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Abstract
The structure of liquid GaSb has been investigated up to 10.1 GPa by means of energy-dispersive x-ray diffraction using a synchrotron radiation source and a multi-anvil apparatus. With increasing pressure up to about 5 GPa, the second and third peaks in the pair distribution functions, $g(r)$, shift remarkably toward smaller r-values, while the first peak shifts toward larger r-values. This shows that the structure of liquid GaSb does not contract uniformly. Corresponding to the shift of the first peak, the coordination number increases. These results show that the local structure in liquid GaSb changes into a more highly coordinated state under pressure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is known that liquid group IV elements have characteristic structure factors, $S(Q)$, and pair distribution functions, $g(r)$. $S(Q)$ has a small hump at the high Q-value of the first peak. The gap between the first and second peaks in $g(r)$ is relatively shallow compared to that for a simple liquid. These characteristics imply that the liquid has non-simple local structure. As for liquid Si and liquid Ge, the local structure is considered to be the same as that of the high-pressure crystalline phase of β-tin [1–3].

GaSb is one of the most popular III–V compounds. The structural and electronic properties are similar to those of the group IV elements. The chemical bonding is, however, more ionic as compared that of group IV elements. It is well known that the crystal structure of the high-pressure phase depends on the ionicity. Since the local structure of the liquid is different from that of the crystalline state for these elements and compounds at ambient pressure, it is very interesting to investigate the effect of the ionicity on the local structure of liquids.

The previously reported P–T phase diagram for GaSb is shown in figure 1. Crystalline GaSb has the following high-pressure sequence: ZnS, β-tin (or *Imma*) and simple hexagonal (sh) structure [4–6]. In the present study, we have performed an *in situ* high-pressure x-ray diffraction study of liquid GaSb to elucidate its local structure at high pressures.
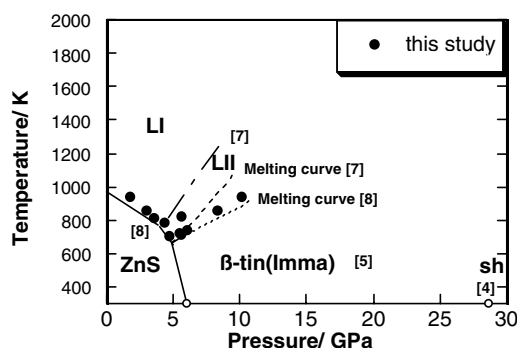
Figure 1. The phase diagram of GaSb [4, 5, 8]. The liquid–liquid phase boundary is shown by the dotted line [7]. The experimental conditions in this study are shown by solid circles.

2. Experimental details

The structure of liquid GaSb was investigated by the energy-dispersive x-ray diffraction method in conjunction with a synchrotron radiation source and a multi-anvil cell high-pressure apparatus [9]. The intensity data were taken by the MAXIII apparatus installed at BL14-C2 in the High Energy Accelerator Research Organization (Photon Factory, KEK). The sample is encapsulated in a BN or NaCl container. The container and the pressure marker (BN + NaCl) are surrounded by a graphite tube heater. These are put in the pressure-transmitting medium of the mixture of boron and epoxy. The P–T conditions in this study are shown in figure 1. These conditions were determined from the lattice parameters of NaCl [10] and the melting temperature. The intensity data were analysed on the basis of the Faber–Ziman form [11]. The density of the liquid at high pressures was estimated from the volume of the crystalline phase at high pressure and at a temperature just below the melting temperature. We calculated the coordination number of the liquid GaSb by fitting the first peak in the radial distribution function with a Gauss function supposing that all partial pair distribution functions, g_{ij}, are equal.

3. Results and discussion

Structure factor, $S(Q)$

The total $S(Q)$ at high pressures are shown in figure 2. With increasing pressure, the first and hump peaks shift toward higher Q-values, while the second and third peak positions remain almost constant. This shows that the contraction of the liquid is not uniform. This contraction mechanism is completely different from the uniform compression of simple liquid [12].

The height of the first peak in $S(Q)$ increases and that of the hump peak decreases with increasing pressure. It is known that the structure factors of the group IV elements show a similar sequence in the order from Si to Pb. The ratios of the peak positions of the second peak to the first peak, $Q2/Q1$ are shown in figure 3, together with those for the liquid group IV elements. With increasing pressure, $Q2/Q1$ for liquid GaSb decreases from the value for Si to that for Pb. The pressure dependences of the peak height and $Q2/Q1$ value suggest that the local structure of liquid GaSb approaches that of liquid Sn or Pb.

Pair distribution function, $g(r)$

The pair distribution functions, $g(r)$, at high pressures are shown in figure 4. With increasing pressure, the second and third peaks shift remarkably toward smaller r-values, while the
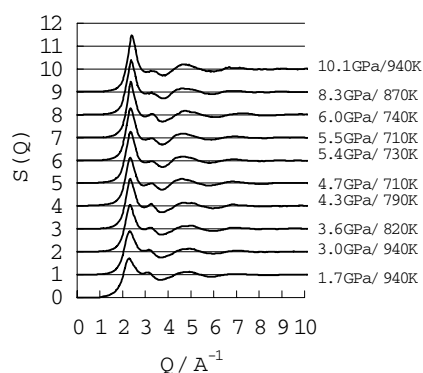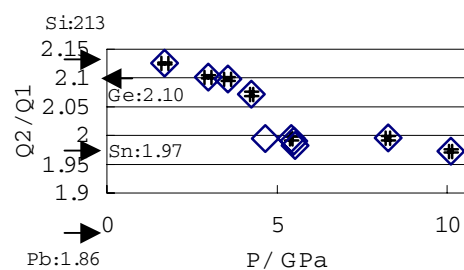
Figure 2. $S(Q)$ for liquid GaSb at high pressures.

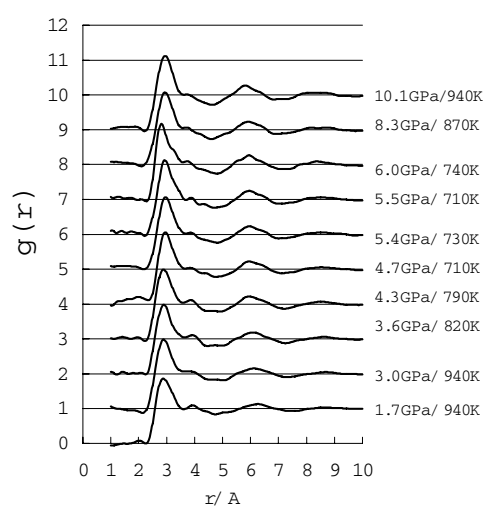**Figure 3.** $Q2/Q1$ for liquid GaSb at high pressures.

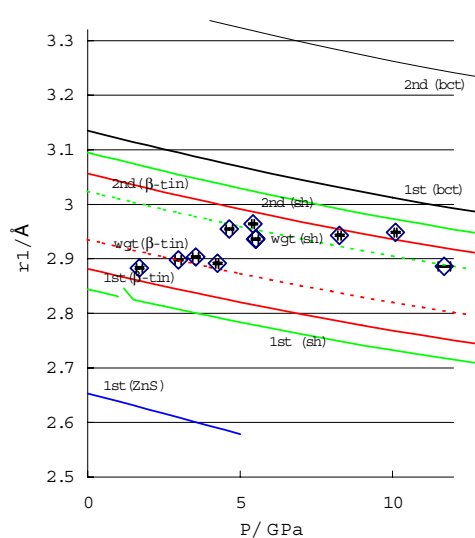**Figure 4.** $g(r)$ for liquid GaSb at high pressures.

Figure 5. The position of the first peak in $g(r)$ for liquid GaSb at high pressures and the interatomic distances for the high-pressure crystalline polymorphs of group IV elements and III–V compounds. Dotted lines show the averaged interatomic distances between the first-and second-nearest distances weighted by the corresponding coordination number.

position of the first peak is almost constant. This also shows the non-uniform contraction of liquid GaSb. The height of the hump peak around 4 Å decreases with increasing pressure.

In order to elucidate the local structure of liquid GaSb at high pressures, the positions of the first peak and the interatomic distances for several high-pressure crystalline phases of group IV elements and III–V compounds are compared, where the interatomic distances are calculated from the volume of liquid GaSb at high pressures (figure 5).

The c/a ratios of the β-tin, sh and body-centred tetragonal (bct) forms are fixed at the values in [4] in the calculation. With increasing pressure up to 4.7 GPa, the position of the first peak shifts toward larger r-values and approaches the averaged interatomic distance for the β-tin structure. Corresponding to the change of the peak position of the first peak, the coordination number increases from about 4.5 to 5.5 (figure 6). It is known that ZnS and β-tin
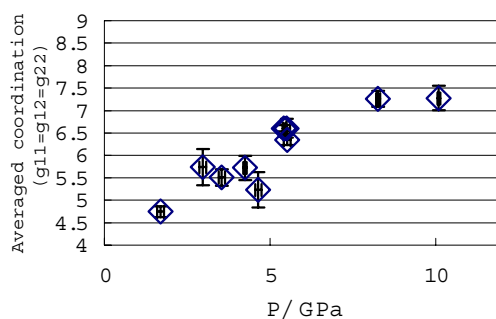
Figure 6. The averaged coordination number in liquid GaSb at high pressures, where the coordination numbers are calculated supposing that all partial pair distribution functions are equal (the chemically disordered model).

have coordination numbers of 4 and 4 + 2, respectively. The observed increase in the peak position and the coordination number suggest that the local structure of liquid GaSb approaches the β-tin structure with increasing pressure up to 5 GPa.

The crystal structure relation between ZnS and β-tin can be understood in terms of the c/a ratio. The change of the c/a ratio for the ZnS cell axes from 1.0 to 0.39 transforms the ZnS structure into the β-tin structure. This change can be performed mainly by the bending of the bond angle, retaining the nearest-neighbour distance. The observed change in the local structure in the liquid GaSb may be interpreted on the basis of this mechanism. At higher pressure, above 5 GPa, the position of the first peak in $g(r)$ approaches the averaged interatomic distance for a sh structure, and the coordination number also approaches the values for the simple hexagonal structure (2 + 6). These findings suggest that the local structure of the liquid approaches sh structure at pressures above 5 GPa.

4. Conclusions

We performed *in situ* x-ray diffraction studies of liquid GaSb under pressure up to 10.1 GPa. Both $S(q)$ and $g(r)$ show non-uniform contraction of the local structure of liquid GaSb.

The positions of the first peaks in $g(r)$ and the coordination number at high pressures suggest that the local structure in the liquid changes from a low-coordination state into a high-coordination state. On comparison of the local structure to that in high-pressure crystalline states of group IV elements, the local structure of GaSb is found to approach the β-tin structure with pressure increasing up to 4.7 GPa.

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