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Ab initio molecular dynamics simulations of liquid structure change with temperature for a GaSb alloy

Tingkun Gu,[1,2] Jingyu Qin,[1] Xiufang Bian,[1] Changye Xu,[3] and Yuanhua Qi[3]
[1]*The Key Laboratory of Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University-Southern Campus, Jinan 250061, People's Republic of China*
[2]*School of Electrical and Engineering, Shandong University, Jinan 250061, People's Republic of China*
[3]*School of Physics and Microelectronics, Shandong University Jinan 250061, People's Republic of China*
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We have performed *ab initio* molecular-dynamics simulation of liquid GaSb at four temperatures: 1073, 1323, 1523, and 1773 K. The calculated total structure factors and pair correlation functions are in good agreement with the experimental results. As temperature rises, some changes in the partial pair correlation functions and bond-angle distributions have been observed. We find that the clusters of Sb atoms have open structure at low temperature, then turn into more close-packed structure at high temperature, and the hetero-atomic coordination of Ga-Sb decreases obviously with increasing temperature in the range of 1073–1523 K. The abnormal changes of diffusion constants D_{Ga}, D_{Sb} and the ratio of $D_{\mathrm{Ga}}/D_{\mathrm{Sb}}$ with temperature, which are consistent with the changes of liquid structure, have been observed in our calculated results. We have also examined electronic properties of the liquid GaSb system and found a small dip at Fermi level as a result of Ga-Sb bonds.

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I. INTRODUCTION

GaSb is one of the popular III–V semiconductors and its structural, electronic properties are similar to those of IV semiconductors. In the crystalline phase, the Ga-Sb bond has a weak ionic nature, and its Phillips ionicity is 0.261.[1] Zinc-blende-type GaSb crystalline phases are stable at ambient condition with a coordination number of 4. Upon melting, the GaSb becomes metallic, similar to Si and Ge, and transforms to a more close-packed structure with the density increased by 8.2%,[2] and parts of the covalent bonds are broken by the thermal motion of atoms and compositional defects or "wrong" bonds exist (bonds between the same type atoms are absent in the crystalline state).

The physical properties of liquid GaSb have been studied extensively. To investigate the synthesis process of a compound semiconductor of GaSb, Kakimoto *et al.*[3] measured the viscosities of ℓ-GaSb and the experimental results indicated that the temperature dependency of the viscosity of ℓ-GaSb did not follow the Arrhenius relation. Further, they found that the viscosity of ℓ-GaSb compound gradually approached the average value calculated as a mixture of gallium and antimony at high temperatures and the difference between the values of viscosity of ℓ-GaSb and ℓ-Sb ($\eta_{\mathrm{GaSb}}-\eta_{\mathrm{Sb}}$) gradually diminished with decreasing temperature. Glazov *et al.*[4] also observed the anomalous changes of viscosity in ℓ-GaSb. But recently, Sato *et al.*[5] have also measured the viscosity of liquid GaSb and found it showed good Arrhenius relation in the range of 991.9–1487.9 K.

To explain the anomalous changes in viscosity, the structure of ℓ-GaSb was measured by neutron diffraction from 1073 to 1323 K,[6] but no obvious changes in total structure factors and pair correlation functions were observed over this temperature range. Recently, Wang *et al.*[7] investigated the structure of ℓ-GaSb with the extended x-ray-absorption fine-structure method and indicated that the covalent bonds of Ga-Sb were preserved in ℓ-GaSb alloy. Because of the great difficulties in experiment, the report on how the partial structure factors or partial pair correlation functions of the ℓ-GaSb alloy change with temperature has not been seen so far. In order to make further investigation on the structure change of ℓ-GaSb, the three partial pair correlation functions of different temperatures should be measured.

In this paper, we have performed *ab initio* molecular-dynamics (AIMD) simulations for ℓ-GaSb at four temperatures. The AIMD simulations are based on density-functional theory (DFT) and the pseudopotential method,[8,9] following the methods pioneered by Car and Parrinello.[10] DFT is generally accurate for metals and semiconductors, and previous AIMD simulations of liquid such as Si,[11] Ge,[12] Ga,[13] GaSe,[14] GaAs,[15,16] CdTe,[17] GeTe,[18] etc., have demonstrated close agreement with experimental results. To our knowledge, Molteni *et al.*[19] had studied the structure of ℓ-GaSb with tight binding molecular dynamics simulation.

The paper is organized as follows: In Sec. II we discuss the theoretical framework and in Sec. III we present the results of static structure and compare with the experimental and other theoretical results. Section IV is a discussion on the dynamical properties. In Sec. V we report the electronic structure of ℓ-GaSb alloy. The final part is the discussion and conclusion

II. COMPUTATIONAL METHODS

Our calculations have been performed by using Vienna *ab initio* simulation program VASP.[20,21] The electronic exchange and correlation are described in the generalized gradient approximation, using the PW91 functional due to Perdew and Wang.[22] The solution of the generalized Kohn-Sham equations is performed with an efficient iterative matrix-

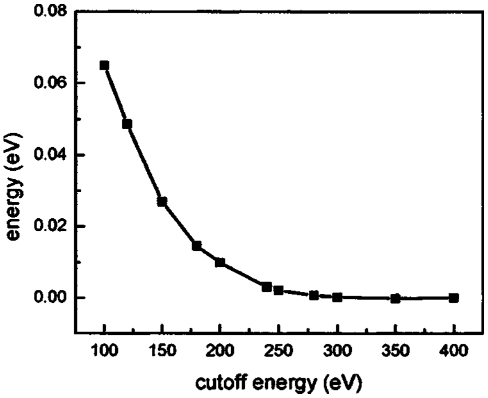

FIG. 1. Calculated total energy for zinc-blende structure of GaSb versus the plane-wave cutoff energy. The total energies are referenced to the total energy obtained with a cutoff energy of 400 eV.

diagonalization routine based on a sequential band-by-band residual minimization method[20] applied to the one-electron energies. An improved Pulay-mixing[23] was used to achieve self-consistency of charge-density and potential.[20] The ultrasoft pseudopotentials (USPP) of Vanderbilt type are used to describe the electron-ion interaction.[24,25] The electronic wave functions are expanded in the plane-wave basis set. To obtain an appropriate plane wave cutoff, we have evaluated the total energy for zinc-blende structure of GaSb as a function of plane-wave cutoff energy and the results are shown in Fig. 1. We find that the calculations are well converged with a cutoff of 250 eV. With this energy cutoff and USPP, we obtain the equilibrium lattice parameter of zinc-blende structure of GaSb to be 0.6189 nm, which is about 2.0% larger than the experimental value (0.6096 nm). Thus, all of the following calculations have been performed with this energy cutoff 250 eV and the USPP.

Our simulations for ℓ-GaSb have been performed with the cubic supercell which contains 80 atoms, and the periodic boundary conditions are imposed. The temperatures are set at 1073, 1323, 1523, and 1773 K and the experimental densities are used.[5] The simulations are performed in a canonical ensemble with a Nosé thermostat for temperature-control.[26] The equation of motion is solved via the velocity Verlet algorithm with a time step 3 fs. The Γ point alone is used to sample the Brillouin Zone of the supercell.

To prepare the liquid, the atoms are initially arranged in cubic supercell randomly. Then, the system is heated up to 3273 K by rescaling the ionic velocities. After equilibrating for 3 ps at this temperature, we gradually reduce the temperature to 1073 K. After equilibrating for 3 ps again, the quantities of interest are obtained by averaging another 12 ps. For other temperatures, we only repeat this procedure and change the final temperature into 1323, 1523, and 1773 K, respectively. In all our simulations, the energy conservation is excellent; we find that the drift is smaller than 0.5 meV/atom/ps.

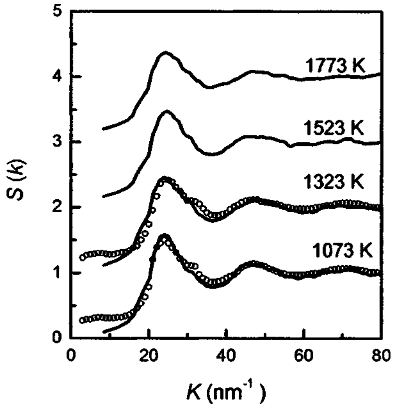

FIG. 2. Calculated total structure factor $S(k)$ of ℓ-GaSb alloy (full line) compared with the result of experiment (circle, Ref. 6).

III. STRUCTURAL PROPERTIES

In a molecular dynamics simulation of liquid state, the structure factor, $S(k)$, serves as a connection with experimental results. The partial structure factors $S_{ij}(k)$ are defined by

$$S_{ij}(k) = \frac{1}{N_i N_j}\left\langle \sum_{\mu=1}^{N_i}\sum_{\gamma=1}^{N_j} e^{ik(r_\mu - r_\gamma)} \right\rangle. \tag{1}$$

The positions of ions $\{r_\mu\}$ are obtained by our *ab initio* MD simulations, N_i is the number of ions of the ith species, and the angular brackets $<>$ mean the time average. The total structure factor is then expressed as a linear combination of the partial structural factors $S_{ij}(k)$ normalized by the neutron scattering lengths of Ga and Sb,

$$S(k) = \sum_i \sum_j c_i^{1/2} c_j^{1/2} \frac{b_i b_j}{c_i b_i^2 + c_j b_j^2} S_{ij}(k), \tag{2}$$

where neutron scattering lengths are: $b_{\mathrm{Ga}} = 7.288$ (Ref. 27) and $b_{\mathrm{Sb}} = 5.57$.[28] c_i is the number concentration.

The structure factors are shown in Fig. 2. In this figure, we compare our theoretical structure factors with the experimental results from neutron scattering and find good agreement between them. Our calculated structure factors also reproduced the small shoulder on the right side of the first peak as in liquid GaAs.[15,16] The liquid structure of III–V compounds (GaAs and GaSb) had been calculated by Molteni *et al.*[19] using tight-bonding molecular dynamics simulation. They failed to reproduce this small shoulder for liquid GaAs and GaSb since tight binding simulation has some restrictions (they are not self-consistent and the basis set is limited). It is instructive to trace how the shoulder is accentuated in liquids of the IV row elements as we move from metallic to covalent liquids. It appears first in liquid Ge and intensifies in the less metallic liquid Si and is absent in liquid Pb and Sn.[29] Thus, this shoulder appears to be a signature of local order resulting from covalent bonding in the liquid. In addition, the shoulder becomes weaker with increasing temperature.

Better insight into the liquid structure is provided by the pair correlation function $g(r)$. The total pair correlation is obtained by weighting the partial pair correlation functions with the neutron scattering length,

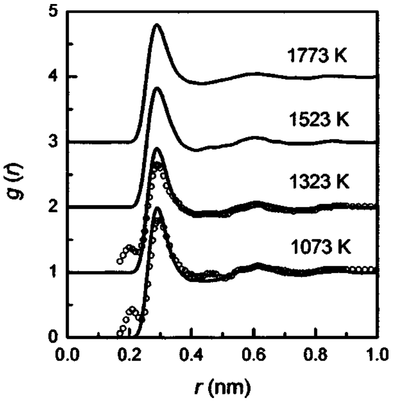

FIG. 3. Calculated total pair correlation functions $g(r)$ of ℓ-GaSb alloy (full line) compared with the results of experiment (circle, Ref. 6).

$$g(r) = \sum_i \sum_j \frac{c_i c_j b_i b_j}{(c_i b_i + c_j b_j)^2} g_{ij}(r). \tag{3}$$

The four total pair correlation functions are shown in Fig. 3. The calculated total pair correlation functions are in good agreement with experimental results. Given the pair correlation function, it is possible to estimate coordination numbers as in Ref. 6,

$$N = 2\int_0^{r_{\max}} 4\pi r^2 \rho g(r)\mathrm{d}r, \tag{4}$$

where $r_{\max}$ is the position of the first peak in radial distribution function $4\pi r^2 \rho g(r)$ (RDF). We find $N=5.5$ for 1073 K. The corresponding experimental vale is 5.4 ± 0.5 at 1073 K.[6]

The calculated partial pair correlation functions at different temperatures are presented in Fig. 4. Comparing $g_{\mathrm{GaGa}}(r)$ and $g_{\mathrm{SbSb}}(r)$ of ℓ-GaSb with that of pure Ga and Sb liquids, we find that the overall features of $g_{\mathrm{GaGa}}(r)$ and $g_{\mathrm{SbSb}}(r)$ in liquid GaSb resemble that in pure Ga (Ref. 13) and Sb (Ref. 30) liquids. Thus, it can be expected that the clusters of Ga and Sb in liquid GaSb would have a tendency to replicate the structural features of pure Ga and Sb liquids, respectively. In the liquid state, pure ℓ-Ga has a compact structure, and pure ℓ-Sb shows semi-metallic behavior. For ℓ-Sb, although the Peierls distortion is almost destroyed upon melting, the results for structure and electronic properties confirm that a Peierls distortion still exists in liquid state.[30,31] Observing the changes of $g_{\mathrm{GaGa}}(r)$, $g_{\mathrm{GaSb}}(r)$, and $g_{\mathrm{SbSb}}(r)$ carefully, we find that there are some changes in partial pair correlation functions with increasing temperature. The heights of the first and second peaks of $g_{\mathrm{GaGa}}(r)$, $g_{\mathrm{GaSb}}(r)$, and $g_{\mathrm{SbSb}}(r)$ decrease with increasing temperature. In addition, for $g_{\mathrm{SbSb}}(r)$, the small shoulder on the right side of the first peak, which locates at ~0.43 nm (the second-neighbor distance of Sb atom in A7 structure), becomes weaker with increasing temperature and disappears as temperature goes up to 1773 K. This indicates that this peculiar local structure of Sb atoms in ℓ-GaSb is destroyed gradually by thermal motion of atoms.

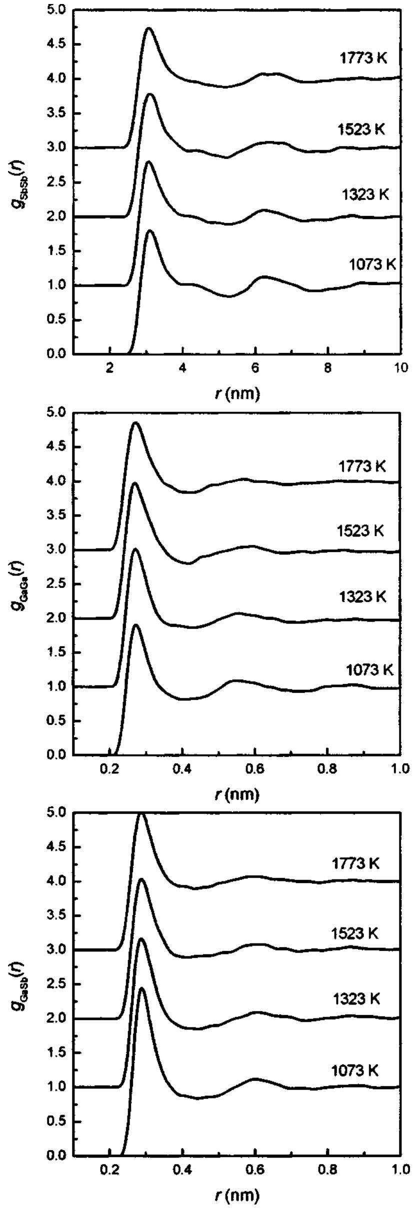

FIG. 4. The partial pair correlation functions of ℓ-GaSb alloy.

In all calculated results, the nearest-neighbor distances of Ga-Ga, Ga-Sb, and Sb-Sb (the coordinate of the first peak of partial pair correlation function, r_{GaGa}, r_{GaSb}, r_{SbSb}) are 0.27, 0.29, and 0.31 nm. This also indicates that the liquid structure of GaSb alloy is different from that β-Sn structure just as what Hottari found in experiment.[32]

Given the partial pair correlation functions, one can estimate partial coordination numbers as

$$N_{\alpha\beta} = \int_0^{r_{\min}} 4\pi r^2 \rho_\beta g_{\alpha\beta}(r)\mathrm{d}r, \tag{5}$$

where $r_{\min}$ is the first minimum coordinate in $4\pi r^2 \rho_\beta g_{\alpha\beta}(r)$ (defined as partial radial distribution function). ρ_β is the number density of the species β. In all calculations we use the total radial distribution at 1073 K to find $r_{\min}$ (0.40 nm) and use it to determine the partial coordination numbers. To estimate compositional defects, a compositional disorder

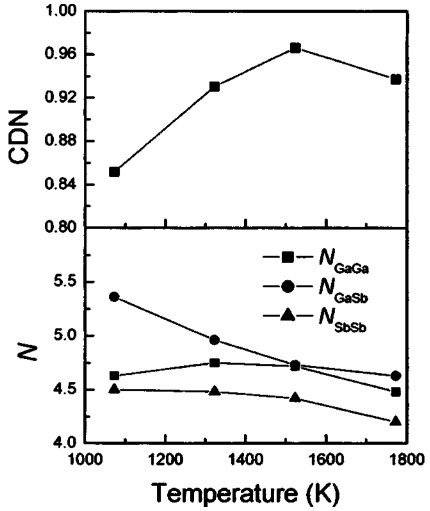

FIG. 5. The calculated partial coordination numbers and CDN of ℓ-GaSb.

number (CDN), defined as the ratio of the numbers of homogeneous and heterogeneous bonds,[15] $(N_{\mathrm{GaGa}}+N_{\mathrm{SbSb}})/2N_{\mathrm{GaSb}}$, is calculated. In Fig. 5, we give the partial coordination numbers and CDN. The coordination numbers of Sb-Sb and Ga-Ga are nearly invariable in the temperature range of 1073–1523 K, and as temperature is beyond 1523 K, these values decrease slightly. But for the coordination number of Ga-Sb, its value decreases with increasing temperature from 1073 to 1523 K and the decreasing rate becomes slower as temperature is beyond 1523 K. The CDN rises with increasing temperature and reaches its maximum at 1523 K. Thus, the calculated results indicate that the bonds of Ga-Sb have been destroyed evidently as temperature is beyond 1523 K.

To gain more insight into the structural changes of Ga and Sb clusters in ℓ-GaSb, we calculate partial bond-angle distributions of Ga-Ga-Ga and Sb-Sb-Sb (Fig. 6). For b_{GaGaGa}, it has a pronounced peak at ~60° indicating close-packed structure of Ga atoms in ℓ-GaSb. The overall feature of b_{GaGaGa} is nearly invariable with temperature; only the part on the right side of the first peak of b_{GaGaGa} becomes more flat at 1773 K, which indicates that the local structure of Ga atoms is not sensitive to temperature. For b_{SbSbSb}, it has two peaks at ~90° and ~180° at 1073 K similar to that of ℓ-Sb.[30] Seifert *et al.*[30] suggested that a weak Peierls distortion should be preserved in ℓ-Sb. As temperature goes up to 1773 K, the small shoulder at ~60° of b_{SbSbSb} at 1073 K turns into a noticeable peak and the other parts of b_{SbSbSb} become flat. This indicates that the local structure of Sb atoms in ℓ-GaSb has a more close-packed stucture at high temperature of 1773 K.

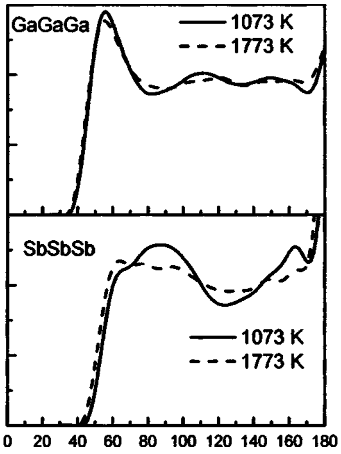

FIG. 6. Partial bond-angle distributions for Ga and Sb clusters normalized by sin(θ). Cutoff distance is 0.34 nm.

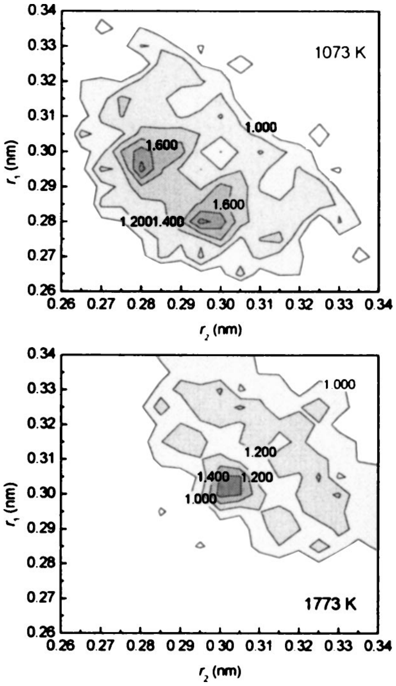

FIG. 7. Angular limited triplet correlation function $P(r_1,r_2)$ of ℓ-GaSb for Sb-Sb-Sb.

To investigate the peak around 180° of b_{SbSbSb} of ℓ-GaSb in detail, we calculate the angular limited triplet correlation function which is plotted in Fig. 7. This function, $P(r_1,r_2)$, is defined as the probability of finding an atom C at a distance r_2 from an atom B, which is at a distance r_1 from the reference atom A. A constraint is placed on the position of atom C. Namely, the BC bond is constrained in a cone of small angular aperture (here, 20°) around the AB axis. For an undistorted disorder structure, the maximum of the distribution should be on the diagonal (i.e., a maximum at $r_1=r_2$). From Fig. 7, we find that an obvious correlation appears at 1073 K: a short bond of length r_1 (0.28 nm) is most probably followed by a longer bond of length r_2 (0.30 nm) and vice versa, but the maximum of $P(r_1,r_2)$ is at (0.305 nm, 0.305 nm) at 1773 K. Thus, the distorted local structure of Sb atoms, i.e., the short-long and long-short bonds correlation, disappears as temperature goes up to 1773 K.

To investigate the bond of Ga-Sb, we calculate the b_{SbGaSb}, b_{GaSbGa} with cutoff distance 0.29 nm (i.e., ~10% larger than the bond length in crystalline states). The results are shown in Fig. 8. The peak in b_{SbGaSb} is at ~109°, i.e., the bond angle of crystalline phases, but for b_{GaSbGa}, this peak shifts to ~90° as a result of the close-packed Ga atoms. As

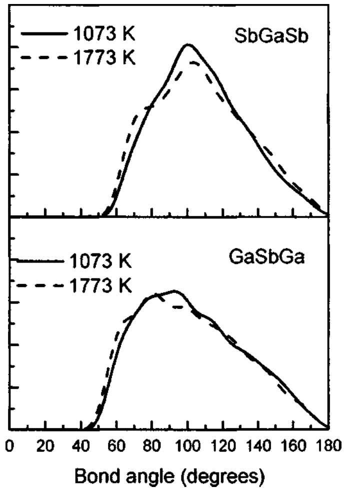

FIG. 8. Bond-angle distributions of SbGaSb and GaSbGa of ℓ-GaSb. Cutoff distance is 0.29 nm.

temperature goes up to 1773 K, no obvious change in b_{GaSbGa} is found, but for b_{SbGaSb}, a noticeable small peak at ~60° occurs as a result of a more close-packed structure of Sb atoms at high temperature.

IV. DYNAMICAL PROPERTIES

We studied the diffusion of atoms in the liquid by calculating the time-dependent mean-square displacement (MSD) defined in the usual way for species α as[33]

$$\langle \Delta r_\alpha(t)^2 \rangle = \frac{1}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} |\mathbf{r}_{\alpha i}(t+t_0) - \mathbf{r}_{\alpha i}(t_0)|^2 \right\rangle, \tag{6}$$

where the sum goes over all N_α atoms of species α, t_0 is an arbitrary time origin and the angular brackets denote a thermal average or equivalently an average over time origins. The calculated results are shown in Fig. 9. For diffusing liquids the MSD is linear in t for large time, and the slope is proportional to the diffusion coefficient D_α of species α,

$$\langle \Delta r_\alpha(t)^2 \rangle \to 6D_\alpha t + B_\alpha, \tag{7}$$

where B_α is constant.

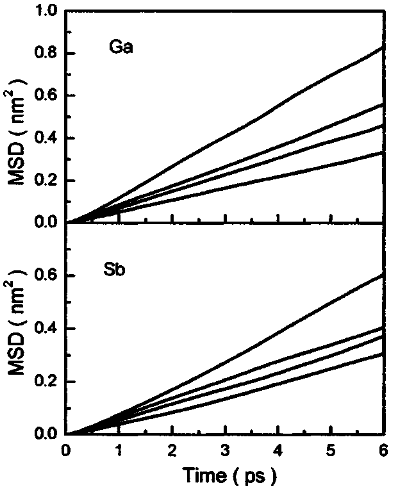

FIG. 9. The time dependence of the mean square displacement of atoms in ℓ-GaSb for all calculated temperatures.

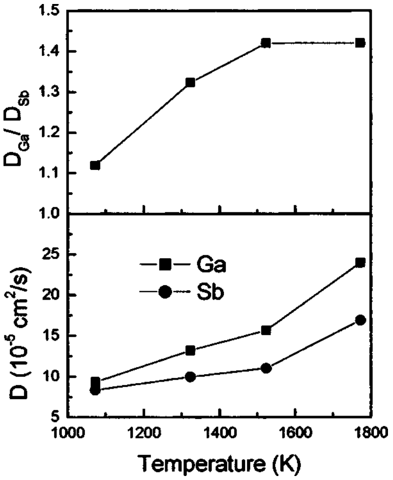

FIG. 10. The calculated diffusion coefficients of Ga and Sb atoms and the ratio of $D_{\mathrm{Ga}}/D_{\mathrm{Sb}}$.

The calculated diffusion coefficients (D_{Ga}, D_{Sb}) and the $D_{\mathrm{Ga}}/D_{\mathrm{Sb}}$ are reported in Fig. 10. In all calculated results, the D_{Ga} is larger than D_{Sb}. We know that self-diffusion coefficients are sensitive to the change of liquid structure and can be served as another way to study the microstructure of liquid.[34] Obviously, the difference between D_{Ga} and D_{Sb} rises with increasing temperature. Because the mass of Ga atom is smaller than that of Sb atom, the smaller ratio of $D_{\mathrm{Ga}}/D_{\mathrm{Sb}}$ indicates that the Ga and Sb atoms have stronger correlations between them. The change tendency of $D_{\mathrm{Ga}}/D_{\mathrm{Sb}}$ with temperature is consistent with that of CDN. Thus, the liquid structure change is also revealed by dynamical properties.

V. ELECTRONIC STRUCTURE

The structure behavior of the liquid alloys can be understood in terms of the electronic structure. Here we have investigated the electronic density of states (DOS) and the local density of states (LDOS), i.e., the DOS for each atomic species is decomposed into angular momentum resolved contributions. The (ℓ, m) angular momentum component of the atom i is the projection onto the spherical harmonic (ℓ, m) of all the wave functions in a sphere of radius R centered on the atom i.[35] The value of the sphere radius R is somewhat arbitrary. We have used the covalent radius of atoms, i.e., $R=0.126$ nm for Ga atom and $R=0.14$ nm for Sb atom.

The DOS and LDOS of ℓ-GaSb are obtained by averaging ten configurations and shown in Fig. 11. Recently, Lu *et al.*[36] have measured the electronic density of states for liquid and crystal GaSb by using XANES spectroscopy method. Our calculated results for GaSb in liquid state are in good agreement with their results. To compare with the electronic structure of GaSb in crystalline state, we have also calculated the electronic density of states of zinc-blende-type GaSb which is shown in Fig. 12. In Figs. 11 and 12, it is shown that there

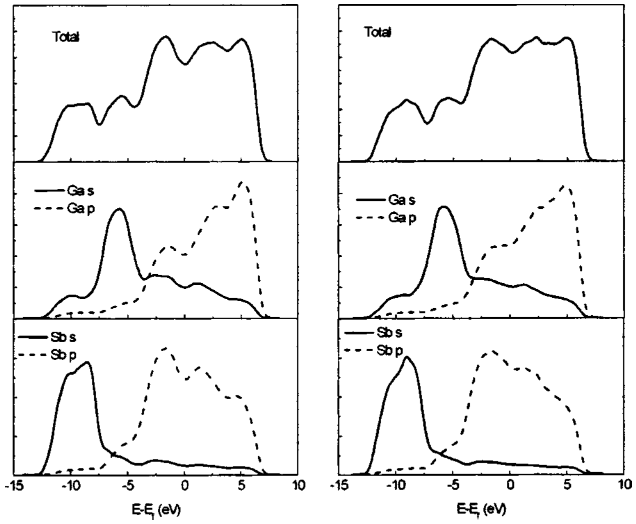

FIG. 11. The total and local electronic density of states for GaSb in liquid state. 1073 K (left panel), 1773 K (right panel).

are some similarities of electronic density of states between ℓ-GaSb and *c*-GaSb. First, ℓ-GaSb and *c*-GaSb have the same positions for all of the main peaks located near -10.0, -6.0, -1.6, $+2.0$, and $+5.0$ eV in DOS. Second, the overall features of LDOS for Ga and Sb atoms in ℓ-GaSb are also similar to those of *c*-GaSb. Orbitals such as Sb (s) and Ga (s) locate at -10 and -6.0 eV and both Sb (p) and Ga (p) orbitals locate at the same position -1.6 eV. Finally, the Ga-Sb bonds mainly result from the overlaps between Ga (p)-Sb (p) orbitals in which bonding and antibonding orbitals locate at -1.6 and $+5.0$ eV, and there are also a few overlaps between Ga (s,p) and Sb (s,p) in which bonding and antibonding orbitals locate at -6.0 and $+2.0$ eV. Certainly, there are also some differences of DOS and LDOS between ℓ-GaSb and *c*-GaSb, such as the boundaries of the peaks in DOS and LDOS become broader and more unclear in ℓ-GaSb, and a gap at Fermi level in *c*-GaSb as a signature of semiconductor turns into a small "dip" in ℓ-GaSb. As temperature rises up to 1773 K, this dip becomes more shallow, and the boundary between the bonding and antibonding states becomes more unclear. This also suggests that the bonds of Ga-Sb become weaker with increasing temperature.

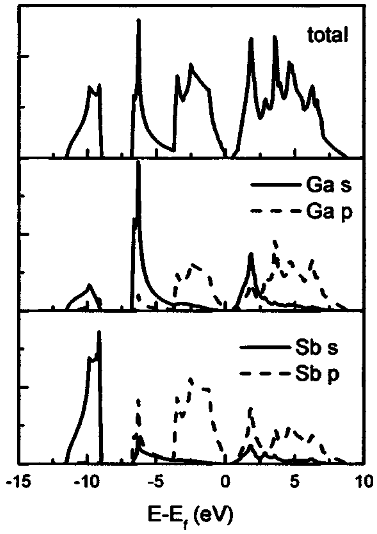

FIG. 12. The total and local electronic density of states for GaSb in crystalline state.

VI. DISCUSSION AND CONCLUSION

So far, three experimental results for the viscosity of ℓ-GaSb have been reported and they are inconsistent with each other. The values of the viscosity of ℓ-GaSb reported by Glazov *et al.*[4] are evidently larger than those of Kakimoto *et al.*[3] and Sato *et al.*.[5] The experimental results reported by Sato *et al.*[5] indicate that the viscosities of ℓ-GaSb show Arrhenius behavior in the temperature range 991.9–1487.9 K. But Kakimoto's results indicate that the temperature dependency of viscosity of ℓ-GaSb at high temperature (beyond 1487.9 K) is different from that of low temperature, and the value of viscosity gradually approached the average value calculated as a mixture of gallium and antimony at high temperatures. Our calculated results of structure and diffusion coefficients of ℓ-GaSb which exhibit different behaviors at low and high temperatures are not in conflict with the experimental results of viscosity by Kakimoto *et al.* and Sato *et al.* At low temperatures, the opened structures of Sb atoms and the high heteroatomic coordination numbers will make the velocity of Ga atoms close to that of Sb atoms which have been shown by the results of D_{Ga}, D_{Sb}, and $D_{\mathrm{Ga}}/D_{\mathrm{Sb}}$. Thus, the difference between the values of viscosity of ℓ-GaSb and ℓ-Sb (η_{GaSb}-η_{Sb}) will diminish gradually with decreasing temperature. Certainly, at high temperatures, the local structure of Sb turns into more close-packed structure and the heteroatomic coordination numbers are reduced evidently. Thus, the viscosity of ℓ-GaSb approaches the average value of ℓ-Ga and ℓ-Sb.

In conclusion, we have performed *ab initio* molecular-dynamics simulations of ℓ-GaSb at four different temperatures and the calculated structure factors and pair correlation functions are in good agreement with available experimental data. The liquid structure of GaSb experiences some changes from near melting point to high temperature. The heteroatomic coordination numbers decrease evidently from 1073 to 1523 K, but the homoatomic coordination numbers are nearly invariant in this temperature range. As temperature is beyond 1523 K, the reverse change tendencies are observed. The local structure of Ga cluster is almost constant with temperature, but for Sb cluster, it changes from distorted open structure into more compact structure with increasing temperature. Our calculated results of diffusion coefficients are consistent with those of liquid structure of GaSb.

ACKNOWLEDGMENTS

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