

Temperature-Induced Density Anomaly in Te-Rich Liquid Germanium Tellurides: *p* versus *sp*³ Bonding?

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The density anomaly of liquid $\text{Ge}_{0.15}\text{Te}_{0.85}$ measured between 633 and 733 K is investigated with *ab initio* molecular dynamics calculations at four temperatures and at the corresponding experimental densities. For box sizes ranging from 56 to 112 atoms, an 8 *k*-points sampling of the Brillouin zone is necessary to obtain reliable results. Contrary to other Ge chalcogenides, no *sp*³ hybridization of the Ge bonding is observed. As a consequence, the negative thermal expansion of the liquid is not related to a tetrahedral bonding as in the case of water or silica. We show that it results from the symmetry recovery of the local environment of Ge atoms that is distorted at low temperature by a Peierls-like mechanism acting in the liquid state in the same way as in the parent solid phases.

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Density anomalies or negative thermal expansion coefficients in liquid or amorphous matter are commonly associated with tetrahedral bonding. A well-documented [1] example is liquid water that displays a density maximum at 277 K and atmospheric pressure. Another well-known example is amorphous silica [2]. In these two cases, directional tetrahedral bonding plays a key role. *p*-bonded elements are another class of materials displaying such a density anomaly. For these, pure tellurium is a prominent example, as its density [3] is maximal at 733 K and decreases when the temperature is lowered below the melting temperature (723 K) in the undercooled regime. Alloys of germanium and tellurium ($\text{Ge}_x\text{Te}_{1-x}$) around the eutectic composition ($x = 0.15$) display an even sharper density anomaly in the stable liquid state [4].

In a recent study of the parent $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) system [5], Kolobov and co-workers proposed an “umbrella-flip” mechanism to account for the differences between crystalline and amorphous phases. In this scheme, Ge atoms surrounded by Te change their local order from *p*-bonded, sixfold coordinated in the crystalline state to *sp*³, fourfold coordinated in the amorphous state. Density and electrical conductivity changes occurring during the amorphization/recrystallization process as well as the bonding type [6] are key features for the use of GST alloys in the upcoming phase change random access memory devices. It is, therefore, essential to validate the mechanisms involved in this transition.

The structural change in liquid $\text{Ge}_x\text{Te}_{1-x}$ is experimentally well-documented, and this system is best suited to theoretical investigation. Investigating this simpler system is particularly relevant since, according to Ref. [5], the

changes in GST alloys are localized in the Te first neighbor shell of Ge atoms. Also, neglecting the small difference in the numbers of *s* and *p* electrons between these two systems (that may play an important role [7]) and in a simple tight binding approximation with equal hopping integrals, adding Sb that is *p*-bonded with *s* and *p* atomic energy levels sitting between those of Ge and Te [8] should not change the hybridization state of Ge. In addition, Ge-Te is very different from Ge-*X* (*X* = O, S, Se) systems, which present a GeX_2 , tetrahedrally bonded compound, while there is no stable GeTe_2 compound in the phase diagram [10].

Owing to the relatively low temperature, accurate measurements of the density [4], the specific heat [11], and the electrical resistivity [12] were performed, leading to a consistent set of data indicating a structural change in the liquid state. Although numerous neutron and x-ray scattering [13,14] and x-ray absorption fine structure [15] measurements have tried to uncover the structural changes associated with the sharp extremum of the thermodynamic response functions, no clear picture of the mechanisms involved emerges. At least two different mechanisms should be considered, assuming different types of bonding states for Ge. According to Kolobov *et al.* [5], a *sp*³ hybridization state of Ge could be assumed, in which case the density anomaly would enter the classical scheme for tetrahedrally bonded systems, or purely *p*-bonding around Ge could be assumed, in which case an explanation for the density anomaly should be provided. With reference to the *p*-bonding scheme, it should be noted that, upon crystallization, the eutectic liquid decomposes into two *p*-bonded phases, namely, pure tellurium and the GeTe

compound that undergoes a phase transition [16] around 700 K between a Peierls distorted low temperature ($R3m$) α phase with three short (2.84 Å) and three long (3.15 Å) Ge-Te distances and a high temperature ($Fm3m$) β phase with six equal first neighbor distances.

This problem has already been tackled [17] by means of *ab initio* molecular dynamics (MD) in the density functional theory (DFT) framework using pseudopotentials and a plane waves basis. The limited statistics prevented a clear-cut answer to the above structure questions. In this Letter, we use a more efficient projector augmented wave (PAW) approach, performing much longer runs (up to 56 ps) on larger simulation boxes (up to 168 atoms). We first carefully analyze some technical points that turn out to be important, such as the often neglected k -point sampling of the reciprocal cell. We then discuss the atomic and electronic structure of the liquid that clearly indicate the absence of sp^3 bonding in the liquid.

The DFT based calculations were performed in the generalized gradient approximation using the Perdew, Burke, and Ernzerhof [18] functional and the PAW [19,20] potentials as implemented in the VASP code [21]. The energy cutoff for the plane waves expansion was set at 130 eV. This cutoff allows the two distinct Ge-Te bond lengths in the α -GeTe phase to be reproduced to within 0.004 Å (0.14%) and 0.008 Å (0.25%) of the experimental values at room temperature. Taking a cutoff of 216 eV reduces the biggest discrepancy to 0.10%. Molecular dynamics runs were performed following the experimental densities [4] at 633 K (0.0277 Å⁻³), 673 K (0.0282 Å⁻³), 733 K (0.0289 Å⁻³), and 943 K (0.0285 Å⁻³), the temperatures corresponding to those of the neutron scattering experiments [13]. The initial MD configurations were generated from random configurations with well separated Ge atoms. Boxes containing 56 (8 Ge + 48 Te) atoms with periodic boundary conditions were used. MD runs under canonical conditions using a Nosé thermostat and micro-canonical conditions were performed and were found to give similar static structure factors. Canonical conditions were retained for production runs of 18 to 54 ps in order to precisely control the temperature. Increasing the k -point sampling of the reciprocal unit cell of a 56 atoms box from the Γ point to 8 k points led to liquid structures in better agreement with the experimental data. In particular, the first peak of the pair correlation function [$g(r)$] is narrower with 8 k points, in better agreement with the data. A check of the k -point convergence on selected disordered structures shows that changing from 1 to 8 k points improves the relative error on the total energy from 0.004 to 0.0003, as compared to a fully converged calculation with 64 k points. The absolute error decreases from 0.70 to 0.05 eV, which is consistent with the energy dispersion of each band that can be as large as 0.10 eV. These simulation characteristics (small simulation box and dense k -point sampling) were preferred over simulations in larger boxes and Γ -point

sampling only in the electronic structure calculation. The drawback of the small number of atoms in the simulation box is the fluctuations in temperature and pressure. The standard deviation on the temperature is less than 70 K at all temperatures and, at 633 K, the pressure is -0.8 ± 4.0 kbar with 8 k points.

In the following, we present results obtained with 8 k -points sampling, on boxes containing 112 atoms at 633 K and 56 atoms at all other temperatures.

The computed total structure factors, properly weighted for neutron scattering (Fig. 1), display the correct temperature dependence as compared to the experimental data from D4 at Institut Laue Langevin. Owing to the small box sizes, the computed structure factors are not physically meaningful below 1.2 Å⁻¹. The first peak in $S(q)$ at 2.2 Å⁻¹ is more prominent than in the experimental data, and the height of the second peak of $S(q)$ is too small at 633 K, but it correctly and significantly (see error bars) decreases with increasing temperature. Although our calculations are effectively converged in terms of the k -point sampling and the plane wave cutoff, the first peak of the calculated $g(r)$ (not shown here) is overestimated by about 0.15 Å. This discrepancy, discussed below, does not hamper our analysis of the structural changes in the liquid. The calculated partial structure factors $S_{ij}(q)$ ($i, j = \text{Ge, Te}$) presented in Fig. 2 show that the temperature-induced decrease of the second peak of $S(q)$ essentially results from the $S_{\text{GeTe}}(q)$ contribution, while $S_{\text{TeTe}}(q)$ does not significantly change with increasing temperature. The second peak of $S_{\text{GeTe}}(q)$ around 3 Å⁻¹ gradually becomes a shoulder, causing the second peak of the total $S(q)$ to decrease. Because of the low ($x = 0.15$) Ge concentration, $S_{\text{GeGe}}(q)$ represents 4% of the total and can be neglected.

To analyze the changes of the local atomic structure upon heating, we first calculate the averages of the distances of the first, second, etc., neighbors up to the ninth neighbor as described in Ref. [17]. The neighbor shells

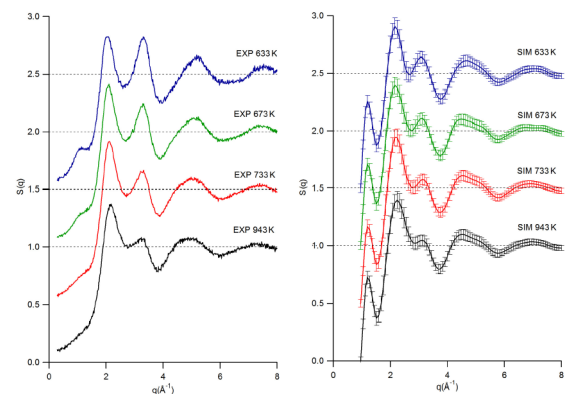


FIG. 1 (color online). Experimental [13] (left panel) and calculated (right panel) total structure factors at 633, 673, 733, and 943 K. The error bars on the calculated $S(q)$ correspond to the rms fluctuations.

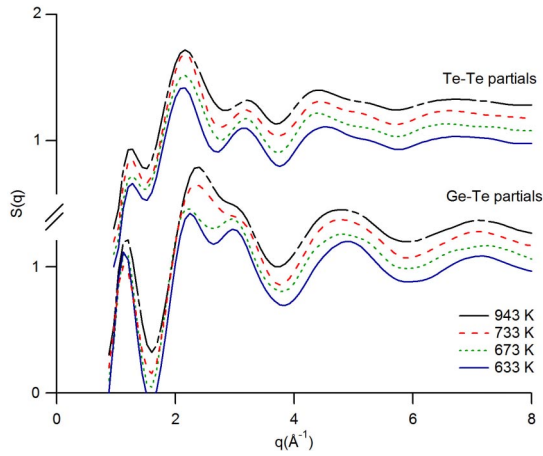


FIG. 2 (color online). Four lower (upper) curves (shifted along y by 0.1): GeTe (TeTe) partial structure factors. Temperatures are 633, 673, 733, and 943 K.

around Ge and Te behave in slightly different ways (see Fig. 3). On heating from 633 to 733 K and shrinking the volume, the three shortest distances around Ge and two shortest distances around Te remain constant or even increase slightly, whereas the distances beyond shrink to accommodate the volume contraction. This is in contrast to the behavior of a classical isotropic fluid and similar to the behavior of the solid phase of pure Te under pressure [22]. We also note that, upon heating from 733 to 943 K, the fourth to sixth distances around Ge and third to sixth distances around Te keep on shrinking although the atomic volume increases.

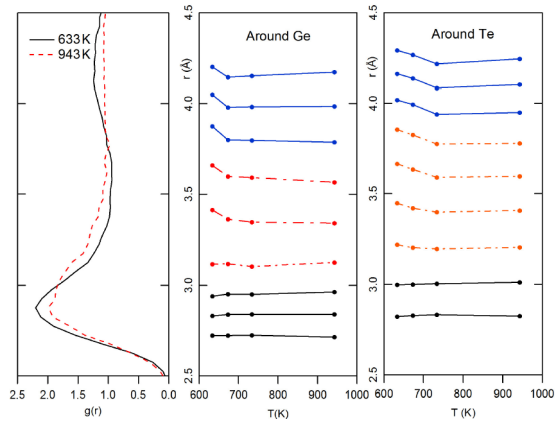


FIG. 3 (color online). Pair correlation functions at 633 and 943 K (left panel) and average distance of the 9 first neighbors around Ge (central panel) and around Te (right panel) atoms. Solid black lines correspond to distances that remain constant or slightly expand with increasing temperature (3 around Ge, 2 around Te). Red dashed-dotted lines correspond to distances that always shrink (3 around Ge, 4 around Te). The 3 thin blue lines correspond to distances that shrink when the average volume shrinks and then slightly expand.

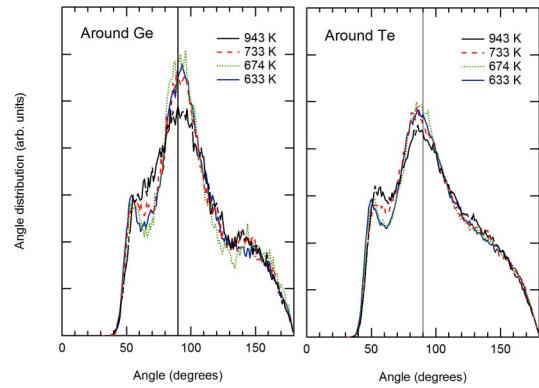


FIG. 4 (color online). Bond angle distributions for the 6 first neighbors of Ge (left panel) and Te (right panel) atoms.

Further insight is gained by analyzing the bond angle distribution. Owing to the better statistics gained from longer runs (as compared to Ref. [17]), it is now clear that the bond angle distributions of the six first neighbors around Ge and Te, plotted in Fig. 4, are very sharply peaked around 93° and 86° , respectively, at all temperatures. The angles between the three closest neighbors are even more sharply peaked around these values.

The density of electronic states (DOS) averaged over 6 independent (separated by at least 3 ps) liquid configurations at each temperature shown of Fig. 5 confirms the

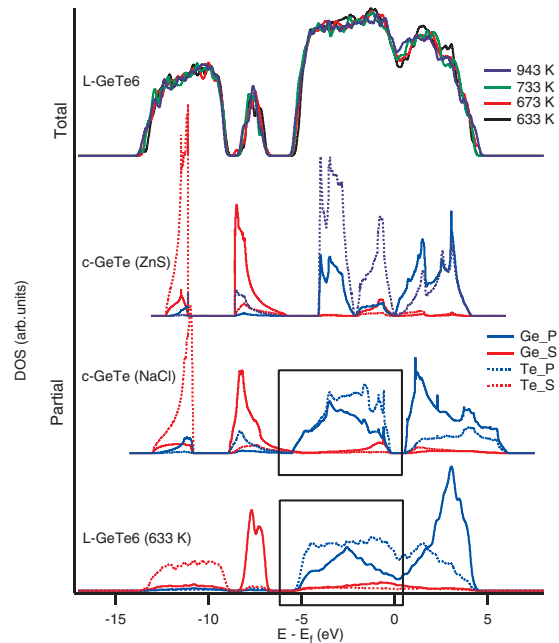


FIG. 5 (color online). Topmost panel: Total DOS averaged on liquid configurations at 633, 673, 733, and 943 K. The pseudogap at the Fermi level ($E - E_f = 0$) gradually fills. Lower panels: Partial densities of s (red) and p (blue) states projected on Ge (solid lines) or Te (dashed lines) atoms. The two rectangles focus on the similarities of Ge p states between the low temperature liquid and the NaCl structures.

absence of sp^3 hybridization and shows a gradual filling of the pseudogap at the Fermi level with increasing temperature. The partial DOS is further analyzed by comparing that of the lowest temperature liquid (lowest density) with those of two crystalline GeTe phases: the purely p -bonded relaxed NaCl structure and the purely sp^3 -bonded relaxed ZnS structure. Since Te-Te bonds are present in $\text{Ge}_{0.15}\text{Te}_{0.85}$ and not in the GeTe compound, the comparison between the Te states is irrelevant. On the contrary, it appears clearly that the valence Ge p states (located between E_f and E_f-5 eV) are similar for the liquid and the NaCl phase, while they are totally incompatible with the sp^3 crystalline phase. As expected, electrical dc conductivities calculated using the Kubo-Greenwood formalism [23] increase from $3000 \pm 500 \Omega^{-1} \text{cm}^{-1}$ at 633 K to $4000 \pm 500 \Omega^{-1} \text{cm}^{-1}$, in qualitative agreement with the experimental data [12].

Despite the major improvements in the simulations of the $\text{Ge}_{0.15}\text{Te}_{0.85}$ system presented here, small discrepancies with the experiment remain, similar to those already noticed by other authors in the case of pure liquid tellurium [24,25] at ambient pressure. The convergence of the electronic structure calculations has been carefully assessed. However, the small system size leads to large temperature (± 70 K) and pressure (± 4 kbar) fluctuations. As a consequence, the experimentally observed structural changes, which take place in a narrow temperature range in the real system, are averaged over a significant temperature range and attenuated in the computer simulation. The low temperature structure effectively corresponds to the $S(q)$ measured at higher temperature displaying a local environment that is too symmetric.

In summary, although limited in size and time scales, *ab initio* simulations are able to qualitatively reproduce the experimental data: The bond angle distribution and the electronic structure analysis clearly support a picture of a p -bonded liquid, with a nontrivial temperature and volume dependence of the distances within the first neighbor shell. In line with the measured increase of the electrical conductivity [12], the pseudogap at the Fermi level gradually fills upon heating.

To conclude, we have shown that the experimentally evidenced negative thermal expansion [4] is clearly not related to a tetrahedral bonding as in the well-known example of water. Another driving force must be identified. Our results suggest that the same symmetry breaking mechanism that stabilizes the α -GeTe low temperature phase (i.e., Peierls distortion in the case of a solid) acts at a local scale in the low temperature liquid. Since this distorted local environment corresponds to a larger atomic volume [7], the symmetry recovery induced by a temperature increase causes a shrinking of the atomic volume and results in the experimentally observed density anomaly. This novel mechanism, different from that observed in tetrahedrally bonded liquids and best characterized in this

$\text{Ge}_{0.15}\text{Te}_{0.85}$ system, might be responsible for similar changes observed in other p -bonded liquids.

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