$_2$O$_3$ and in ferro and antiferro electric and piezoelectric materials in general.

In a recent paper T.L. Lee \textit{et al.} 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 of rapidly at energies just beyond the edge. The intensity of this reflection at the edge corresponds to a structure factor of 0.45 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 because, even if we take into account the non spherical 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 \textsuperscript{2, 3, 4, 5} and V$_2$O$_3$ \textsuperscript{6, 7, 8} cannot contribute to this reflection as discussed below. Recently Templeton and Templeton \textsuperscript{9} suggested that the lowest order process which will allow such a reflection is one involving a product of a dipole and a quadrupole like matrix element for the scattering. In this paper we show that band structure calculations provide a natural and detailed explanation for the observed behaviour and that the resonance behaviour is a direct measure of the energy dependence of the $p$-$d$ hybridization in the conduction band of Ge. This is, in a way equivalent to Templeton’s suggestion but here is caused by a natural $p$-$d$ mixing due to a lack of inversion symmetry at the Ge atomic sites.

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 \textsuperscript{10, 11, 12}. Non the less 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 behaviour of recently discussed controversial materials like V$_2$O$_3$, Fe$_2$O$_3$ 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 antiferro electric 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 8 atoms per unit cell as depicted in Fig.\ref{fig:fig1} showing also the location of these atoms in a simple cubic notation. We notice immediately that if all the Ge atoms are equivalent then reflections like the 600 and 222 reflections will 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 will 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.\ref{fig:fig2} more carefully however and at the Ge atoms connected by a bond it is easy to see that in fact Ge\textsubscript{1} and Ge\textsubscript{2} are not really equivalent in that the charge distribution around atom 1 is the, by 180 degrees,
rotated image of that around atom 2. In Thomson scattering this difference will not be noticed however. This difference between Ge₁ and Ge₂ is caused by a change in sign of the hybridization between s and p and the p and d wave functions forming the eigenstates of the occupied valence and unoccupied conduction band states. For example if we take the Ge₁-Ge₂ direction to be the z direction then a wave function like occupied valence and unoccupied conduction band states.

We note that s, p, d can mix in this structure because of the lack of inversion symmetry about the Ge atoms.

Following Templeton we expand the exponential as the translation band part of the band structure in a LDA 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 life time. This core hole life time is about 3 eV. The 600 and 222 reflection structure factors in this 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.

The two terms are obviously not equal yielding a net result for each. For the K-edge we see that the r² 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 visa versa. Immediately we see that the phase of the p-d mixing in the eigenstate enters and therefore the two Ge atoms discussed above will in fact scatter differently. Now one might say that this would also be the case for the s-p transition is not quadrupole allowed because an s-p hybridization has no quadrupole moment. This kind of hybridization could only be observed 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.
number of $d$ and $p$ orbital respectively

$$T_{lm, l'm'} = \sum_j \int d\vec{k} \frac{C^{ij}_{lm}(\vec{k}) C^{*}_{l'm'}(\vec{k})}{E_{1s} - E_j(\vec{k}) + i\hbar\omega/2}$$

$$p^i_m = \int dr R_{1s}(r) r^3 R_{4p}(r) \int d\Omega Y_{00}^{*} Y_{lm}$$

$$d^{ij}_{m} = \int dr R_{1s}(r) r^4 R_{4d}(r) \int d\Omega Y_{00}^{*} r^2 Y_{2m}$$

$j$ is a band index, $C^{ij}_{lm}(\vec{k})$ 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. 3 we show the $4p$ projected partial density of states and this convoluted with a Lorentzian of width $3eV$. 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 11107 eV the scattering angle is 36.35 degrees for the 600 reflection and 20.01 degrees for a photon energy equal to 11107 eV the scattering angle is determined by the Bragg conditions for the given energies. At 0 $< \phi < 90$ or 180 $< \phi < 270$; $\sigma-\pi$ with $-40 < \phi < 40$ or $140 < \phi < 220$; $\pi-\sigma$ with $40 < \phi < 140$ or $220 < \phi < 320$. To obtain the phase for other $\phi$ angles one needs to shift these by 180 degrees.

We notice that the resonant intensity goes to zero at about 1135eV 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 $3\pi$. This change of phase should change the interference with the omweg scattering dramatically and also this should be studied as a function of energy.

In agreement with the paper by Templeton and Templeton 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 quadrupole term in Eq. (4) is essentially proportional to local partial $p$ or $d$ density of states projected on a particular site. Due to the fact that there is no difference in the correspondent partial densities of states of the 8 germanium atoms in the unit cell and the reverse of signs in structure factor the intensity of resonant scattering in dipole-dipole or quadrupole-quadrupole channels is zero. Secondly, 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 will not contribute to this scattering.

The net tensor has then only two significant contributions which, in for example the $p-d$ dipole-quadrupole
As changing from $\pi$ compare our calculations with experiment we define the

tion factor and the Debye-Waller factors to be 1. To
Colella and Merlini [11] where we choose the polariza-
value of the structure factor following the paper by
$
$ and the incident beam is approximately parallel to this

The upper panel shows 600 reflection at energy 11109.2 eV. The upper panel shows 600 reflection at $\theta = 20.01^\circ$.

transition has a symmetry:

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

Here $C$ is some constant for each particular energy and independent on azimuthal angle $\phi$. The rows and columns of this matrix are numerated according to quantum number order ($m = -l \ldots l$). The reverse transition has exactly the same symmetry and sign but both of them have opposite sign 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. Fig shows that the intensity of the 600 reflection follows a $(\sin \phi \cos \phi)^2$ behaviour in $\sigma-\sigma$ and $\pi-\pi$ channels with $\phi$ equal to zero when the (001) axis is in the scattering plane and the incident beam is approximately parallel to this axis. For the 222 reflection it changes to more like $\cos^2 \phi$ behaviour whereas the period in $\sigma-\pi$ ($\pi-\sigma$) channel is changing from $\pi$ to $2\pi$.

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 \( \sum_s I_{s,s}^2 + I_{s,-s}^2 \) were $s$ is a spin index. In that case for an azimuthal angle of 25 degrees the integrated intensity is calculated to be $1.656 \cdot 10^{-10}$ and the structure factor 0.44 which is in excellent agreement with 0.475 determined from the experimental data by Colella [11].

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 only allowed 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$_2$O$_3$ in particular.

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