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Electronic structure of liquid gallium antimonide tested with x-ray absorption near-edge-structure spectroscopy

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Abstract. On the basis of the measured K-edge x-ray absorption near-edge-structure (XANES) spectra of Ga and Sb in crystalline and liquid gallium antimonide (c-GaSb and l-GaSb), the electronic structures near the Fermi level of l-GaSb have been studied. A multiple-scattering simulation of the XANES spectra and a self-consistent calculation of the density of states (DOS) have been carried out. The configuration models used in the data analysis for l-GaSb were generated by means of a reverse Monte Carlo simulation based on the measured extended x-ray absorption fine-structure data. The calculated spectra agree very well with the measured ones. The strong white line for the Ga K edge is attributed to the high density of states in the conduction band and partially to the excitonic effect. The DOS of l-GaSb is quite high around the Fermi level, as for metals, while that for c-GaSb exhibits a gap there. Some features of the c-GaSb DOS remain in that of the liquid.

1. Introduction

The covalent semiconductors, such as Si, Ge, GaSb, and InSb, become metallic and increase their densities upon melting [1–3]. These anomalous phenomena have attracted much attention and motivated efforts to achieve an understanding of the mechanism. Investigation of the atomic and the electronic structures of the liquids in comparison with those of the related solids should be helpful as regards explaining this special phase transition. However, experimental studies of the electronic structure are still limited because of the practical difficulties, especially for compound semiconductors such as GaSb, which is emerging as an important optoelectronic material. Photoelectronic spectroscopy can hardly be applied due to the vapour pressure problem of the liquid at high temperature. As is well known, x-ray absorption near-edge-structure (XANES) spectroscopy provides direct information on the local electronic structure of unoccupied states for a selected atomic species [4, 5]. Nevertheless, results on the electronic structures of melts studied by means of XANES spectra remain lacking because of the difficulties both in measuring the spectra at high temperature and in analysing the data for a system in which the atomic configuration is not well defined. In this paper, we present Ga and Sb K-edge XANES spectra of l-GaSb measured by using an improved sample holder, and a theoretical analysis by means of which we derive electronic pictures of the unoccupied states near the Fermi level E_F by solving the atomic configuration. For comparison, the results for c-GaSb are also given.

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2. Experiment

The XANES and extended x-ray absorption fine-structure (EXAFS) spectra measurements using an improved sample holder were carried out in transmission mode at the beam line BL-10B equipped with a Si(311) channel-cut monochromator at the Photon Factory synchrotron radiation source in Japan. The experimental arrangements were detailed elsewhere [6]. The Ga K-edge and Sb K-edge XANES spectra of c-GaSb at room temperature and l-GaSb at 993 K are plotted in figure 1(a) and figure 1(b) respectively. The Ga K-edge spectrum of c-GaSb shows an intense white line with a strong hump on the high-energy side and many features beyond the white line, while the white line for l-GaSb is wider without shoulder features and the spectrum is quite smooth beyond the white line as a result of disorder. The Sb K-edge XANES spectra are quite similar to those for the Ga edge; however, they are smoother, and the feature E cannot be recognized due to the shorter core-hole lifetime and poorer energy resolution at high energy, and the white line is weaker. The threshold of the Ga K edge for l-GaSb is shifted towards lower energy by about 1.45 eV relative to that of c-GaSb, and the shift of the Sb K edge is about 1.9 eV.

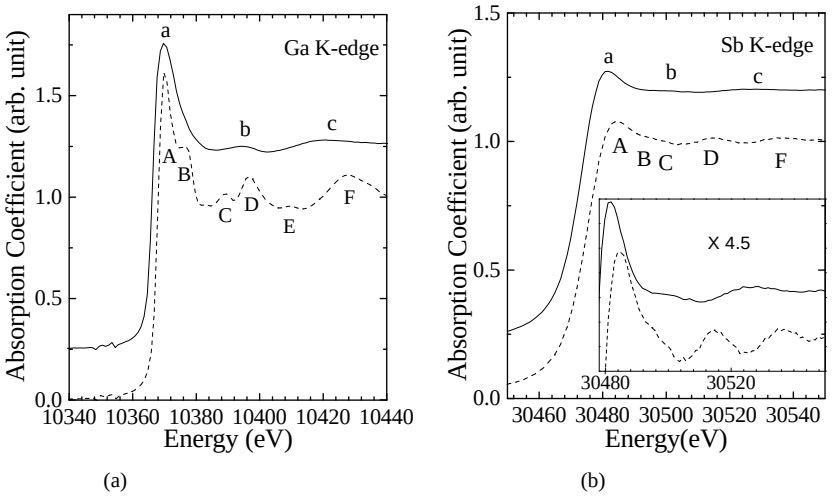

Figure 1. (a) Ga K-edge XANES spectra of c-GaSb measured at room temperature (dashed) and of l-GaSb measured at 993 K (solid). (b) Sb K-edge XANES spectra of c-GaSb measured at room temperature (dashed) and of l-GaSb measured at 993 K (solid). The inset shows an enlarged plot.

3. Multiple-scattering simulation of XANES spectra

The XANES spectra have been simulated in real space by using the *ab initio* one-electron full multiple-scattering (MS) [4, 7, 8] formalism. The x-ray absorption coefficient is determined, according to the Fermi Golden Rule, as the product of the electron transition matrix element and the selected partial density of unoccupied states. Following the core-hole excitation, the excited photoelectron 'sees' a new potential which evolves over the time following the rearrangement of the passive electrons. According to the final-state rule, this many-body effect can be described by the one-electron fully relaxed potential simulated by the $Z + 1$ approximation [9]. In this work, the absorption cross sections were calculated for an unperturbed potential describing the ground-state properties, and for a fully relaxed potential including the core-hole effect to study

the electronic structure [10, 11]. The real Hedin–Lundqvist self-energy [12] was included as an exchange–correlation potential. The muffin-tin radii were chosen according to the Norman criterion [13]. The calculated spectra were convoluted with a Lorentzian to account for the core-hole lifetime, chosen to have a width of 2.13 eV for the Ga K edge and a width of 10.72 eV for the Sb K edge [14].

The calculated Ga and Sb K-edge XANES spectra of c-GaSb in relaxed and unrelaxed potentials for a cluster including 99 atoms are presented in the lower parts of figure 2 and figure 3 respectively. Empty spheres are placed in the tetrahedral holes of the zinc-blende lattice. The spectra show an increase of the white-line intensity at the Ga K edge due to the core-hole-induced relaxation, while the effect at the Sb K edge is negligible since there are more passive electrons to screen the core hole. It is obvious that the calculated spectra including the relaxation effect are more consistent with the measured ones. All features of the XANES spectrum are well reproduced, indicating that the potential used here is acceptable.

In the case of l-GaSb, the atomic configuration which has to be known first was solved on the basis of the EXAFS data. We have performed a reverse Monte Carlo (RMC) simulation [15] with 1728 atoms based on the EXAFS data for l-GaSb measured in the same experiment as was performed to obtain the XANES spectra, and obtained a series of independent configurations [6]. Then the Ga and Sb K-edge XANES spectra of l-GaSb were calculated with an *ab initio* full MS approach by using atomic clusters with radii of about 9 Å created according to the independent converged configurations. The calculated spectra averaged over 16 configurations are given in the upper parts of figure 2 and figure 3. The predictions agree with the experiments quite well. The intensity of the white line at the Ga edge is increased by the core-hole relaxation effect, while that at the Sb edge remains almost unchanged when the core-hole effect is included. This indicates that the screening of the core holes at Ga sites is still incomplete, although l-GaSb is metallic as will be discussed later. We also calculated the spectra by using 16 smaller clusters with radii of about 3.8 Å, and obtained essentially the same results, indicating the long-range disorder in l-GaSb.

In order to compare the features of the XANES spectra for c-GaSb and l-GaSb, we have calculated the spectra of c-GaSb using different atomic cluster sizes around the absorbing

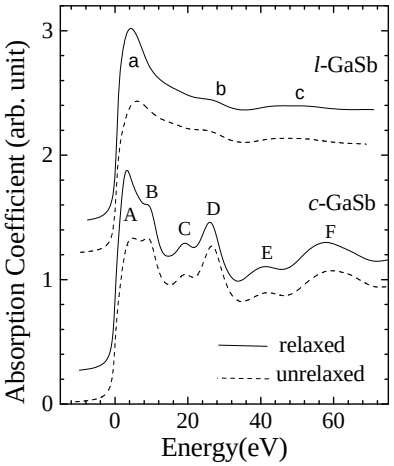

Figure 2. Calculated Ga K-edge XANES spectra for a fully relaxed (solid) and an unrelaxed (dashed) potential. Upper curves: c-GaSb; lower curves: l-GaSb.

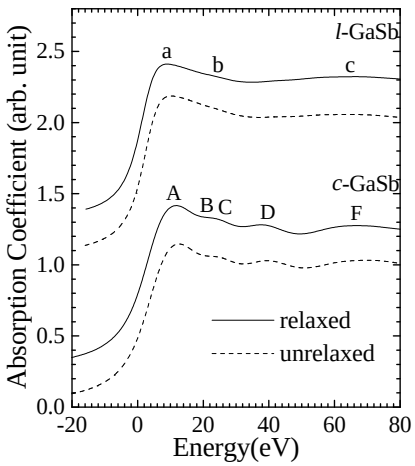

Figure 3. Calculated Sb K-edge XANES spectra for a fully relaxed (solid) and an unrelaxed (dashed) potential. Upper curves: c-GaSb; lower curves: l-GaSb.

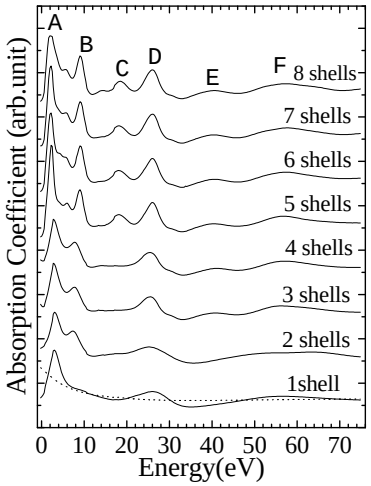

Figure 4. Calculated Ga K-edge XANES spectra of c-GaSb with different atomic cluster sizes around the absorber.

atom, and we plot the spectra without broadening in figure 4. A sharp feature A and wider features D and F are predicted for a small cluster, with only the first shell of neighbouring atoms located at the four apices of the tetrahedron. The peak A is almost unchanged when the cluster size is altered. Hence the final states of this feature show the character of the sp^3 hybrid orbital antibonding states. The peak B is well defined when the second shells including twelve neighbouring atoms are added, and the peaks C and E appear when more atomic shells are included, showing that the final states cannot be described in terms of a simple cluster formed by the absorbing atom and its first neighbours. The peaks D and F arise from εp-like derived bands. The calculation for the Sb edge gives similar results.

Both the experimental and the calculated XANES spectra of GaSb show that the features B, C, and E are smeared, while the peaks A, D, and F remain as the features a, b, and c upon melting. The calculation shows that the features A, D, and F for c-GaSb are well defined with the four tetrahedrally covalent neighbours, and the features a, b, and c for l-GaSb can be predicted with small clusters with radii of 3.8 Å. Thus some covalent characteristics persist in the liquid, and keep the features a, b, and c nearly unchanged.

4. LMTO-ASA calculation of the density of states

The densities of states (DOSs) of c-GaSb and l-GaSb were calculated by using the self-consistent linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA) [16, 17] in order to check the electronic structure near E_F. Spare empty spheres were used for the c-GaSb calculation. 64-atom super-cells from independent-atomic configurations created in RMC simulations were used for the l-GaSb DOS calculation. The DOS of l-GaSb was averaged over 16 independent configurations. In figure 5 and figure 6 we show the DOS together with the partial contributions of p-like and s-like states centred on Ga and Sb sites for c-GaSb and l-GaSb respectively. The energy origins are at the calculated E_F. The total DOS of c-GaSb is consistent with the pseudopotential calculation [18].

Above E_F, the p-like projected DOSs of c-GaSb at Ga and Sb sites are quite high. Between $\sim$1 eV and $\sim$11 eV, the density of the empty states centred on Ga sites is higher than that of those centred on Sb sites. This is consist with the XANES white line of Ga being stronger than that of Sb. However, the p-like projected DOS of Ga is not high enough to fit the measured intense white line; thus the core-hole effect must be included. This is consistent with the

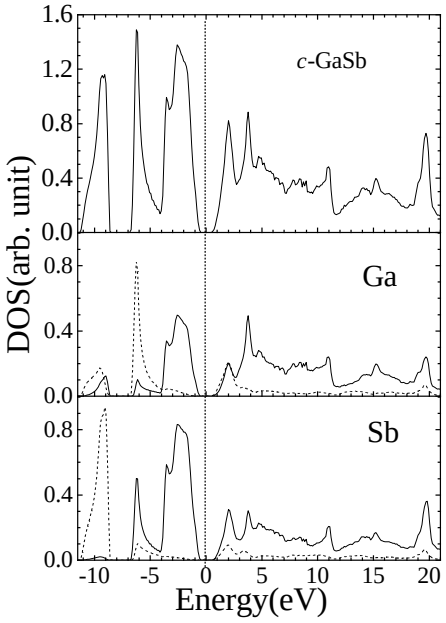

Figure 5. The DOS of c-GaSb. Top panel: total DOS; middle panel: p-like (solid) and s-like (dashed) DOSs at Ga sites; bottom panel: p-like (solid) and s-like (dashed) DOSs at Sb sites.

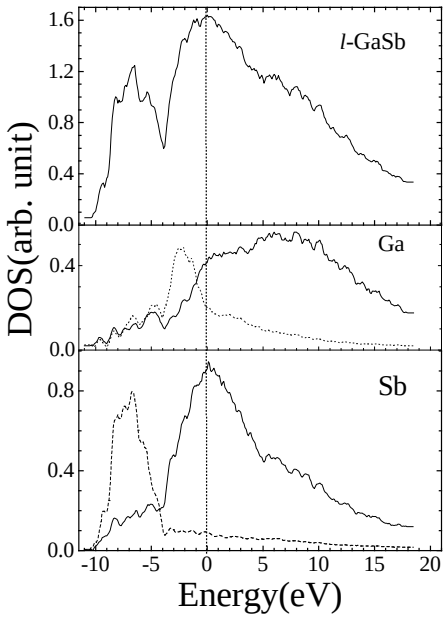

Figure 6. The DOS of l-GaSb. Top panel: total DOS; middle panel: p-like (solid) and s-like (dashed) DOSs at Ga sites; bottom panel: p-like (solid) and s-like (dashed) DOSs at Sb sites.

XANES calculation as shown in figure 2. Comparing figures 4 and 5, the projected DOS for c-GaSb gives evidence that the XANES features A, B, and C attribute to the same p-derived band and correspond to the features of the p-like DOS centred at about 3, 10, and 19 eV respectively.

The DOS of l-GaSb remains high around E_F, as for metals, in contrast with that of c-GaSb for which a gap opens there. The p-like band above E_F for l-GaSb is narrower than that of c-GaSb, as shown by the XANES spectra. The band on the Sb sites is even narrower and higher than that on the Ga sites, but has not led to a sharper XANES white line due to the shorter photoelectron lifetime.

Some features of the DOS for c-GaSb are visible in that for l-GaSb, such as the fact that there is a band of s-like states originating from Sb atoms at low energy.

From either the measured XANES spectra or the calculations, we can see that the DOS features at Ga sites are quite similar to those at Sb sites for c-GaSb, since the two components are covalently bonded, while, in contrast, they are quite different—as the covalent bonding has been destroyed—in l-GaSb.

Using more configurations in the calculation might give a more precise sampling of the configuration space of the liquid GaSb system. 16 configurations have already given a quite good result, consistent with the experimental data.

5. Conclusions

In summary, by using the combined analysis of our measured Ga and Sb K-edge XANES spectra of molten and crystalline gallium antimonide, the electronic structures near E_F have been studied. A MS simulation and a self-consistent DOS calculation have been carried out.

In the case of l-GaSb, the configurations needed for the spectra and DOS calculations were generated by a RMC simulation with experimental EXAFS data. The spectra calculated in the framework of the one-electron approximation are in good agreement with the measurement. The strong Ga K-edge white line of l-GaSb shows a high DOS near E_F and is partially due to the core-hole Coulomb final-state effect. The electronic structure of the p-like empty states was obtained from the XANES spectra taking the core-hole effect into account. The DOS of l-GaSb is quite high around E_F, as for metals, while that for c-GaSb has a gap opening there. Some crystalline features and covalent characteristics persist in the liquid.

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