Evidence of a Reentrant Peierls Distortion in Liquid GeTe

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The local atomic order of semiconducting liquid GeTe is studied using first-principles molecular-dynamics simulations. Our work points out a high degree of alternating chemical order in the liquid and demonstrates the presence of a Peierls distortion close above the melting temperature. This distortion, absent in the high temperature crystalline structure of NaCl type, is a remnant of the atomic arrangement in the $A7$ low temperature crystalline phase. It disappears slowly with temperature, as the liquid evolves from a semiconducting to a metallic state.

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The melting of semiconductors has been the subject of many studies since the initial work of Glazov *et al.* [1], especially because of the variety of behaviors that have been observed. For most IV and III-V semiconductors (SC), melting is accompanied by a transition toward a metallic state (MT) and a jump of coordination number from the value of 4 in the crystalline phase to the value of ~6 in the melt [2]. At variance, some II-VI materials (e.g., CdTe, ZnTe, and HgSe) retain their semiconducting properties as they melt. In those cases, the structure of the liquid phase remains open with the coordination number being equal to ~4 [1]. The empirical Joffe and Regel rule suggests that the semiconducting character is preserved in the liquid when its local order is close to the order of the crystalline phase [3]. For example, for SC liquid II-VI materials both neutron diffraction experiment [4] and molecular-dynamics simulations [5] indicate that the coordination number is ~4 and the number of homopolar bonds is significantly smaller than for III-V compounds [5]. Such small deviation of the local order from the crystalline phase explains the SC behavior of the melt. Similarly, for the lightest IV-VI compounds (SnS, SnSe, and GeS) which remain SC as they melt, the coordination number measured in the liquid ($Z \approx 3-4$) [6] remains close to that in their $Pbnm$ crystalline structure ($Z = 3$).

In comparison to lightest IV-VI compounds, the behavior of GeTe appears unique in many respects. First, solid GeTe undergoes a crystalline phase transition on cooling at 430 °C [7], from the $B1$ phase with $Z = 6$ (NaCl structure) to an $A7$ rhombohedral phase that consists of a stack of corrugated planes of alternating threefold coordinated atoms ($Z = 3$) [8]. A similar transition is observed in crystalline GeSe. This transition is the result of a Peierls distortion: the half filling of the valence p band favors the alternation of short and long bonds in three almost orthogonal directions of space by opening a gap at the Fermi level. The concept of Peierls distortion, established in the context of low dimensional, periodic, structures, has been recently generalized for aperiodic systems using a direct space method [8]. The covalent bonding in both phases of GeTe has been described extensively in Ref. [9] and has been attributed mainly to $pp\sigma$ resonances. This study shows that covalency is increased in the low temperature, Peierls distorted phase. Second, the liquid phase of GeTe, semiconducting close above the melting temperature ($T_m = 725$ °C), evolves gradually to a metallic state: the dc conductivity, σ, varies little upon melting (from 2400 to 2600 $\Omega^{-1}\,\mathrm{cm}^{-1}$), but then increases rapidly with temperature in the liquid phase [1]. Third, at 900 °C, temperature at which the system may still be considered as semiconducting, the average coordination number, deduced from neutron diffraction data [6], is equal to 5.1 ± 0.5. This value appears significantly smaller than in the NaCl structure below T_m ($Z = 6$) if we notice that the estimate of Z in the liquid is an upper bound, obtained under the assumption of perfect chemical ordering.

The lowering of Z in the liquid was tentatively explained by the appearance of numerous coordination defects (vacancies), also responsible for the large and positive variation in atomic volume observed upon melting (+6.7%). However, additional measurements at 740 °C yield $Z = 3.9 \pm 0.5$ [10], making this hypothesis less plausible. Another possibility is that the local ordering in the liquid could be significantly different from that of the crystalline form as it was recently suggested for GeSe, which exhibits features similar to GeTe in both the solid and the molten phases [11,12]. In any case, the evolution of Z upon melting, combined with the persistence of a semiconducting behavior, is unusual as it seems to invalidate the Joffe and Regel rule, and may question the hypothesis of perfect chemical ordering in the liquid. Also, the reasons of the gradual evolution of the liquid system to a metallic state remain unclear.

In this work, we study the microscopic structure of the liquid GeTe, using first-principles molecular-dynamics simulations. We first highlight the high level of alternating

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chemical order. Using "triplet correlation functions" inaccessible to the experiment, we then demonstrate that the evolution of the structure upon melting results in fact from the reentrance of the Peierls distortion present in the low temperature (LT) crystalline phase. This distortion is characteristic of the SC liquid and disappears with increasing temperature as the system evolves to a MT state.

In the simulation, an ensemble of 64 atoms is used in a supercell geometry. The size of the supercell is fixed to correspond to the experimental liquid density ($\rho = 0.0335$ atoms/Å^3 [13], $a = 12.4$ Å). To prepare the liquid ensemble, we perform Langevin dynamics [14–16]. The time step used to integrate the equation of motion is taken as 300 a.u. (1 a.u. $= 2.4 \times 10^{-17}$ s). The interatomic forces are computed quantum mechanically within the density functional theory and the local density approximation. We adopt a pseudopotential approach with a plane wave expansion of the electronic wave function [15]. We use Troullier-Martins pseudopotentials [17] with Ceperley-Alder correlation [18] for the electrons. The energy cutoff is equal to 9 Ry. With these potentials, the cell parameters of the $A7$ phase of GeTe are reproduced within 1% ($a = 5.95$ Å, $\alpha = 89.09°$, and $u = 0.2335$). Starting from a $B1$ configuration, we thermalize the liquid at 6000 K for 3 ps. Then we gradually cool the system down to the final temperature of 1000 K during a period of 3 ps. Once the melting temperature is reached, we conduct the simulation during another 3 ps.

The partial structure factors calculated from the Fourier transform of the partial correlation functions obtained by simulation are combined using the bound coherent scattering wavelengths of the hot-neutron diffraction experiment (see Ref. [6]) to get the total structure factor of Fig. 1. The overall agreement with the experiment is excellent, especially for the right shoulder of the first peak around 3 Å^{-1}. Similarly, every feature of the total pair correlation $g(r)$ is accurately reproduced by the simulation. The partial pair correlation functions are given in Fig. 2. Defining the outer limit of the first coordination shell by the location of the first minimum of the total $g(r)$, we estimate the total and partial coordination numbers. The major contribution to the total $g(r)$ is due to Ge-Te bonds ($Z_{\text{Ge-Te}} = 2.87 \pm 0.09$), but a relatively high proportion of homopolar Ge-Ge bonds exists in the liquid ($Z_{\text{Ge-Ge}} = 2.56 \pm 0.09$), to the contrary of Te-Te bonds ($Z_{\text{Te-Te}} = 1.11 \pm 0.09$). The total coordination of Ge atoms (Z_{Ge}) is equal to 5.43 ± 0.19, while it is only equal to 3.98 ± 0.18 for Te atoms. These values exclude the possibility of tetrahedrally bonded Ge as suggested recently in Ref. [19] for amorphous GeTe.

At this stage of the description, the local order in the liquid seems to differ widely from both LT and HT crystalline forms. It is the conclusion which rose recently for GeSe from the inspection of similar partial $g(r)$ obtained by neutron diffraction with isotopic substitution [11,12]. However, it is worth noticing that the heteropolar coordination number is very close to the value of 3 found in the Peierls distorted structure of the LT crystal. This suggests that the SC liquid structure just above melting could be closely related to the crystalline LT phase, while the associated local ordering gradually disappears with increasing temperature in favor of homopolar Ge-Ge bonds, simultaneously to the evolution to the MT state. Two questions must be addressed to confirm this hypothesis: (i) what is the degree of chemical ordering in the liquid, and (ii) does the molten phase exhibit a Peierls distortion?

To quantify the ordering, we use the Warren-Cowley parameter as generalized for liquids by Wagner and Ruppersberg [20],

$$\alpha_x = \frac{1 - Z_{\text{Te-Ge}}/[c_{\text{Te}} c_{\text{Ge}}(Z_{\text{Te}} + Z_{\text{Ge}})]}{1 - Z_x/[c_{\text{Te}} c_{\text{Ge}}(Z_{\text{Te}} + Z_{\text{Ge}})]}, \tag{1}$$

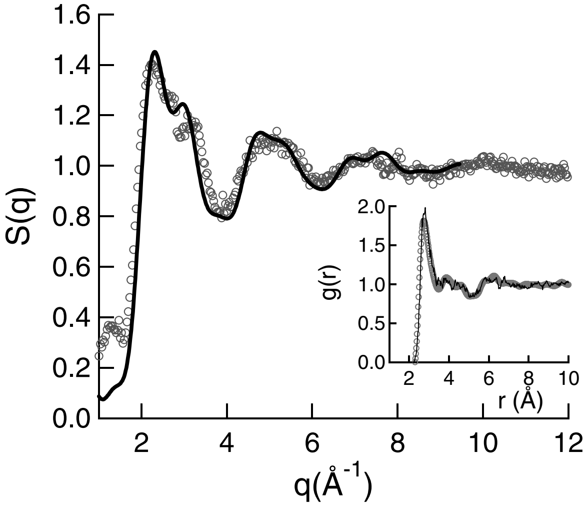

FIG. 1. Calculated structure factor $S(q)$ at 1000 K (solid line) compared with neutron diffraction $S(q)$ at 1013 K from [6] (symbols). Inset: Pair correlation functions $g(r)$.

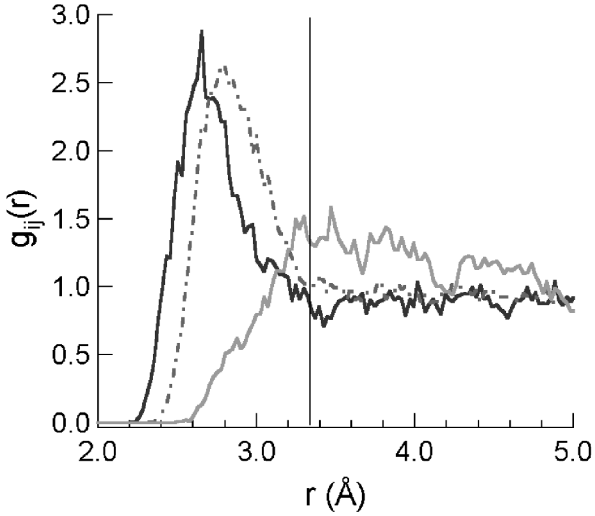

FIG. 2. Partial pair correlation functions $g_{ij}(r)$ calculated by simulation at 1000 K: g_{GeGe} (solid curve), g_{GeTe} (dash-dotted curve), and g_{TeTe} (grey curve). The vertical line corresponds to the first minimum of the total $g(r)$.

where $c_{\mathrm{Te}} = c_{\mathrm{Ge}} = 0.5$ are the concentrations in Te and Ge, and the subscript $x = \mathrm{Ge}, \mathrm{Te}$. The value of 1 corresponds to a complete chemical ordering (alternating species), $\alpha = 0$ is obtained for a random mixing of the atoms, and $\alpha = -1$ would be a synonym of phase separation. We obtain $\alpha_{\mathrm{Ge}} = 0.17 \pm 0.02$ and $\alpha_{\mathrm{Te}} = 0.32 \pm 0.05$ at 1000 K. This means that the environment, though not fully, remains partly ordered especially around Te atoms.

As evidence that this order is similar to the Peierls distortion of the crystal, we plotted in Fig. 3 the angular limited bond-bond correlation function as introduced in Ref. [21]. It is the probability $P(r_1, r_2)$, relative to a perfect gas at the same density, 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, under the constraint that the B-C bond is contained in a cone of small angular aperture whose axis is A-B. It appears that if at high temperature (initial configuration thermalized at 6000 K), there is no correlation between the lengths of two successive bonds, this is no more true at the final temperature of 1000 K. A correlation appears, the maximum of probability being that a "short" first distance is followed, within the angular aperture of the cone, by a longer distance, and vice versa. This is the fingerprint of the Peierls distortion of the LT crystal. Further inspection of the "almost aligned" triplet partial correlation functions shows that if correlation is negligible for nonalternating triplets it gets very large when the triplet is alternating (Ge-Te-Ge or Te-Ge-Te triplets) as represented in Fig. 4. The correlation maximum is located at $(r_1, r_2) \approx (2.7$ Å$, 3.1$ Å$)$, values very similar to

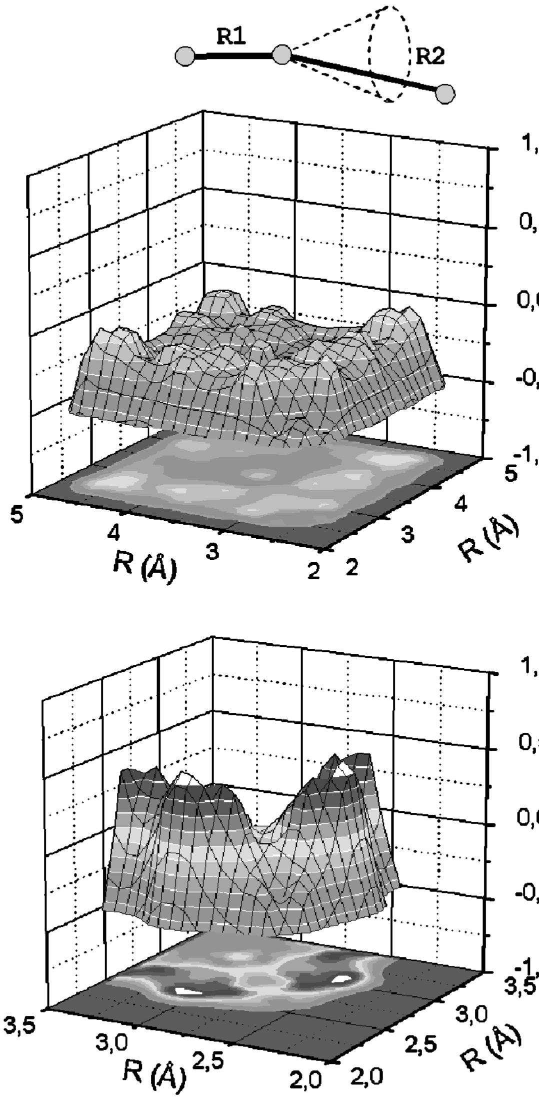

FIG. 3. Comparison of the angular limited bond-bond correlation function $P(r_1, r_2)$ (see text) at $T = 6000$ K (upper) and $T = 1000$ K (lower). The cone aperture is of 15°. Horizontal axes: r_1 and r_2; vertical axis: probability $P(r_1, r_2)$ [with $P_{gaz}(r_1, r_2)$ as origin]. The correlation surfaces are drawn from $P = -0.5$. Contour lines are drawn on the bottom for further clarity. All surfaces are obtained by averaging over 300 time steps (2.1 ps).

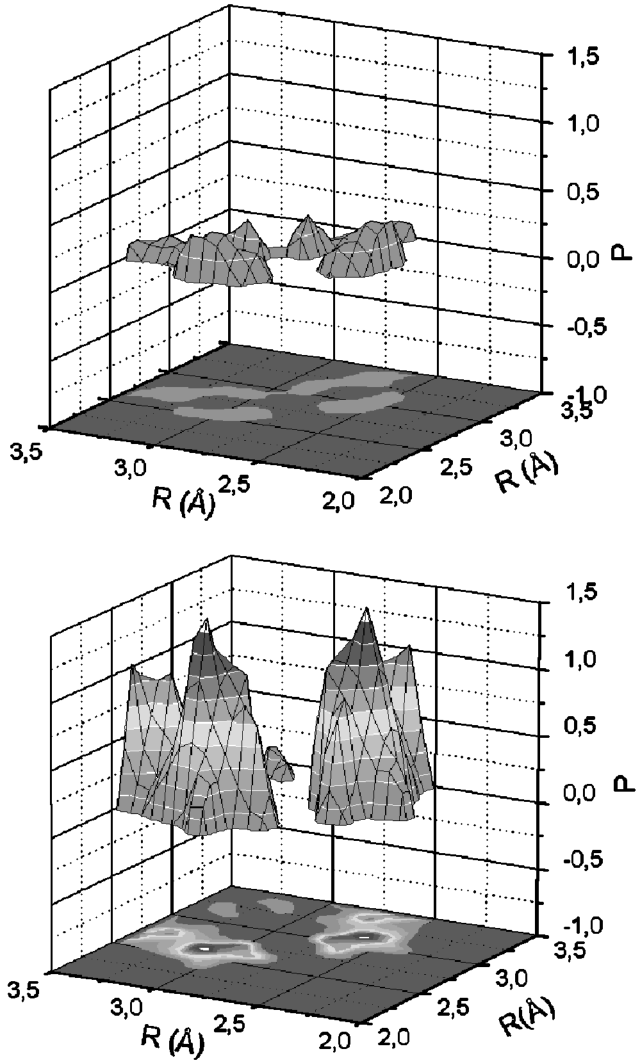

FIG. 4. Comparison of the angular limited bond-bond correlation function $P(r_1, r_2)$ (see text) for nonalternating A-A-A and A-A-B triplets (upper) and alternating A-B-A triplets (lower) at $T = 1000$ K. The correlation surfaces are drawn from $P = 0.0$.

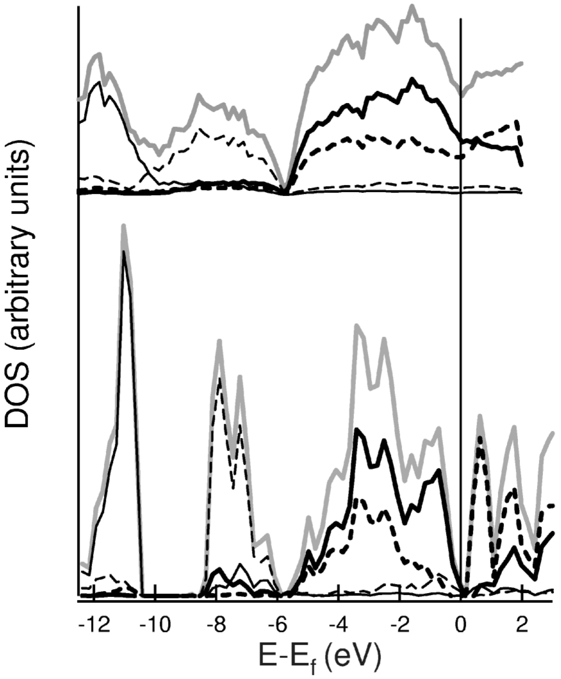

FIG. 5. Calculated electronic densities of states of the NaCl phase (lower part) and averaged over 10 time steps in the liquid phase (upper part). The total density of states (thick grey line) is projected on Ge-p (thick black line), Ge-s (thin black line), Te-p (thick dotted line), and Te-s orbitals (thin dashed line).

the first and the second neighbor distance within the LT crystal (2.84 Å and 3.15 Å, respectively).

The density of states of the liquid, represented in Fig. 5, shows a dip at the Fermi level due to the fluctuations in the Fermi level position. The major contribution to the density of states at the Fermi level is due to Ge and Te p orbitals. Moreover, the angular distribution around Te atoms shows a maximum close to 90°. These are indeed the two conditions that have to be fulfilled to allow a Peierls distortion of the *local* atomic environment as explained in Ref. [8]. The value of the dc electrical conductivity, σ, calculated as in Ref. [5], is between 3000 and 4000 Ω^{-1} cm. This agrees with the experimental value measured at 900 °C (3100 Ω^{-1} cm^{-1} [1]). Also, we found that the frequency dependence of the electrical conductivity is typical of a SC rather than of a MT [22].

In conclusion, the local order of liquid GeTe is shown to be partly Peierls distorted. Although evidence of a Peierls distortion in a disordered system has already been observed for elemental liquid As [23], this is the first evidence for the Peierls distortion in a liquid alloy, the striking feature being here that the distortion is reentrant from a nondistorted HT crystalline structure. This reentrant Peierls distortion is directly related to the chemical ordering. At the melting point, the degree of remaining chemical ordering is sufficient to maintain the Peierls distortion, even if the Ge atoms tend to form homopolar bonds, not present in either the LT or the HT crystal. This explains why the average coordination number decreases upon melting and, alternatively, why liquid GeTe is a semiconductor. As temperature increases, both the chemical ordering and the Peierls distortion vanish, explaining the rapid augmentation of σ. This study suggests that related compounds such as GeSe could exhibit a similar behavior.

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[1] V. M. Glazov, S. N. Chizhevskaya, and N. N. Glagoleva, *Liquid Semiconductors* (Plenum, New York, 1969).
[2] J. E. Enderby and A. C. Barnes, Rep. Prog. Phys. **53**, 85 (1990), and references therein.
[3] A. Joffe and A. Regel, *Progress in Semiconductors* (Heywood, London, 1974), Vol. 4, p. 237.
[4] J.-P. Gaspard, J.-Y. Raty, R. Céolin, and R. Bellissent, J. Non-Cryst. Solids **205–207**, 75 (1990).
[5] V. V. Godlevsky, J. J. Derby, and J. R. Chelikowsky, Phys. Rev. Lett. **81**, 4959 (1998).
[6] J.-Y. Raty, J.-P. Gaspard, M. Bionducci, R. Céolin, and R. Bellissent, J. Non-Cryst. Solids **250–252**, 277 (1999).
[7] A. Schlieper, Y. Feuetelais, S. G. Fries, B. Legendre, and R. Blachnik, Calphad **23**, 1 (1999).
[8] J.-P. Gaspard, A. Pellegatti, F. Marinelli, and C. Bichara, Philos. Mag. B **77**, 727 (1998), and references therein.
[9] H. M. Polatoglou, G. Theodorou, and N. A. Economou, J. Phys. C **16**, 817 (1983).
[10] J.-Y. Raty, Ph.D. thesis, University of Liège, 1990.
[11] P. S. Salmon and J. Liu, J. Phys. Condens. Matter **6**, 1449 (1994).
[12] I. Petri, P. S. Salmon, and H. E. Fisher, J. Phys. Condens. Matter **11**, 7051 (1999).
[13] V. M. Glazov and O. D. Shchelikov, Sov. Phys. Semicond. **18**, 411 (1984).
[14] R. Biswas and D. Hamann, Phys. Rev. B **34**, 895 (1986).
[15] R. N. Binggeli, J. L. Martins, and J. R. Chelikowsky, Phys. Rev. Lett. **68**, 2956 (1992).
[16] J. R. Chelikowsky, N. Troullier, and N. Binggeli, Phys. Rev. B **49**, 114 (1994).
[17] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[18] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[19] S. Hosokawa, Y. Hari, T. Kouchi, I. Ono, M. Taniguchi, A. Hiraya, Y. Takata, N. Kosugi, and M. Watanabe, J. Phys. Condens. Matter **10**, 1931 (1998).
[20] C. Wagner and H. Ruppersberg, At. Energy Rev. **1**, 101 (1981).
[21] C. Bichara, A. Pellegatti, and J.-P. Gaspard, Phys. Rev. B **47**, 5002 (1993).
[22] All details of those calculations will be given in a forthcoming paper.
[23] R. Bellissent, C. Bergman, R. Céolin, and J. P. Gaspard, Phys. Rev. Lett. **59**, 661 (1987).