Structures of Liquid GaSb and InSb Studied with the Extended X-Ray-Absorption Fine-Structure Method

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The extended x-ray-absorption fine-structure technique is applied to study the local atomic structures of liquid GaSb and InSb using an improved sample holding method. The partial pair distribution functions and coordination distributions of the two liquids are given by using reverse Monte Carlo simulation. The coordination numbers in liquid GaSb are mostly 5 and 6, in addition to which there are about 15% of 4 coordination and about 10% of 7 coordination. On average, the coordination number is 5.4. The results are similar in liquid InSb. This structural study provides some hints of the metallic behavior and density increase in the liquid. [S0031-9007(97)04456-6]

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The phase transition from solids to liquids is accompanied by marked changes in both the structure and the properties. The melting of the covalent semiconductors such as Si, Ge, GaSb, InSb, etc., exhibits a special feature, that is, the covalent bond is broken, the density increases and a semiconductor-metal transition occurs. To understand the mechanism of the transition and the origin of the property changes, as well as to improve the crystal growth of these important materials, the structural study of these melts has attracted increasing attention in recent years [1,2,3].

The fundamental difficulties of the structural study on the melts are the sample holding at high temperature in the experiment and the large disorder distribution of the atoms in the analysis. Moreover, the technique for measuring the structure of a multicomponent liquid is still under development, although the total pair distribution function can be obtained with a conventional x-ray or neutron scattering technique. To determine partial pair distribution function of a multicomponent system, anomalous x-ray scattering or neutron scattering with isotopic substitution [4] must be used. In the former, the measurements should be performed at different wavelengths, for instance, the scattering scans at three wavelengths have to be carried out for a two-component sample. In addition, the minute difference among the real parts of the scattering factors causes considerable error in the result. Alternatively, neutron scattering with isotopic substitution can provide a better result, but it is costly.

The extended x-ray-absorption fine-structure (EXAFS) technique is a powerful alternative for probing the liquid structure [5,6,7], which can be applied to determine the local structure surrounding a specific kind of atom and can nicely complement the structure factor information derived from the x-ray or neutron diffraction. Nevertheless, there are several problems which should be solved in studying the melt structure with the EXAFS technique. The weak absorption oscillating signal and asymmetrical distribution of the near-neighbor atoms make it hard to achieve desirable results by a conventional analysis method, for instance, cumulant expansion. The measurement of the melt at high temperature requires reconsidering a suitable arrangement for the sample mounting.

In this Letter we report the studies on the structure of GaSb and InSb melts by an improved XAFS experiment and analysis method. The crystalline GaSb and InSb are two important compound semiconductors of zinc blende structure. The nearest neighbors are four heterogeneous atoms composed of a tetrahedron at distances 2.639 and 2.835 Å, respectively, from the central atom. The next nearest neighbors consist of twelve of the same kind of atoms. The densities of GaSb and InSb increase 8.2% and 12.5%, respectively, when they melt (melting points are 982.6 and 783 K, respectively). In the molten state the conductivity and temperature coefficient show a metallic behavior. In the previous work on the liquid GaSb structure by neutron diffraction, only the total pair distribution function was given [1]. In this paper the EXAFS data of liquid GaSb and InSb are treated with the reverse Monte Carlo (RMC) simulation, and the results of the partial pair distribution functions and the structural units are reported.

The main difficulty in the data collection of the EXAFS signal for the liquid system is how to keep a uniform thin liquid film vertical at high temperature during the measurement with a transmission mode. In order to resolve this problem the sample preparation and the experimental procedure in our measurement were as follows. The fine powders of GaSb or InSb (about 10 μm size), which were prepared from single crystals by grinding and sieving, was sufficiently mixed with LiF powder made from a single crystal. The mixed powder was pressed into tablets of diameter 10 mm and thickness 1 mm. The ratio of GaSb or InSb to LiF powder was optimized by calculating and measuring the x-ray absorption to ensure that the absorption jump $\triangle \mu x \approx 1$ at the absorption K edge could be measured. The tablet was sealed in a vacuum quartz tube and sintered at 773 K for about 4 h and then put into a quartz sample holder with two thin windows (of thickness 200 μm) sealed in the vacuum. There are several advantages to using LiF as a matrix for holding the droplet of GaSb or InSb melt. Its soft and wetting properties are helpful in making the droplet stick to the tablet, thus avoiding any leakage, unlike in the case of using a BN matrix. The x-ray absorption of LiF is quite low, and the melt point (1113 K) is high enough for use as a matrix material. In addition, it was verified by x-ray diffraction that GaSb or InSb did not react with LiF at high temperature, even at temperatures above the melting point of GaSb or InSb.

The EXAFS measurements were carried out on the beam line 10B at the synchrotron radiation source of the Photon Factory in Japan. A transmission mode was used in the measurement with a Si(311) channel-cut monochromator. The electron energy in the storage ring was about 2.5 GeV with a current of 200 mA. Two ion chambers filled with a mixture of Ar and N_2 gases were used to detect incident x-ray intensity and transmitted intensity simultaneously. The Ga K edge and Sb K edge EXAFS spectra of GaSb were measured at room temperature, 773 K, 973 K, and 993 K, while the In K edge and Sb K edge EXAFS spectra of InSb were measured at room temperature, 658 K and 813 K. Figure 1 shows the Ga K-edge EXAFS oscillations at room temperature and 993 K. A high-quality liquid spectrum was well collected in our experiment. It should be noted that the EXAFS signal of the melt is quite different from that of the solid, and the EXAFS magnitude of the melt is much reduced, indicating a large disorder in the melt. The raw x-ray-absorption spectra are given in the inset of Fig. 1 which illustrates that there is no evidence of changes of absorption jumps in the melting procedure. That means the droplets of the sample disperse uniformly in the LiF matrix after melting, rather than collapsing to the bottom of the sample holder as usually encountered in such types of measurement.

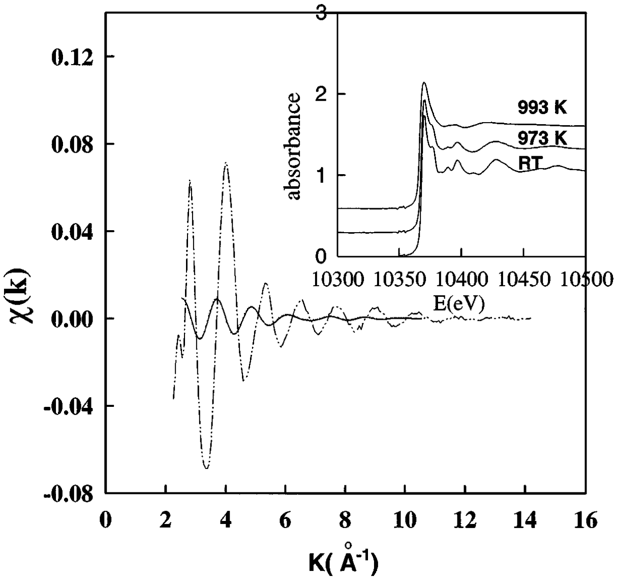

FIG. 1. Ga K-edge EXAFS oscillations of GaSb at room temperature (RT) (long-dashed line) and 993 K (solid line). The raw x-ray-absorption spectra at RT, 973 K, and 993 K are shown in the inset.

In the first step of data analysis, the absorption background should be carefully removed, because the EXAFS oscillation magnitude for the liquid system is faint (generally in the order of 10^{-3}), otherwise the EXAFS oscillation may be distorted seriously. Several methods were put forward to tackle this problem. The optimum one we have chosen is similar to that developed by Li *et al.* [8]. A weighted exponential function was used to simulate the feature of atomic distribution for a disordered system, and the cubic spline smoothing method was used to fit the background. As an example, the Ga K-edge x-ray-absorption spectrum for liquid GaSb at 993 K and its background are shown in Fig. 2, in which a multielectron excitation feature at 48 eV behind the threshold is also accounted for in the background removal.

The EXAFS oscillation for a disordered system can be expressed by the following formula:

$$\chi_\alpha(k) = \sum_\beta 4\pi\rho \int_0^\infty r^2 g_{\alpha\beta}(r)\chi_{1\beta}(k,r)\,dr\,,$$

where α and β represent the chemical types of the central and backscattering atoms, respectively, $\chi_{1\beta}(k,r)$ is the contribution from a single β-type atom at distance r, ρ is the average number density in the liquid, and $g_{\alpha\beta}(r)$ is the partial distribution function. In order to get $g_{\alpha\beta}(r)$ from EXAFS data of a disordered system the cumulant expansion [5], model-dependent analysis [9,10], and RMC method [11] can be used. In our experience with the first two methods, it is hard to get a reliable result in the case of large disordered systems such as liquid GaSb and InSb. The RMC algorithm is based on a Metropolis Monte Carlo procedure for simulating the partial configuration in a

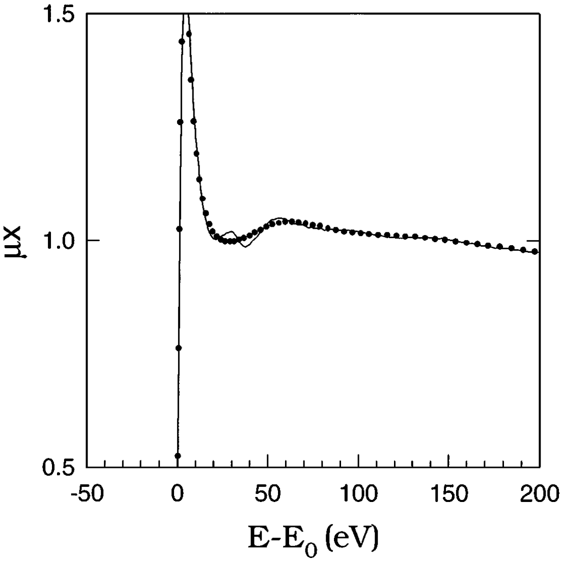

FIG. 2. Ga K-edge spectra (solid line) and its background (dotted line) of liquid GaSb at 993 K.

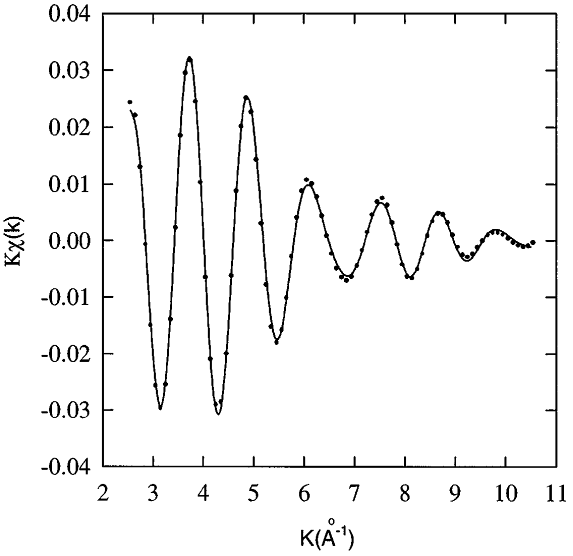

FIG. 3. Experimental data (solid line) and RMC fitting (dotted line) of GaSb Ga K-edge XAFS oscillation at 993 K.

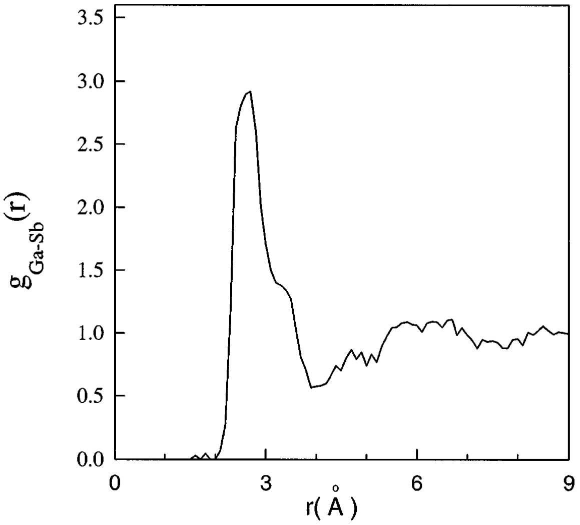

FIG. 4. Ga-Sb pair distribution function of GaSb melt at 993 K.

liquid. Instead of minimizing the system energy to reach equilibrium, RMC decreases the difference between the experimental spectrum and the calculated one. The advantage of this method is that it is a fitting method based on the measured data and hence gives the structural information directly from the experiments with no hypothetical model. In addition, the possible structural units and their distributions can be derived from the simulated configurations. In this work, the RMC simulation was employed to extract the structure information.

One feature of the RMC method is that multiedge EXAFS data can be hosted in one simulation. This means that the derived configurations fit the requirement of multiedge EXAFS data in one simulation routine and the results can be confirmed more confidently. Both the Ga K-edge and Sb K-edge EXAFS data of liquid GaSb were put in the simulation simultaneously. As shown in Fig. 1, the Ga K-edge EXAFS oscillation of liquid GaSb can be discerned up to 10.5 Å^{-1}. The Fourier transform ranges were determined according to the maximum range in which the XAFS signal could be discerned. The structural information up to 6 Å in the Fourier transform spectra was used in the simulation. $\chi_{1\beta}(k, r)$ was calculated with a FEFF program [12]. The S_0^2 was determined by comparison of the FEFF calculation with the room temperature experimental data.

In our calculation, 1728 atoms were proposed with a normal periodical boundary condition. The radial distribution function can be calculated up to 15 Å, which is accurate enough for the EXAFS analysis. The simulations with 200, 500, and 1000 atoms were also tested, and it was found that the result calculated from the system with 1000 atoms was close to that with 1728 atoms. The crystalline structure parameters were used as the initial configuration. The step length in the simulation was about 0.5 Å to keep the system from falling into any local minimum. The stochastic simulation was run more than 600 000 times. Figure 3 shows the experimental EXAFS oscillation and the RMC fitting result, which demonstrates that the fitting is quite good. The same procedure was carried out for the InSb system.

The Ga-Sb pair distribution function of GaSb melt is shown in Fig. 4. It can be seen that the near-neighbor atoms are distributed in the range of 2.4 to 4.0 Å and the main peak is located at about 2.7 Å, while a shoulder appears in the distance at 3.2 Å. The average coordination number is 5.4, which is calculated from the area of the main peak in the pair distribution function. The statistical distribution of the coordination number can be calculated from the derived configurations of RMC simulation in which all

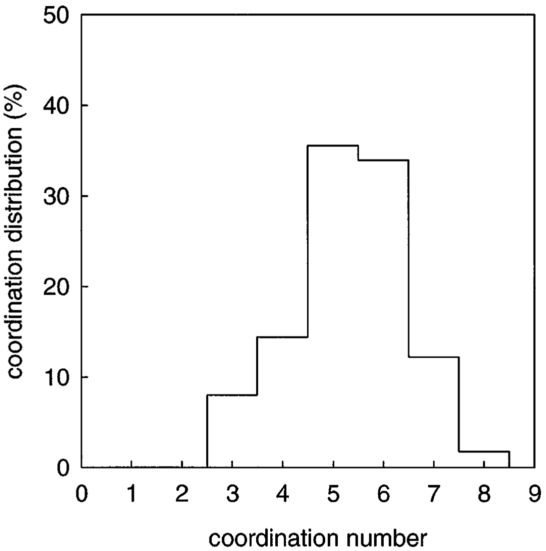

FIG. 5. The coordination number distribution of liquid GaSb at 993 K.

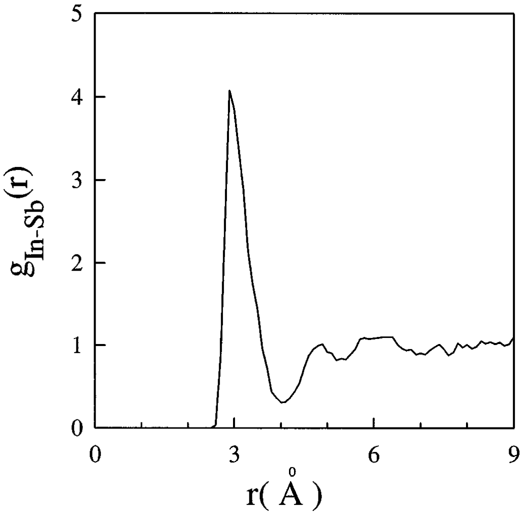

FIG. 6. In-Sb pair distribution function of liquid InSb at 813 K.

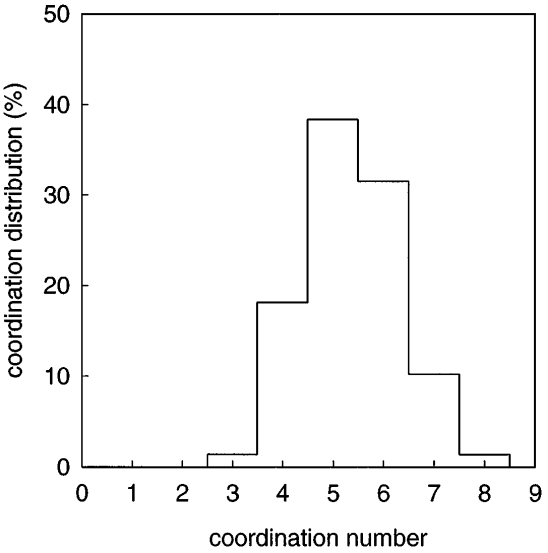

FIG. 7. The coordination number distribution of liquid InSb at 813 K.

possible positions of atoms around a central atom are obtained. Here, the shortest bond length is defined as the first minimum in the distribution function. The coordination distribution of GaSb melt is summarized in Fig. 5, from which we can see that there are several coordinating states in liquid GaSb. The coordination numbers are mostly 5 and 6, besides which there are some 4 (about 15%) and 7 (about 10%) coordinations. Because there is a large enough difference in the backscattering amplitudes of Ga and Sb atoms, the chemical type of the coordination atoms can be distinguished in our analysis. The result shows that there is heterogeneous atomic coordination essentially in liquid GaSb, i.e., Ga is surrounded by Sb atoms and Sb by Ga atoms, and on average the coordination number is 5.4. Comparing with the coordination number 4 in the solid, the coordination distribution in liquid GaSb indicates that more than 80% of the local coordinates deviate from the regular tetrahedra. The analysis of the structure of liquid InSb has been performed and a similar result has been obtained. The pair distribution function and the coordination distribution are shown in Figs. 6 and 7, respectively. The average coordination number is 5.2. Our results demonstrate that for GaSb and InSb the melting has destroyed the covalent network. However, heterocoordination in the liquid state is not sufficient to sustain a pseudogap [13]. The structural information of liquid GaSb and InSb should be helpful for understanding the metallic behavior and density increase, although no quantitative theory appears to have been put forward in these terms.

In conclusion, the EXAFS technique has been applied to study the local atomic structure of liquid GaSb and InSb by using an improved sample holder. The partial pair distribution functions and coordination distributions of the two liquids have been obtained by the RMC analysis method. The coordination configuration and properties of the liquids have been discussed.

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