PHYSICAL REVIEW B **74**, 184202 (2006)

Ab initio molecular dynamics simulations on structural change of liquid eutectic alloy $Ge_{15}Te_{85}$ from 573 to 1073 K

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(Received 27 June 2006; revised manuscript received 27 September 2006; published 1 November 2006)

We have performed *ab initio* molecular dynamics simulations of liquid $Ge_{15}Te_{85}$ alloy at seven different temperatures from 573 to 1073 K. The structural and electronic properties of liquid $Ge_{15}Te_{85}$ alloy and their temperature dependence were studied. Comparing with available experimental data, the calculated pair-correlation functions are acceptable. In the low-temperature region from 573 to 733 K, the total coordination number N_{Total} increases gradually with increasing temperature in contrast to the behavior of a classical isotropic fluid; but in the high-temperature region from 833 to 1073 K, it nearly remains a constant. The partial coordination number N_{GeTe} nearly remains a constant 4.7 in the whole temperature region from 573 to 1073 K. The partial coordination number N_{TeTe} first increases in the low-temperature region with increasing temperature and then nearly keeps a constant in the high-temperature region, showing the same temperature dependence as N_{Total}. The calculated angular limited triplet correlation functions of Te-Te-Te and Te-Ge-Te suggest that at low temperatures there exist Peierls-type distorted local structure around both Ge and Te atoms, i.e., the short-long and long-short bonds correlation, however, it is no more true at high temperatures. At low temperatures (573–733 K) the Te *p* states form an obvious dip at Fermi level E_F; but at high temperatures (833–1073 K) this dip disappears, approaching the free-electron form. Our results suggest that besides the contribution from the modification of the local environment around Ge atoms with the temperature the unexpected temperature dependence of the local environment around Te atoms is also responsible for the structural change of liquid $Ge_{15}Te_{85}$ characterized by anomalous temperature behaviors of thermodynamic quantities.

DOI: 10.1103/PhysRevB.74.184202 PACS number(s): 61.20.Ja, 61.25.Mv, 71.15.Pd

I. INTRODUCTION

In the phase diagram of Ge-Te alloys the eutectic composition lies at 15 at. % Ge with melting temperature of 648 K.[1] The crystalline eutectic alloy $Ge_{15}Te_{85}$ is composed of pure Te and the equiatomic compound GeTe, which is known to have three modifications: rhombohedral α-GeTe, β-GeTe, and the orthorhombic low temperature form γ-GeTe. α-GeTe is stable from 638 K up to 673 K, where the transition to β-GeTe takes place. The structure of α phase results from a Peierls distortion of the β phase, that is, β-GeTe has a more symmetric structure ($Fm3m$) with six equal GeTe bonds and α-GeTe has a Peierls distorted structure ($R3m$) with three short and three long GeTe bonds.

The Peierls distortion of *p*-bonded atoms has been established to simply and successfully explained the valence three of group-V elements in their crystalline structures.[2–4] The six lobes of the *p* orbitals pointing at right angles lead to a simple cubic (or related) structure. But, such a structure is unstable against doubling of the periodicity for a half filled band. Doubling of the periodicity in the three principal directions of the simple cubic structure can be achieved by the alternation of short (covalent) bonds and long (weakly covalent) van der Walls bonds. Although the concept of Peierls distortion was established in the context of low dimensional, periodic structures, it has been recently generalized for aperiodic systems using a direct space method. It has already been substantiated that in many liquids, such as As, there exists a Peierls distorted local structure.

In the liquid state, $Ge_{15}Te_{85}$ is marked by strong and anomalous variations of many physical properties, which are indicative of the microstructure changes in liquid $Ge_{15}Te_{85}$. By drop calorimetry, Castanet and Bergman have investigated the temperature dependence of the enthalpy in liquid $Ge_{15}Te_{85}$,[5] and suggested that, from supercooled to normal liquid, a second-order transition takes place around the eutectic temperature 648 K. Such a behavior was explained by the destruction of the short-range order in the liquid phase by heating. Experimental investigations by Neufville[6] and Tsuchiya[7,8] have also shown some anomalous behaviors of thermodynamic quantities in liquid eutectic composition $Ge_{15}Te_{85}$. With decreasing temperature, the volume of liquid $Ge_{15}Te_{85}$ shows an anomalous increase from around 773 K to the liquidus temperature. Correspondingly, the thermal-expansion coefficient, adiabatic compressibility, and the heat capacity at constant pressure show very sharp extrema at around 680 K, moreover, the magnitude of the electrical conductivity shows an increase of three orders in the temperature range from 573 to 773 K.[9] These facts indicated the occurrence of rapid structural change in liquid $Ge_{15}Te_{85}$ from 650 to 773 K. But the driving mechanism for the structural change is still a controversial question. Before the results of Tsuchiya, by neutron and x-ray diffractions, Neumann and co-workers[10,11] have suggested that significant structural change in melt $Ge_{15}Te_{85}$ takes place from 653 to 823 K and the changes in the first maximum of the structure factor $S(Q)$ are caused by scattering contributions associated with Te. The partial structure factor $S_{\mathrm{TeTe}}(Q)$ near the eutectic temperature significantly differs from the structure factor of pure liquid Te but tends towards the form of pure Te with increasing temperature. However, by first-principle molecular dynamics simulations and reverse Monte Carlo analysis on liquid $Ge_{15}Te_{85}$ above the eutectic temperature, Bichara and co-workers[12–15] showed that the anomalous volume contraction from 650 to 750 K observed in the liquid corresponds to a significant change of the Ge-Te partial structure factor, whereas the Te-Te partial structure factor remains essentially unaffected except for the usual damping effect due to the increase of temperature. From the microscopic view, they suggested that the structural change can be explained in terms of the competition between two types of local environment of Ge atoms—a symmetrical coordination octahedron at high temperatures and an asymmetrical octahedron at low temperatures. Also, based on the thermodynamic measurements and neutron-scattering results of liquid $Ge_{15}Te_{85}$, Bergman *et al.*[16] proposed an analysis of the experimental data and provided a simple model for the structural change observed: with increasing temperature, an increasingly large number of Ge-Te bonds become shorter, leading to a more compact local environment with a smaller atomic volume.

The liquid structure is usually understood with reference to its crystal structure. As mentioned above, the crystalline eutectic alloy $Ge_{15}Te_{85}$ is composed of pure Te and equiatomic compound GeTe. Crystalline Te forms a trigonal lattice, with helical chains of atoms running along the axes of the hexagonal cell. The electronic mechanism stabilizing the chain structure is usually described as a Peierls distortion, within either a tight-binding or a pseudopotential formalism (Ref. 17 and references therein). With decreasing temperature, pure supercooled liquid Te undergoes a smooth structural change in a slightly lower temperature range, being accompanied with an anomalous expansion of volume.[7,18] For equiatomic GeTe, on cooling at 673 K the crystalline phase transition occurs from a symmetric β phase structure with six equal Ge-Te bonds to a Peierls distorted structure α phase with three short and three long Ge-Te bonds.[19] For liquid equiatomic GeTe, *ab initio* molecular dynamics calculations recently pointed out a high degree of alternating chemical order and demonstrated the presence of a Peierls distortion close above the melting temperature 1000 K.[20,21]

To obtain more microscopic atomic structure and electronic properties of liquid $Ge_{15}Te_{85}$ and investigate possible structural correlations with the macroscopic properties, we performed *ab initio* molecular dynamics simulations from 573 to 1073 K, including supercooled and normal liquid. The paper is organized as follows: in Sec. II, we describe the method of our simulations; the results of our simulations and the corresponding discussion are reported in Sec. III; a short summary is given in Sec. IV.

II. COMPUTATIONAL METHODS

Our simulations were performed within the framework of the density-functional theory (DFT).[22] We used the Vienna *Ab initio* Simulation Package (VASP),[23,24] and employed the projector augmented-wave (PAW) potential,[25,26] with the generalized gradient approximation (GGA) formulated by Perdew and Wang (PW91) to the exchange-correlation energy.[27,28] We have also performed the simulations with GGA using the Perdew, Burke, and Enrzerhof (PBE) functional[29] at 943 and 633 K. As can be seen from Fig. 1, the pair-correlation functions $[g(r)]$ simulated by PW91 and PBE functional have an acceptable agreement with the experimental data, though the first peak of $g(r)$ is shifted to the right by about 0.02 nm (a classical problem with *ab initio* molecular dynamics) and is a little broad as compared to the experimental data. In addition, it seems that the PW91 functional yields a slightly narrower and lower first peak of $g(r)$ than the PBE functional. In order to estimate the finite-size effects, we compared the results of 60 atoms (9 Ge+51 Te) with those of 80 atoms (12 Ge+68 Te) at 943 K. As shown in Fig. 2, the result of 80 atoms is in good agreement with experimental data, and is better than that of 60 atoms. As shown in Fig. 3, increasing the k point of the reciprocal cell of an 80-atom system from the Γ point to 4 k points does not lead to liquid structure in better agreement with the experimental data. Therefore, in our present simulations, we adopt the 80-atom system (12 Ge+68 Te) with periodical boundary conditions and the Γ point was used to sample the Brillouin zone of the supercell. The electronic wave functions were expanded in the plane-wave basis set, with an energy cutoff of 175 eV. Our canonical ensemble simulations have been performed at 573, 633, 673, 733, 833, 943, and 1073 K with a Nosé thermostat for temperature control.[30] The experimental densities are used at different temperatures except at 573 K.[7,16] The density at 573 K is derived by adjusting the box size to keep the internal pressure approximately equal to that at 673 K. The Verlet algorithm was used to integrate Newton's equations of motion and the time step of ion motion was 4 fs. The Kohn-Sham energy functional was mini-

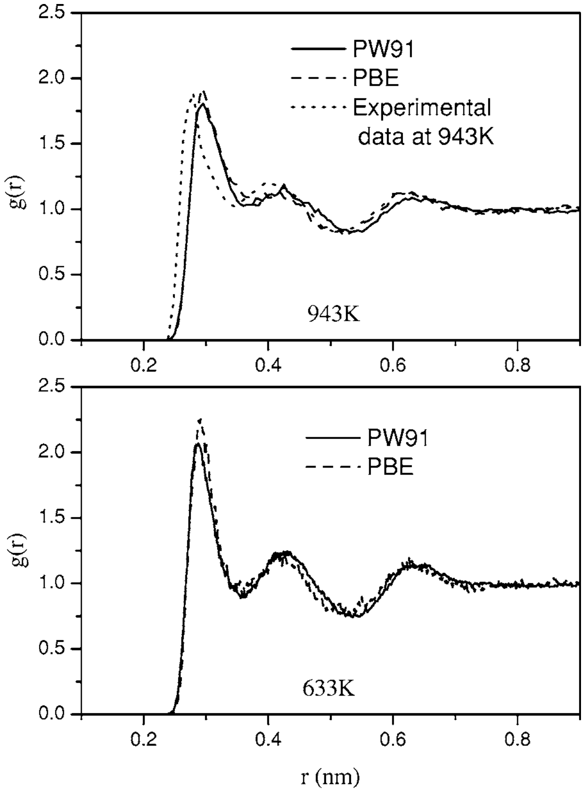

FIG. 1. Simulated pair-correlation functions $g(r)$ of liquid $Ge_{15}Te_{85}$ at 943 and 633 K using PW91 (solid line) potential, PBE (dash line) potential, and experimental data (dot line) from Ref. 16.

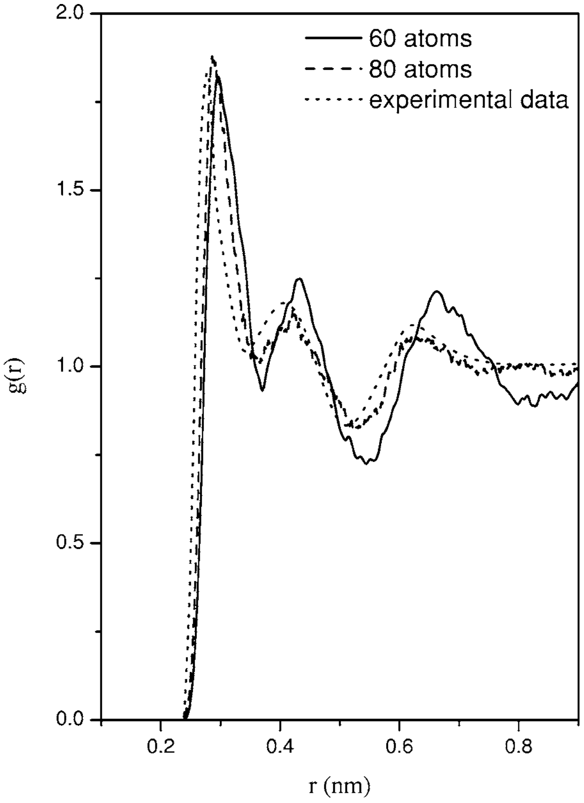

FIG. 2. Pair-correlation functions $g(r)$ of liquid $Ge_{15}Te_{85}$ at 943 K: comparison of simulations for the 60-atom system (solid line) and the 80-atom system (dash line), and the experiment (dot line) from Ref. 16.

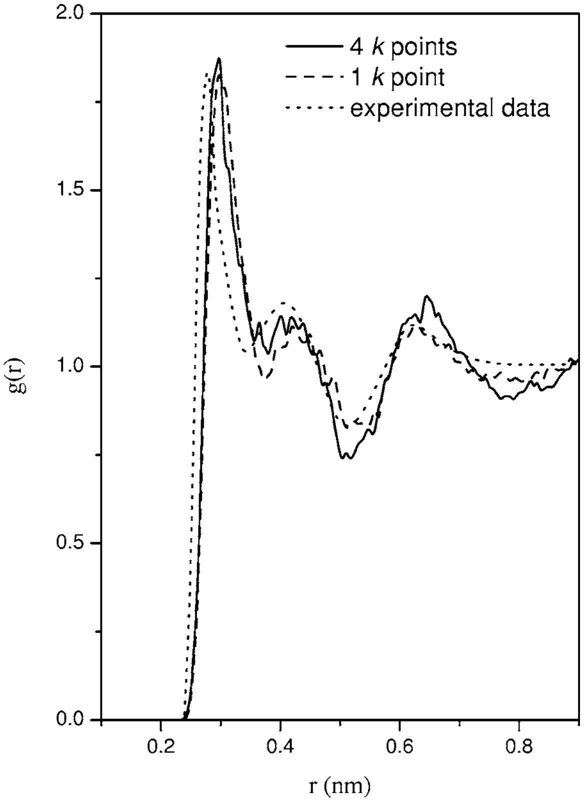

FIG. 3. Pair-correlation functions $g(r)$ of liquid $Ge_{15}Te_{85}$ at 943 K using 4 k points (solid line) and the Γ point (dash line), the dotted line is for experimental data from Ref. 16.

mized by the preconditioned conjugate-gradient method.

The initial atomic configuration adopted was a random distribution of 80 atoms on the grid, which was constructed by dividing the supercell into $5\times5\times5$ square segments. Then, the system is heated up to 1500 K by rescaling the ionic velocities. After equilibration for 4 ps at this temperature, we gradually reduce the temperature to 1073 K. For other temperatures, we only repeat this procedure and change the final temperature into 943, 833, 733, 673, 633, and 573 K, respectively. At each temperature, the physical quantities of interest were obtained by averaging over 16 ps after the initial equilibration taking 4 ps.

III. RESULTS AND DISCUSSION

The structure factor $S(Q)$ is an important physical quantity, serving as a connection with experimental results. In a liquid two-component alloy, the Ashcroft-Langreth (AL) partial structure factor $S_{ij}(Q)$ can be obtained by Fourier transformation of the partial pair-correlation function $g_{ij}(r)$,[31]

$$S_{ij}(Q) = \delta_{ij} + 4\pi\rho_0\sqrt{c_ic_j}\int_0^\infty [g_{ij}(r)-1]\frac{\sin(Qr)}{Qr}r^2dr, \quad (1)$$

where i and j denote the two components of the binary alloy, ρ_0 is the average number density, c_i and c_j are their number concentrations, respectively. The total structure factor is expressed as a linear combination of three partial structure factors, normalized by the neutron-scattering lengths of the two elements in the alloy,[31]

$$S(Q) = \sum_{i=1}^{2}\sum_{j=1}^{2}\frac{(c_ic_j)^{1/2}b_ib_j}{c_1b_1{}^2+c_2b_2{}^2}S_{ij}(Q), \quad (2)$$

where the neutron-scattering lengths are $b_{\mathrm{Ge}}=8.185$ and $b_{\mathrm{Te}}=5.68$.[32] Considering that the calculation of the structure factor by Eq. (1) on a small simulation box may lead to significant errors, a direct computation by Eq. (3) was also performed.

$$S_{ij}(Q) = \frac{1}{\sqrt{N_iN_j}}\left\langle \sum_{\alpha=1}^{N_i}\sum_{\beta=1}^{N_j}\exp\{-iQ(r_{i\alpha}-r_{j\beta})\}\right\rangle - \frac{\delta_{Q,0}}{\sqrt{N_iN_j}}, \quad (3)$$

The results are shown in Figs. 4(a)–4(c). Comparison of the simulated total structure factors displayed in Fig. 4(a) with the experimental presented by Bergman[16] shows that (i) on the whole, the calculated structure factors by the two methods are in agreement with the experimental and correctly reproduce the temperature dependence, (ii) the direct calculation by Eq. (3) leads to the structure factor in better agreement with experimental result than that by the Fourier transform of $g(r)$, especially, the ratio of the heights of the first two peaks at low temperatures. But we can also notice that the evolution of structure factor with temperature in two

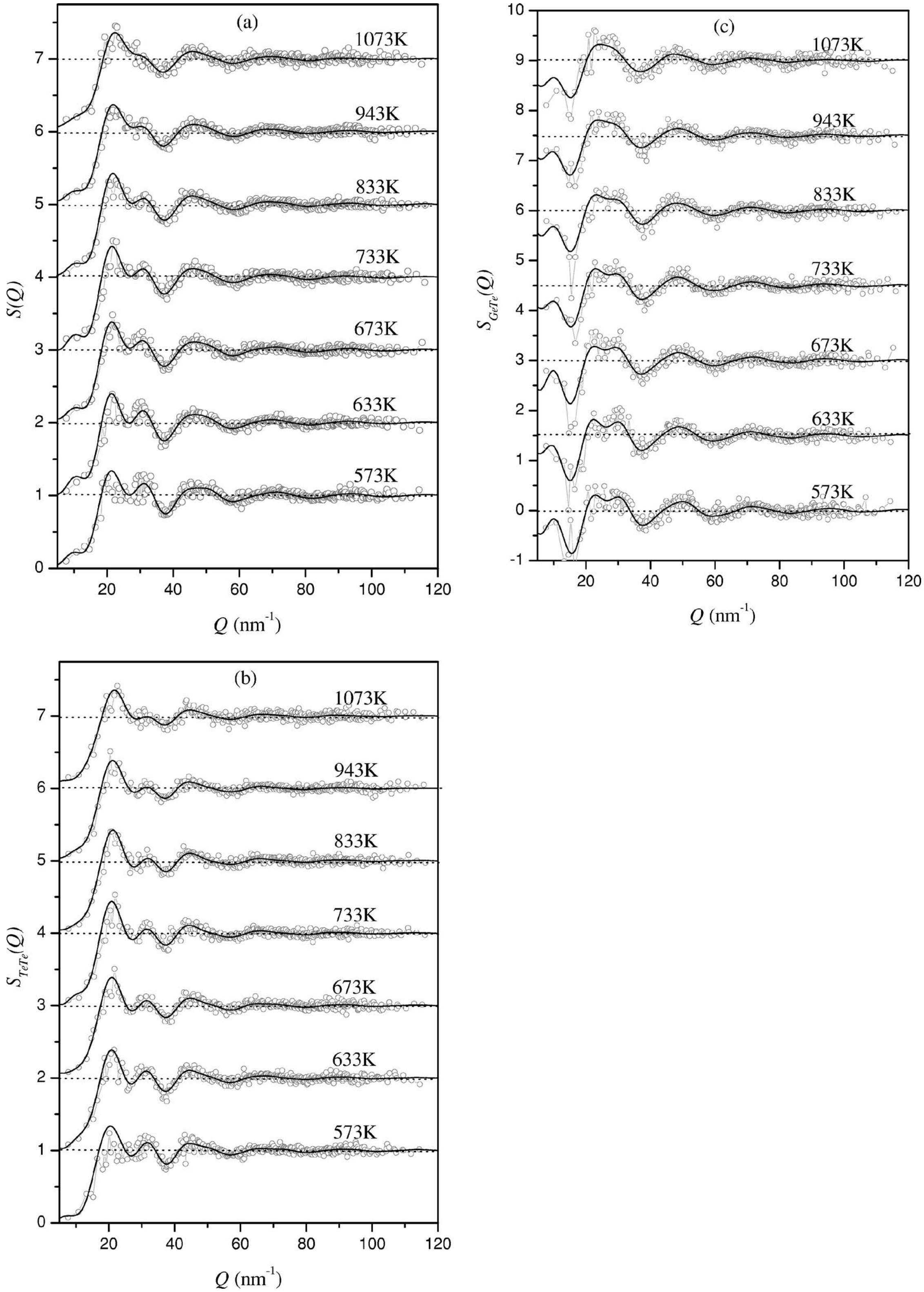

FIG. 4. Structure factors of $Ge_{15}Te_{85}$ calculated by Fourier transform (solid line) and direct calculation (grey line and circle) at seven different temperatures. (a) Total structure factor; (b) partial structure factor of Te-Te; and (c) partial structure factor of Ge-Te.

cases is coincident with each other. The total structure factors of liquid $Ge_{15}Te_{85}$, shown in Fig. 4(a), were calculated at seven different temperatures from 573 to 1073 K. With increasing temperature, the position of the first peak presents a little shift towards large Q value. However, the position of the second peak is almost unchanged, the height of second peak obviously decreases with temperature and the second peak becomes a shoulder at 1073 K. The trough between the first peak and the second one becomes more and more shallow with the increase of temperature. The evolution of these features is in good accordance with experimental observation.[16] The partial structure factors $S_{\mathrm{TeTe}}(Q)$ are plotted in Fig. 4(b). The positions of the first and the second peaks show the same evolution with the increase of temperature as that in total $S(Q)$. The height of the second peak decreases with increasing temperature. Figure 4(c) gives the partial structure factors $S_{\mathrm{GeTe}}(Q)$. We can see that, with increasing temperature, the two peaks at low temperatures become one peak along with a shoulder at the right side at high temperatures, and the position of the first peak also presents a little shift towards large Q value.

In the physics of fluids, the pair-correlation function is also an important physical quantity because, in principle, various properties of liquid materials can be estimated from the pair-correlation function when coupled with an appropriate theory. In a two-component alloy, the total pair-correlation function $g(r)$ is obtained by weighting the partial pair functions $g_{ij}(r)$ with the neutron-scattering length:

$$g(r)=\sum_{i=1}^{2}\sum_{j=1}^{2}\frac{c_ic_jb_ib_j}{(c_1b_1+c_2b_2)^2}g_{ij}(r), \qquad (4)$$

where the neutron-scattering lengths (b_{Ge} and b_{Te}) are the same as defined in Eq. (2). $g_{ij}(r)$ is calculated by the following definition:

$$g_{ij}(r)=\frac{1}{\rho_0c_ic_jN}\left\langle\sum_i\sum_{j\neq i}\delta(\vec{r}-\vec{r}_{ij})\right\rangle, \qquad (5)$$

where r_{ij} is the interatomic distance between atom i and j. Using the atomic coordinates from the molecular dynamics simulations, the total pair-correlation functions of liquid $\mathrm{Ge_{15}Te_{85}}$, shown in Fig. 5(a), were calculated at seven different temperatures ranging from 573 to 1073 K. As can be seen from Fig. 5(a), the position of the first peak and that of the second one are around 0.287 and 0.426 nm at 943 K, which is very close to the experimental results at 943 K—0.286 nm for the first peak and 0.412 nm for the second one.[16] The heights of both the first and the second peaks decrease with increasing temperature and the trough between them becomes more and more shallow. The partial pair functions $g_{\mathrm{TeTe}}(r)$ and $g_{\mathrm{GeTe}}(r)$ were also calculated according to Eq. (4). The partial pair-correlation functions between Te atoms at different temperatures are plotted in Fig. 5(b). The first peak position in $g_{\mathrm{TeTe}}(r)$ is around 0.30 nm, which shift slightly towards the right with increasing temperature. Its height decrease gradually and its width becomes large with increasing temperature. The second peak is located at around 0.426 nm. With the increase of temperature, its position shows a slight shift towards the left and its height decreases obviously. At 1073 K, the second peak becomes almost a shoulder, and the trough between the first and the second peaks becomes more and more shallow. The partial pair-correlation functions between Ge and Te atoms are shown in Fig. 5(c). The first peak position of $g_{\mathrm{GeTe}}(r)$ is around 0.28 nm and there is almost no shift with temperature. Its height decreases with the increase of temperature. The second peak is around 0.426 nm, which seems not sensitive to temperature, but its height shows a distinct decrease with increasing temperature and at high temperatures it presents a flat shape.

According to the total and partial pair-correlation functions given above, the average coordination number can be obtained by the integration of $g_{ij}(r)$ to its first minimum,

$$N_{ij}=\int_0^{R_{cutoff}}4\pi r^2\rho_jg_{ij}(r)dr, \qquad (6)$$

where $\rho_j=\rho_0c_j$ is the partial number density of the atom j. Here, the cutoff distance R_{cutoff} is chosen to be 0.35 nm, corresponding to the position of the first minimum of the total pair-correlation function. The calculated results are shown in Fig. 6. In the low temperature region from 573 to 733 K the total coordination number increases steadily with the increase of temperature, which is in contrast to the behavior of a classical isotropic fluid. This suggests that on heating from 573 to 733 K the volume shrinks and hence a negative thermal-expansion coefficient is observed. However, in the high-temperature region from 833 to 1073 K, it hardly depends of the temperature. In order to draw a comparison between calculated and experimental results, the experimental total coordination numbers[16] at different temperatures are also given in Fig. 6. As demonstrated in Ref. 33, the right shift and the overestimation of the width of the first neighbor peak lead to an overestimation of the number of first neighbors, however, the evolution of the total coordination number with the temperature is in good accordance with the experimental results. From Fig. 6 we can also see that the partial coordination number N_{GeTe} nearly remains a constant $\approx$4.7 in the whole temperature region from 573 to 1073 K. With increasing temperature the partial coordination number N_{TeTe} first increases in the low-temperature region and then nearly keeps a constant in the high-temperature region, indicating that the nearest Te neighbors around a Te atom becomes more and more compact from 573 to 733 K. N_{TeTe} shows the same temperature dependence as N_{Total}. It should be pointed out that a fixed cutoff distance (0.35 nm) for all partial quantities and at all temperatures may lead to the overestimation of N_{GeTe} at low temperatures. Taking into account the difference in the concentration of elements Ge and Te, we may conclude that the change of N_{Total} may mainly results from the changes of N_{TeTe}. Therefore the unexpected temperature dependence of N_{TeTe} may play an important role in the structural change of liquid $\mathrm{Ge_{15}Te_{85}}$ characterized by anomalous temperature behaviors of thermodynamic quantities.

In Ref. 16 Bergman *et al.* have studied the thermodynamic properties (molar volume, thermal-expansion coefficient and heat capacity) of $\mathrm{Ge_{15}Te_{85}}$ in the range of 150 K above the eutectic temperature. They have also performed measurements of its total structure factors by neutron scattering at four different temperatures. They analyzed the thermodynamic and neutron-scattering data, and concluded that the structural change of liquid $\mathrm{Ge_{15}Te_{85}}$ mainly consists in a modification of the first neighbor shell of the Ge atoms similar to the $\alpha\rightleftharpoons\beta$ transition in the solid GeTe compound. That

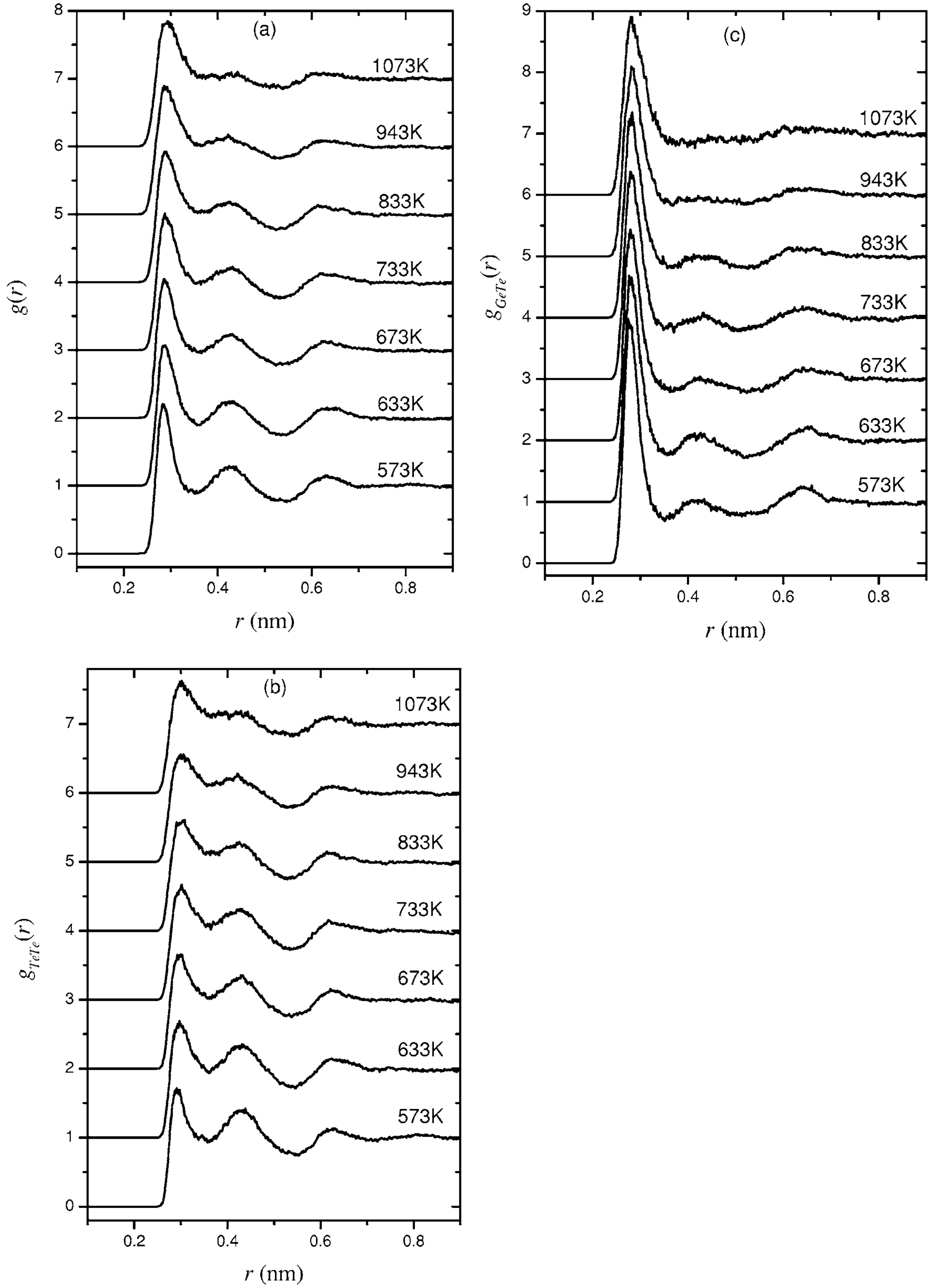

FIG. 5. Pair-correlation functions of liquid $Ge_{15}Te_{85}$ at seven different temperatures. (a) Total pair-correlation function; (b) partial pair-correlation function for Te-Te; and (c) partial pair-correlation function for Ge-Te.

is, with increasing temperature an increasingly large number of Ge-Te bonds become shorter, leading to a more compact local environment with a smaller atomic volume, whereas the TeTe partial structure factor remains essentially unaffected except for the usual damping effect due to the temperature increase. As they pointed out in their paper, both direct measurements of the partial structure factors and a complete computer simulation of the liquid state would be

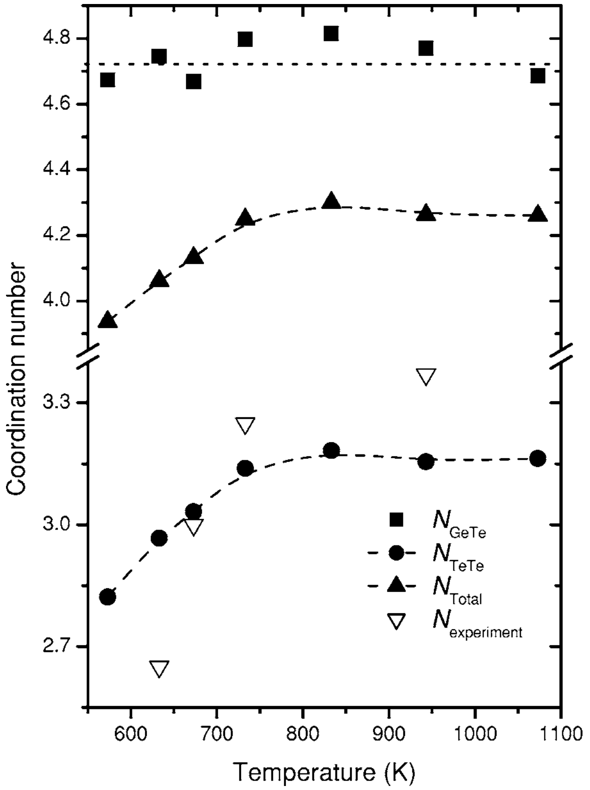

FIG. 6. Temperature dependence of the total and partial coordination number.

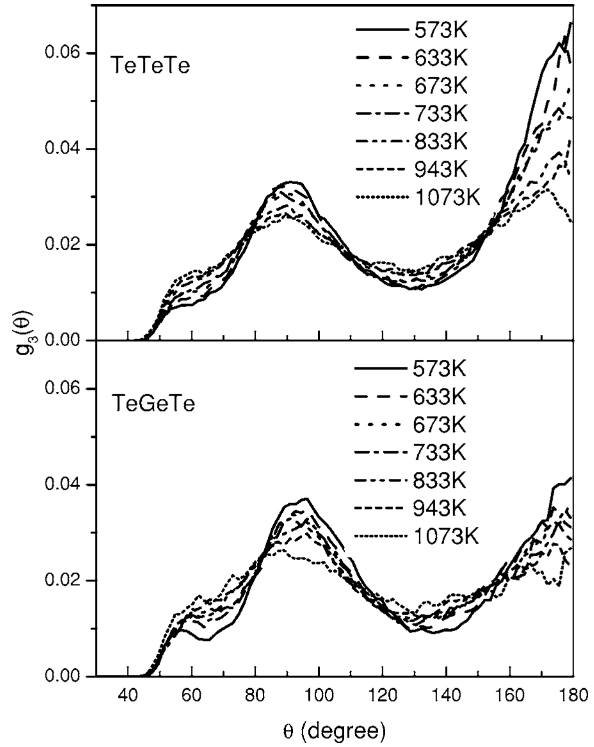

FIG. 7. Partial bond-angle distribution functions of Te-Te-Te and Te-Ge-Te normalized by $\sin(\theta)$ at seven different temperatures. The cutoff distance is 0.35 nm.

useful to confirm their interpretation. Our present *ab initio* molecular dynamics (MD) simulations on liquid $Ge_{15}Te_{85}$ in a large temperature range show that, in the whole temperature region from 573 to 1073 K, the partial coordination number N_{GeTe} nearly keeps a constant, whereas the partial coordination number N_{TeTe} varies in the same way as the total coordination number. Based on these results of the whole and partial coordination number and taking into account the overestimation of the partial coordination number at low temperatures due to the choice of a fixed cutoff distance (0.35 nm) for all partial quantities and at all temperatures, we think the modification of the nearest Te neighbors of the Te atoms is an important factor in the structural change of liquid $Ge_{15}Te_{85}$.

The bond-angle distribution function $g_3(\theta)$ is one type of three body distribution functions. The angle noted in $g_3(\theta)$ is formed by a pair of vectors drawn from a reference atom to any other two atoms within a sphere of cutoff radius r_{cutoff}. To gain further insight into the structural change in liquid $Ge_{15}Te_{85}$, we calculated the partial bond-angle distributions of Te-Ge-Te and Te-Te-Te normalized by $\sin(\theta)$ from the atomic configuration obtained in our simulations. Figure 7 gives the partial bond-angle distribution functions $g_{\mathrm{TeGeTe}}(\theta)$ and $g_{\mathrm{TeTeTe}}(\theta)$ of liquid $Ge_{15}Te_{85}$ at seven different temperatures with the bond length $r_{cutoff}=0.35$ nm. One can easily find that both $g_{\mathrm{TeTeTe}}(\theta)$ and $g_{\mathrm{TeGeTe}}(\theta)$ show three peaks. For the first peak, its position is around 60°, invariable with the variation of temperature; but its height increases with increasing temperature. This indicates that close-packed structure of atoms in liquid $Ge_{15}Te_{85}$ becomes more close-packed with increasing temperature. The second and the third peaks, located at around 90° and 180°, respectively, indicate a Peierls-like distorted local atomic structure is preserved in liquid $Ge_{15}Te_{85}$. For both partial bond-angle distribution functions, the height of the 90° peak decreases with the increase of temperature; however, for the 180° peak, the height decreases more sharply in $g_{\mathrm{TeTeTe}}(\theta)$ than in $g_{\mathrm{TeGeTe}}(\theta)$. This suggests that the local environment around a Te atom may be more sensitive than that around a Ge atom with increasing temperature.

To further investigate the variation of the peak around 180° of $g_{\mathrm{TeTeTe}}(\theta)$ and $g_{\mathrm{TeGeTe}}(\theta)$ and the Peierls distortion in liquid $Ge_{15}Te_{85}$, we calculated the angular limited triplet correlation functions of Te-Te-Te and Te-Ge-Te as introduced in Ref. 34. 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 disordered structure, the maximum of the distribution should be on the diagonal (i.e., a maximum at $r_1=r_2$) in the angular limited triplet correlation function; for a distorted structure, there should be two peaks corresponding to the short-long and long-short correlations. The angular limited triplet correlation functions $P(r_1,r_2)$ of Te-Te-Te and Te-Ge-Te in liquid $Ge_{15}Te_{85}$ at 573 and 1073 K are shown in Fig. 8. At 573 K, (i) the maxima of Te-Ge-Te triplet correlation function are centered at (0.303, 0.303 nm) and the other two smaller regions are centered at (0.290, 0.320 nm) and (0.320, 0.290 nm); (ii) two maxima of

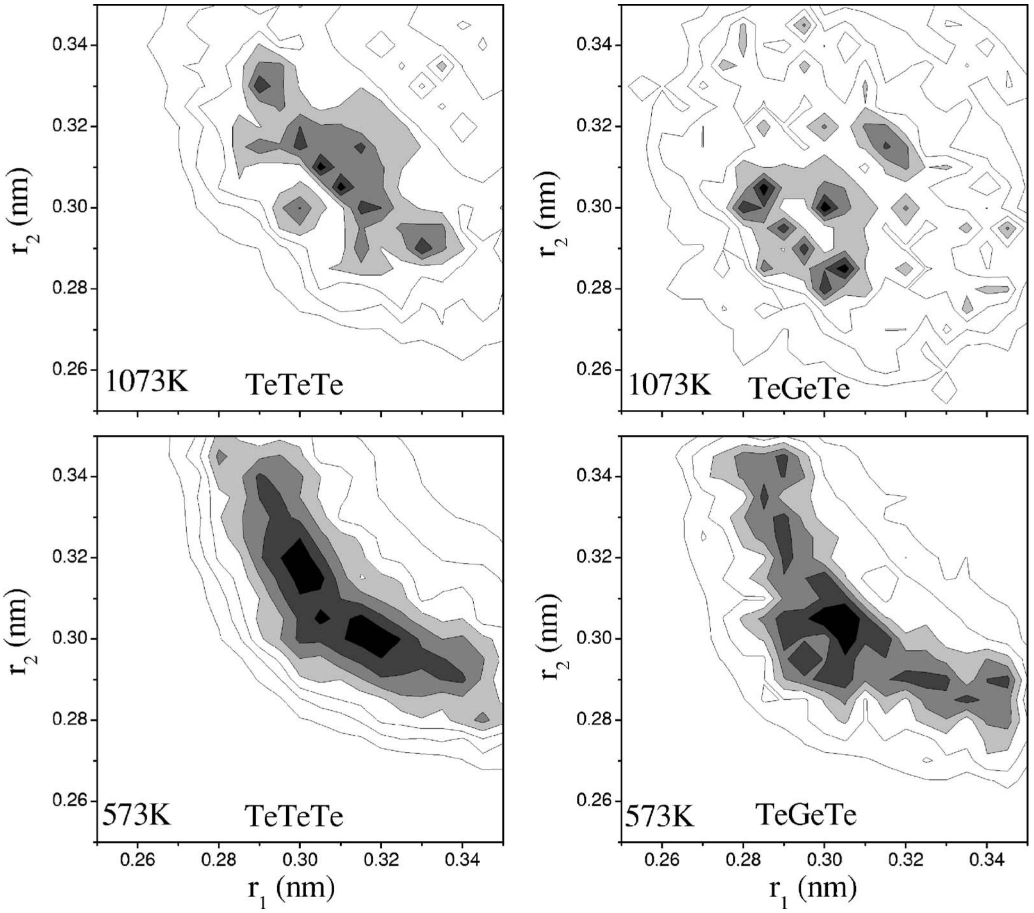

FIG. 8. Angular limited triplet correlation function $P(r_1,r_2)$ of Te-Te-Te and Te-Ge-Te in liquid $Ge_{15}Te_{85}$ at 573 K (lower panel) and 1073 K (upper panel).

Te-Te-Te triplet correlation function are (0.317, 0.300 nm) and (0.300, 0.317 nm). These indicate that there is a much stronger tendency to alternate long and short bonds (the signature of Peierls distortion mechanism) around Te atom than around Ge atom, which is in agreement with the result that $g_{\mathrm{TeTeTe}}(\theta)$ has a higher 180° peak than $g_{\mathrm{TeGeTe}}(\theta)$. At 1073 K, several very small regions of short-long and long-short bonds correlation are observed in the distribution of both Te-Ge-Te and Te-Te-Te, suggesting that the local structures around Te and Ge atoms are hardly Peierls-type distorted. That is, with increasing temperature the local Te arrangements around Ge and Te atoms become less Peierls-like distorted.

The microscopic atomic structure is correlated with the electronic structure. Experimental results[9] have suggested that the magnitude of the electrical conductivity shows an increase about three orders in the temperature range from 573 to 773 K. Here we also studied the electronic density of state (DOS) and the local density of states (LDOS), i.e., the DOS for each atomic species is decomposed into angular-momentum-resolved contributions. By projecting all the wave functions in a sphere of radius R around atom i onto the spherical harmonic (l,m), we obtained the (l,m) angular momentum component of the atom i. For binary system, there is no unambiguous way to define the value of the sphere radius R and several choices are possible. Here, we have used the covalent radius of atoms, $R_{\mathrm{Ge}}=0.122$ nm and $R_{\mathrm{Te}}=0.136$ nm. The calculated DOS and LDOS of liquid $Ge_{15}Te_{85}$ are represented in Fig. 9. We can see that the major contribution to the density of states at the Fermi level E_F is due to Ge p and Te p orbitals, and there is an obvious dip in DOS at E_F, but it should also be noticed that the dip at 943 K is more shallow than that at 573 K. From LDOS, we can conclude that the variation of the dip in DOS mainly results

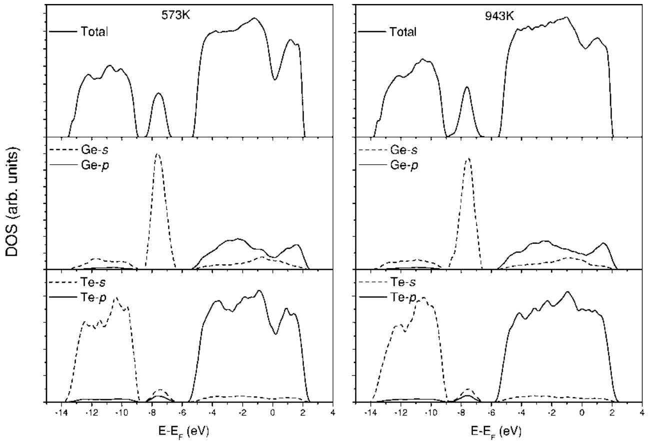

FIG. 9. The total and local electronic density of states for liquid $Ge_{15}Te_{85}$ at 573 K (left panel) and 943 K (right panel).

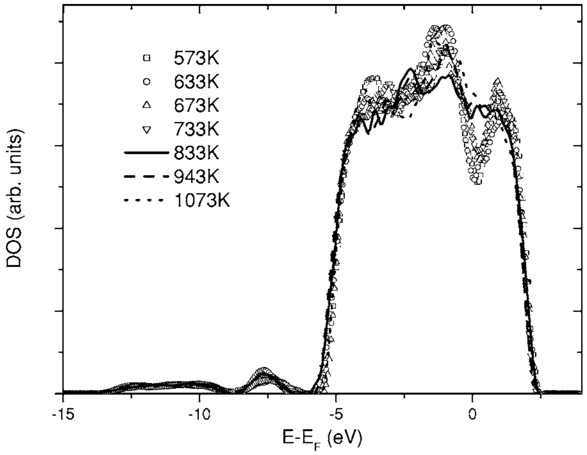

FIG. 10. The local electronic density of states for Te *p* orbitals at seven different temperatures in liquid $Ge_{15}Te_{85}$.

from the change of Te *p* orbitals. With increasing temperature, the variation of Ge *p* orbitals is almost negligible, but the deep dip at low temperature in Te *p* orbitals at E_F disappears at high temperature. Figure 10 gives the LDOS of Te *p* orbitals at seven different temperatures. One can easily find that at low temperatures (573–733 K), there is an obvious dip at E_F, but at high temperatures (833–1073 K), the dip disappears, approaching the free-electron form. These facts indicate that the Te atom also plays a prominent role in the structural change of liquid $Ge_{15}Te_{85}$ from 573 to 733 K.

IV. CONCLUSIONS

In summary, *ab initio* molecular dynamics simulations were performed on liquid $Ge_{15}Te_{85}$ by using the supercell size of 80 atoms. The structural and electronic properties of liquid $Ge_{15}Te_{85}$ alloy and their temperature dependence were studied. The structure factors, pair-correlation functions, average coordination numbers, bond-angle distribution functions, and DOS at each temperature were calculated. The calculated structure factors and pair-correlation functions are acceptable with available experimental data. With increasing temperature, in the low-temperature region from 573 to 733 K, the total coordination number increases gradually; but in the high-temperature region from 833 to 1073 K, it nearly remains a constant, indicating rapid structural change of liquid $Ge_{15}Te_{85}$ in the temperature region from 573 to 733 K. The calculated partial coordination number indicates that the unexpected temperature dependence of N_{TeTe} may play an important role in the structural change of liquid $Ge_{15}Te_{85}$ characterized by anomalous temperature behaviors of thermodynamic quantities. The calculated angular limited triplet correlation functions of Te-Te-Te and Te-Ge-Te suggest that at low temperatures there exists a Peierls-type distorted local structure around both Ge and Te atoms, i.e., the short-long and long-short bonds correlation, however, it almost disappears at high temperatures. Our calculated LDOS suggests that the increase of electronical conductivity of liquid $Ge_{15}Te_{85}$ from 573 to 773 K observed in experiments may mainly result from the variation of the Te *p* orbital. At low temperatures (573–733 K), there is an obvious dip at Fermi level E_F, but at high temperatures (833–1073 K), the dip disappears, approaching the free-electron form.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 10374089 and Grant No. 10674135) and the Knowledge Innovation Program of Chinese Academy of Sciences (Grant No. KJCX2-SW-W17), and by the Center for Computational Science, Hefei Institutes of Physical Sciences.

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