PHYSICAL REVIEW B **79**, 184203 (2009)

Negative thermal expansion coefficient in supercooled liquid Te

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(Received 12 February 2009; published 18 May 2009)

The local atomic structure of supercooled liquid Te is studied using *ab initio* molecular-dynamics simulations and inherent structure formalism. Compared to experimental results, our calculated results reproduce the correct temperature dependence of structure factor, pair-correlation function, and average coordination number. Our results present direct evidence of a Peierls-type distorted local atomic structure in supercooled liquid Te. Moreover, our results suggest that the change in Peierls-type distorted local atomic structure around Te atoms with temperature is responsible for the negative thermal expansion coefficient of supercooled liquid Te. This mechanism is different from that observed in tetrahedrally bonded liquids.

DOI: 10.1103/PhysRevB.79.184203 PACS number(s): 61.20.Ja, 72.80.Ph, 71.15.Pd

I. INTRODUCTION

In liquid or amorphous matter, there are two cases about abnormal volume expansion with the decrease in temperature, i.e., negative thermal expansion coefficient. In the first case, for example, liquid water shows an abnormal volume expansion with decreasing temperature from 277 to 273 K at atmospheric pressure.[1] Another prominent example is amorphous silica.[2] In these two examples, directional tetrahedral bonding plays a key role. The second case is that negative thermal expansion coefficient is also shown in *p*-bonded element such as liquid $Ge_{15}Te_{85}$ alloys and supercooled liquid Te.[3,4] For liquid $Ge_{15}Te_{85}$, based on Kolobov *et al.*,[5] two different mechanisms should be considered, a sp^3 hybridization state of Ge or purely *p* bonding around Ge. Recently Bichara *et al.*[6] showed that no sp^3 hybridization of the Ge bonding is observed in liquid $Ge_{15}Te_{85}$. They suggested that the negative thermal expansion coefficient of liquid $Ge_{15}Te_{85}$ results from the symmetry recovery of the local environment of Ge atoms as in the parent solid phases. For pure liquid Te, a minimum volume was presented at about 733 K. With decreasing temperature from melting point (723 K) to 573 K, supercooled liquid Te undergoes an abnormal volume expansion. However, the atomic structure of supercooled liquid Te and the involved driven mechanism for the abnormal volume expansion have been open.

The liquid structure is usually understood with reference to its crystal structure. The trigonal structure of crystalline Te is usually discussed in terms of a Peierls distortion of simple cubic lattice: the *s* bands are completely filled and nonbonding, the *p* bonds directed along three orthogonal axes lead to a simple cubic structure.[7] However, for Te, the *p* bands is two-thirds filled so that the lattice is unstable against a Peierls distortion dividing the six nearest-neighbor bonds into two short intrachain bonds (d_1=0.284 nm) and four long interchain bonds (d_2=0.349 nm).[8] Also, this Peierls distortion was correctly reproduced by *ab initio* calculations in Refs. 7 and 9. Although the concept of Peierls distortion was established in the context of low-dimensional and periodic structures, recently it has been generalized for aperiodic systems using direct space method.[8] Over the past several decades, with reference to the crystal structure, there are many data about the structure of liquid Te. Most of the experimental results showed that the coordination number in liquid Te is about 3 at higher temperature and 2.5 at melting point, which is larger than that in crystalline Te, indicating not a pure chain structure in liquid Te. Based on the extended x-ray-absorption fine structure (EXAFS) data of Tsuzuki *et al.*,[10] there is a strong interchain correlation between the chains at melting point, which is reduced with decreasing temperature. By a tight-binding Monte Carlo simulation, Bichara *et al.*[11] showed that upon melting, the chain structure of the crystal is preserved and a short-long alternation (0.280 and 0.290 nm) of the bonds takes place within the chains. The local environment of each atom changes from two short and four long neighbor distances to two short, one medium, and three long neighbor distances. Although these works have tried to uncover the structural changes associated with the negative thermal expansion coefficient, no clear picture of the mechanisms involved emerges.

The inherent structure formalism, introduced by Stillinger and Weber,[12,13] is an insightful approach to study the local atomic structure of liquid and amorphous states. The idea is to separate the statistical-mechanical description of the many-body system into two distinct parts—the mechanically stable packing part and the vibrational part. The former is called inherent structures.[12,13] Molina and Lomba[14] pointed out that a more clear picture about the microscopic atomic structure of liquid Te can be obtained if the inherent structure is derived. In this work, using *ab initio* molecular-dynamics simulations and inherent structure formalism, we studied the general and inherent structures of supercooled liquid Te with decreasing temperature from 673 to 573 K. The aim is to gain more detailed information about the microscopic structure in supercooled liquid Te and find out the reason for negative thermal expansion efficient. 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; and a short summary is given in Sec. IV

II. COMPUTATIONAL METHODS

We used the Vienna *ab initio* simulation package (VASP) (Ref. 15) based on density function theory (DFT) (Ref. 16)

TABLE I. Main features of $S(Q)$ and general $g(r)$. ρ_0: number density used; pressure: the pressure in simulation box; h_1: first-peak height of $S(Q)$; R_1: first-peak position of $g(r)$; R_{min}: first minimum position of $g(r)$; r_{max}: first-peak position in RDF; and CN: average coordination number.

Temp. (K)	ρ_0 (at/Å^3)	Pressure (kbar)	h_1	R_1 (Å)	R_{min} (Å)	r_{max} (Å)	CN
573	0.0262	0.63	1.39	2.89	3.70	2.95	2.25
623	0.0266	0.34	1.40	2.92	3.82	2.98	2.51
673	0.0271	0.75	1.48	2.95	3.73	3.04	3.04

and employed the projector augmented-wave (PAW) potential.[17,18] As demonstrated in Refs. 7 and 9, the local-density approximation (LDA) underestimates the equilibrium volume of crystalline Te and predicts a more isotropic crystal structure than observed; however, the generalized-gradient approximation (GGA) gives a more reasonable result. So in the present paper, we used the generalized-gradient approximation formulated by Perdew and Wang to the exchange-correlation energy.[19,20] The experimental density,[4] listed in Table I, was used. The corresponding calculated pressure at each temperature is also listed in Table I. It can be seen that the pressure is very close to zero at each temperature and the pressure variation is very small. That is to say the density which yields a vanishing pressure at each temperature is very close to the experimental density. Although the anomalous pressure-induced structural change in liquid Te is observed by synchrotron x-ray-diffraction techniques[21] and *ab initio* molecular-dynamics simulations,[22] the pressure variation range is very large (0 ~ 22 GPa) and the anomalous structural change happens at about 6 GPa. We believe such a small pressure variation (about 0.4 kbar) in our simulations will not bring significant errors for the comparison of structural properties at different temperatures. The system (80 Te atoms) was put in a simple cubic box with periodical boundary conditions, and the Γ point was used to sample the Brillouin zone of the supercell. To check the k-point convergence on selected disordered structure, we have performed a fully converged calculation with a grid of $4\times4\times4$ k points (64 k points). When Γ point is used, compared to a fully converged calculation with 64 k points, the absolute error of average binding energy of each atom is 0.007 eV and the relative error is 0.002. We believe that such an error does not hamper our analysis on the temperature dependence of the structural properties of supercooled liquid Te. The electronic wave functions were expanded in the plane wave basis set, with an energy cutoff of 175 eV. Our canonical ensemble simulations were performed at 673, 623, and 573 K with a Nosé thermostat for temperature control.[23] 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 minimized 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. At first, the system was heated up to 1073 K. After a run of 20 ps at this temperature, the system arrived at an equilibrium liquid state. Then gradually reducing the temperature to 673 K, after the equilibration taking 8 ps, the physical quantities of interest were obtained by averaging over 16 ps to obtain 4000 configurations (called general structure configurations). For other temperatures, we only repeated this procedure and changed the final temperature into 623 and 573 K, respectively. At 673 K, we obtained 20 configurations during the run of 16 ps. For each configuration, keeping the volume of the supercell constant, we only relaxed the configurational coordinates of the atoms to the closest local minima (inherent structure configurations) on the potential-energy hypersurface by a conjugate-gradient energy minimization algorithm.[12,13] Then we analyzed the inherent structure of liquid Te by averaging the 20 inherent structure configurations. At 573 K, we repeated this procedure.

III. RESULTS AND DISCUSSION

The structure factor $S(Q)$ of supercooled liquid Te, obtained by Fourier transformation of pair-correlation function $g(r)$, is shown in Fig. 1. Considering that the calculation of $S(Q)$ by Fourier transformation of $g(r)$ on a small simulation box may lead to significant errors, a direct calculation from atomic coordinates in our simulations was also performed. The calculated results along with the experimental data at 603 K from neutron diffraction are also shown in Fig. 1. It can be found that the calculated structure factors by the two methods are in good agreement with each other, which indicates that the errors in the calculation of $S(Q)$ by Fourier transformation of $g(r)$ on our simulation box are negligible. At 623 K, compared to experimental data at 603 K,[24] although the shifts from 30 to 60 nm^{-1} are obvious, the overall agreement between them is acceptable. Especially, it should be noticed that, compared to experimental results,[24] our calculated results reproduce the evolution of $S(Q)$: as listed in Table I, the height of the first peak increases with increasing temperature from 573 to 673 K, which is in contrast to the behavior of a classical isotropic fluid. So we believe that the discrepancy in $S(Q)$ between our results and experimental data does not hamper our analysis of the structural changes in supercooled liquid Te.

The pair-correlation function, obtained from the atomic coordinates in our molecular-dynamics simulations, is shown in Fig. 2. It can be seen that there are three peaks located at about 0.290, 0.430, and 0.620 nm, respectively. It should also be noticed that the first peak is asymmetry and there is a shallow trough between the first peak and the second one, which indicate a nonsimple local structure in supercooled liquid Te. With increasing temperature, the position of the first peak presents a little shift toward large r value, and the height decreases. According to $g(r)$, the average coordination

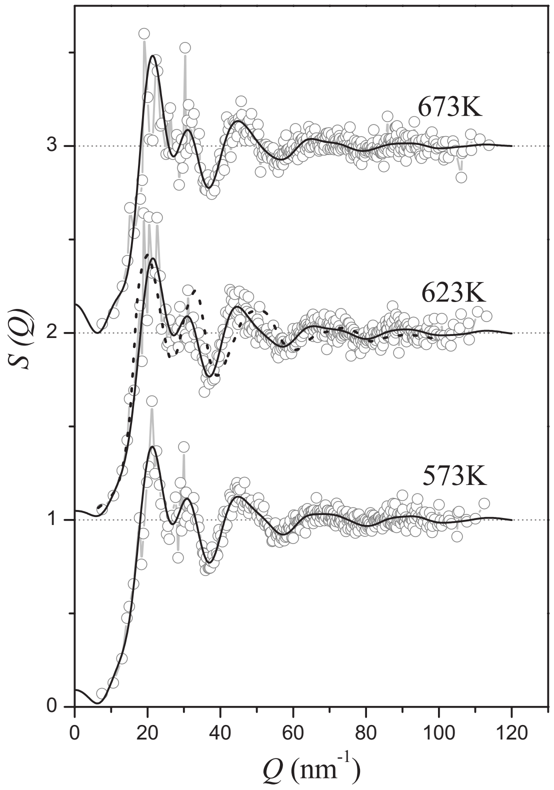

FIG. 1. $S(Q)$ of supercooled liquid Te calculated by Fourier transform (solid line) and direct calculation (gray line and circle), compared with experimental data (dash line) at 603 K from Ref. 24.

number (CN) was also calculated as in Ref. 25,

$$N = 2\int_0^{r_{\max}} 4\pi r^2 \rho_0 g(r) dr, \tag{1}$$

where $r_{\max}$ is the position of the first peak in radial distribution function (RDF) $4\pi r^2 \rho_0 g(r)$. The results are also listed in Table I. It can be seen that the coordination number decreases gradually with a decrease in temperature from 673 to 573 K, which is in contrast to the behavior of a classical isotropic fluid. This suggests that, with decreasing temperature from 673 to 573 K, the volume expands and hence a negative thermal expansion coefficient is observed. The evolution of these features is in good agreement with experimental results.[10,24] As mentioned in Sec. I, Bichara *et al.*[11] showed that upon melting, the chain structure of the crystalline Te is preserved and a short-long alternation of the bonds takes place within the chains so that the splitting of the first peak of $g(r)$ appears in liquid Te and remains in supercooled liquid Te. In order to verify whether the case is true or not, we calculated the pair-correlation functions from the inherent structure of supercooled liquid Te at 673 and 573 K. From the inherent $g(r)$, also shown in Fig. 2, we do not find the splitting of the first peak. On the contrary, the first peak located at about 0.290 nm becomes more sharp than that in general pair-correlation function. Moreover, we can easily find that at 673 K, a new peak located at around 0.330 nm appears, which becomes very low at 573 K. It should also be noticed that two other shoulders located at about 0.315 and 0.345 nm appear at 573 K. We noticed that the first-peak position 0.290 nm and the shoulder position 0.345 nm are very close to lengths of two characteristic bonds of Peierls distortion in trigonal Te [two shorter interchain bonds 0.284 nm and four longer interchain bonds 0.349 nm (Ref. 8)]. Does the local atomic structure of supercooled liquid Te exhibit a Peierls distortion similar to that in crystalline Te? As explained in Ref. 8, two conditions have to be fulfilled to allow a Peierls distortion of the local atomic environment around Te atoms: (i) the angular distribution function around Te atoms shows a maximum close to 90°; (ii) the major contribution to the density of states (DOS) at the Fermi level is due to Te p orbitals. To confirm this question, the angular distribution function and the DOS were also calculated.

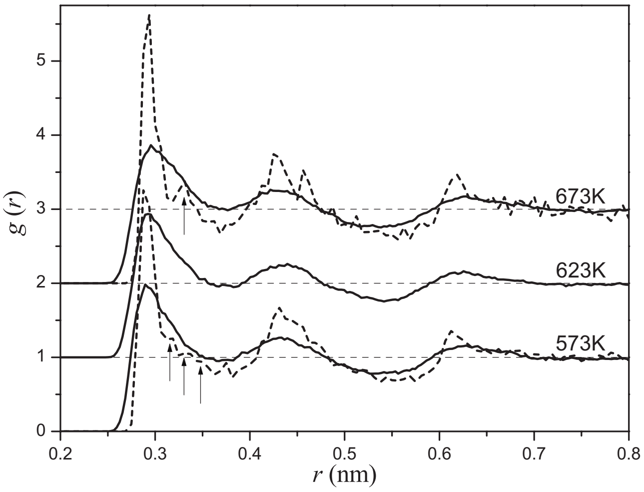

FIG. 2. Inherent (dash line) and general (solid line) $g(r)$ of supercooled liquid Te.

The calculated inherent angular distribution functions, $g_3(\theta)$, are shown in Fig. 3. When $r_{\text{cutoff}}=0.360$ nm, including the second peak in the inherent $g(r)$, $g_3(\theta)$ mainly shows three peaks located at around 60, 95, and 167°, respectively. But it should be noticed that their heights and positions are almost unchanged with temperature. The 60° peak is related to close-packed structure of atoms in supercooled Te. Although 95° is slightly less than the characteristic angle of Peierls distortion in trigonal Te [101.0° (Ref. 7)], the second and the third peaks seem to indicate that a Peierls-type distorted local structure similar to that in crystalline Te is still preserved at 673 and 573 K. This is consistent with that found in inherent $g(r)$ (as shown in Fig. 2). When $r_{\text{cutoff}}=0.300$ nm, not including the second peak in the inherent $g(r)$, the 167° peak disappears completely. This suggests that at least one of the two bonds which form the 167° angle is included in the second peak of inherent $g(r)$.

The total density of states, represented in Fig. 4, shows a dip at the Fermi level due to the fluctuations in the Fermi level position. From the calculated partial density of states, we can see that the major contribution to the total density of states at the Fermi level is indeed due to Te p orbital. Moreover, it can be found that the dip at the Fermi level in Te p orbital becomes more shallow from 573 to 673 K. As demonstrated in Ref. 11, the reason is that one of the interchain distances is shortened, and a resonance effect arises between

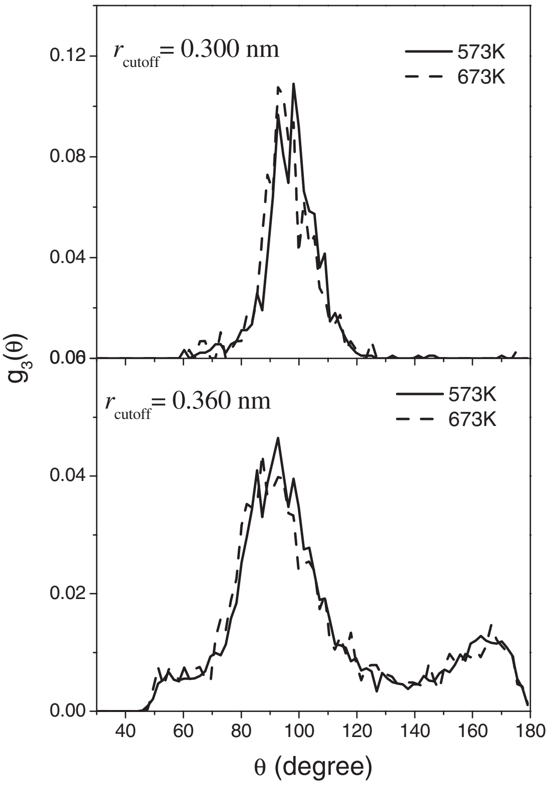

FIG. 3. Angular distribution functions of supercooled liquid Te for $r_{\text{cutoff}}=0.360$ nm (lower) and $r_{\text{cutoff}}=0.300$ nm (upper).

two neighboring lone pair orbitals, leading to the broadening of lone pair band. Through the analysis on angular limited bond-bond correlation functions, we positively find that some of the interchain distances are shortened, as will be seen in the following parts of this section.

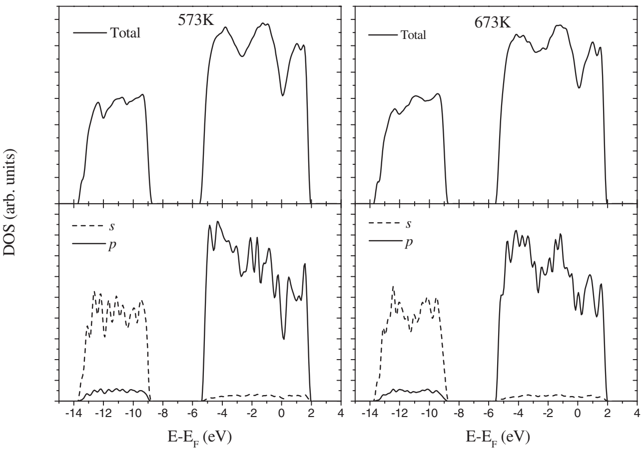

FIG. 4. Total and local electronic density of states of supercooled liquid Te at 573 and 673 K.

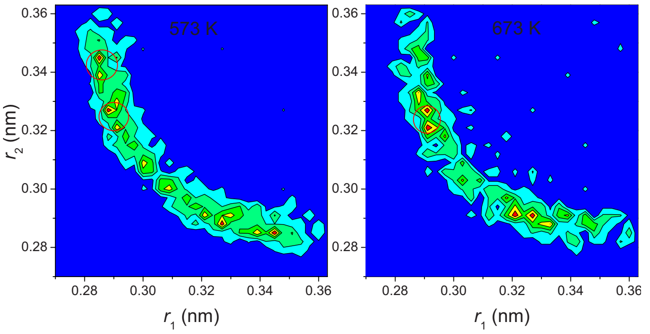

FIG. 5. (Color online) Angular limited bond-bond correlation functions at $T=573$ K (left) and $T=673$ K (right).

To obtain direct evidences of a Peierls-type distorted local structure in supercooled liquid Te and analyze the reason for negative thermal expansion efficient, we have also calculated the angular limited bond-bond correlation function from inherent structures as introduced in Ref. 26. The angular limited bond-bond correlation function is shown in Fig. 5. It is the probability $P(r_1,r_2)$ of finding an atom C at a distance r_2 from an atom B which is itself at a distance r_1 of the reference atom A. A constraint is placed on the position of atom C. Namely, the angle θ formed by vectors $\overrightarrow{BA}$ and $\overrightarrow{BC}$ is constrained in a small range. Here, in order to investigate the correlation of two bonds which form the angle at about 167° [i.e., the third peak in inherent $g_3(\theta)$], θ is chosen between 155 and 175°. It can be easily found that at 673 K, the maxima of $P(r_1,r_2)$ are mainly centered at two regions (0.290 and 0.325 nm) and (0.325 and 0.290 nm). This indicates that a shorter bond of length $r_1=0.290$ nm is most probably followed by a longer bond of length $r_2=0.325$ nm, and vice versa. This is the fingerprint of the Peierls distortion in crystalline Te, suggesting that Peierls-type distorted local structure similar to that in crystalline Te is preserved at 673 K. But we should notice that $r_2=0.325$ nm is shorter than the interchain bond 0.349 nm in crystalline Te, indicating that interchain correlation at 673 K is stronger than that in crystalline Te. Compared to the results at 673 K, one can find that, at 573 K, besides two maxima of $P(r_1,r_2)$ at (0.290 and 0.325 nm) and (0.325 and 0.290 nm), two other maxima at (0.285 and 0.345 nm) and (0.345 and 0.285 nm) appear. The values that $r_1=0.285$ nm and $r_2=0.345$ nm are very close to the two characteristic bond lengths of Peierls distortion in trigonal Te (0.284 and 0.349 nm). The longer bond in Peierls-type distorted local structure changes from 0.325 nm at 673 K to 0.345 nm at 573 K, indicating that interchain correlation reduces when decreasing temperature from 673 to 573 K. These correlation maxima are also in good accordance with the positions of the first and the second peaks in the inherent pair-correlation functions.

Based on our present results, we now turn to the negative thermal expansion coefficient of supercooled liquid Te. Obviously, the Peierls-type distorted local atomic structure, i.e., a shorter bond followed by a longer one, is preserved in supercooled liquid Te from 673 to 573 K. From the inherent angular distribution functions, we can conclude that the local environment of Te atoms is dominated by the Peierls-type distorted local atomic structure since the 95° peak and the 167° peak are apparently higher than the 60° peak. With decreasing temperature from 673 to 573 K, the heights of the 95° peak and 167° peak are almost unchanged, indicating that the percentage of the Peierls-type distorted local atomic structure is unchanged with temperature. However, from the angular limited bond-bond correlation functions, it can be concluded that some of the Peierls-type distorted local structure around Te atom changed with temperature—the longer bond changing from 0.325 nm at 673 K to 0.345 nm at 573 K. Apparently, the Peierls-type distorted local atomic structures at 573 K occupy larger atomic volume than that at 673 K so that the volume of supercooled liquid Te expands when decreasing temperature from 673 to 573 K, leading to a negative thermal expansion coefficient. Obviously, this mechanism is different from that observed in tetrahedrally bonded liquids.

IV. CONCLUSIONS

In summary, the local atomic structure of supercooled liquid p-bonded element Te is studied using *ab initio* molecular-dynamics simulations and inherent structure formalism. The structure factor, pair-correlation function, average coordination number, angular distribution function, density of states, and angular limited bond-bond correlation function were calculated. Compared to experimental results,[10,24] our calculated results reproduce the correct temperature dependence of $S(Q)$, $g(r)$, and CN. Our results from inherent $g(r)$, $g_3(\theta)$, DOS, and angular limited bond-bond correlation function present direct evidence of a Peierls-type distorted local atomic structure in supercooled liquid Te. Moreover, our results showed that, when decreasing temperature from 673 to 573 K, some of the longer bonds in the Peierls-type distorted local atomic structures change from 0.325 to 0.345 nm so that the Peierls-type distorted local atomic structures at 573 K occupy larger atomic volume than that at 673 K, and the volume of supercooled liquid Te expands when decreasing temperature from 673 to 573 K, leading to a negative thermal expansion coefficient.

ACKNOWLEDGMENTS

This work was supported by the School Scientific Research Foundation of Ludong University.

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