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# Properties of molten Ge chalcogenides: an *ab initio* molecular dynamics study

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## Abstract

In this study, we perform first-principles molecular dynamics simulations of the eutectic alloy Ge<sub>15</sub>Te<sub>85</sub> at five different densities and temperatures. We obtain structures in agreement with the available diffraction data and obtain a new view of the molten Ge chalcogenides. We show that the anomalous volume contraction observed in the liquid 30 K above the eutectic temperature corresponds to a significant change of the Ge–Te partial structure factor. The detailed structural analysis shows that volume variations observed upon melting in Ge<sub>15</sub>Te<sub>85</sub>, as in liquid GeSe and GeTe, can be explained in terms of the competition between two types of local environment of the germanium atoms. A symmetrical coordination octahedron is entropically favoured at high temperature, while an asymmetrical octahedron resulting from the local manifestation of the Peierls distortion is electronically favoured at lower temperatures.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Besides having a good glass-forming ability, binary germanium chalcogenides exhibit a unique variety of behaviours in the liquid state. The melting of the GeSe and GeTe compounds takes place with a clear local order change (reduction of the atomic coordination number [3, 4] and atomic volume expansions of 11 and 7% respectively [2]), while the liquids remain semiconducting, with GeTe rapidly becoming metallic with increasing temperature [1]. These modifications are totally different from what is usually observed when melting other semiconductors (e.g. Si, Ge, III–V and the heavier II–VI compounds). An *ab initio* molecular dynamics method has recently succeeded in explaining this peculiar behaviour [5–8]. GeSe and GeTe remain semiconducting in the liquid phase by recovering locally the atomic arrangement of their low-temperature Peierls distorted crystalline  $\alpha$ -phases.

Away from the compound (50% Te) composition, the eutectic  $\text{Ge}_{15}\text{Te}_{85}$  alloy also exhibits another unique thermodynamic behaviour in the liquid phase. Experimental evidence for a strong structural change in a small temperature range around 680 K (about 30 K above the eutectic temperature) is provided by a set of experimental data that show a sharp maximum in the temperature evolution of the specific heat [9] accompanied by a negative thermal expansion coefficient [2].

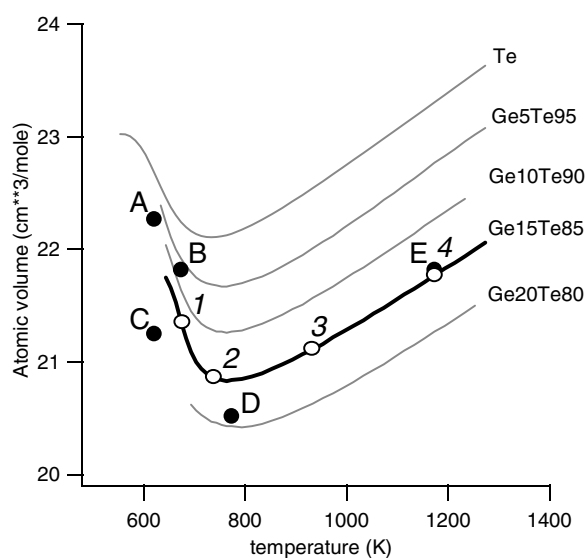
The recent experimental discovery of liquid–liquid (LL') transitions in elemental liquid semiconductors under pressure [10, 11] and in undercooled water [12] has emphasized the need for simulations which would unambiguously determine the driving mechanism for these transitions. The  $\text{Ge}_{15}\text{Te}_{85}$  compound is the ideal system for this purpose since a large set of experimental data exists [13, 14] although no clear picture emerges of the phenomena involved. It is interesting to notice that the phases in equilibrium with the eutectic liquid also undergo a structural change or a phase transition in the same temperature range. In undercooled liquid Te, a semiconductor-to-metal transition accompanied by a volume contraction and a decrease of the distance between the chains of twofold-coordinated atoms is observed [21]. The crystalline GeTe compound undergoes the  $\alpha$ – $\beta$  phase transition at 703 K, corresponding to the disappearance of the Peierls distortion in the solid  $\alpha$ -GeTe phase.

In this paper, we present results from first-principles molecular dynamics simulation of the eutectic  $\text{Ge}_{15}\text{Te}_{85}$  alloy at five different temperatures and densities which span across the experimental 'transition' domain. We obtain structures in agreement with the available diffraction data and provide a detailed structural analysis. By comparing these results with our previous studies of liquid GeSe and GeTe, we present evidence that the structural change in  $\text{Ge}_{15}\text{Te}_{85}$  is not due to modifications in the Te local environment, but to a gradual reduction of the 'Peierls-like' distortion of the local Ge coordination octahedron that is stabilized in the liquid just above the eutectic temperature. This distortion evolves strongly with temperature and density, its total disappearance coinciding with the onset of a normal fluid behaviour.

## 2. Methods

The *ab initio* calculations were performed using the ABINIT code [15]. The total energy of the system was calculated within the density functional theory framework [16]. The computations were done in the local density approximation (LDA) and in the generalized gradient approximation (GGA) [17], with Troullier–Martins pseudopotentials representing the core electrons [18]. A convergence study on our plane-wave-basis cut-off energy led to a maximal energy of 20 Ryd. At this energy, all GeTe bulk structural parameters ( $\alpha$ -phase) were reproduced within <1%. The ion movement equations were integrated using the velocity Verlet algorithm and a 200 au time step was used. All simulations were done at constant temperature using a Langevin thermostat. In this scheme, the equations of motion are modified by introducing a friction coefficient (here equal to 0.0006 friction units) and this dissipated energy is randomly redistributed into the system [19]. Using this thermostat, the relative temperature fluctuations of the system remained smaller than 15%.

To mimic the  $\text{Ge}_{15}\text{Te}_{85}$  system with a reasonable number of atoms, we studied a system of 8 Ge and 48 Te atoms, for an actual stoichiometry of  $\text{Ge}_{14.2}\text{Te}_{87.8}$ . We started from a completely random structure and performed a high-temperature thermalization at 3000 K for 3 ps to avoid retaining any memory of the initial structure. We then progressively cooled the system and kept monitoring the diffusivity of the ions. After a linear cooling of 5 ps, the liquid was equilibrated at the final temperature of 673 K for 15 ps. A 3 ps average over the structural data indicates clearly that the LDA approximation is insufficient to accurately reproduce the liquid structure factor obtained by means of neutron diffraction. This is not totally unexpected, since the LDA



**Figure 1.** Atomic volume versus temperature [2]. The dots A–D and the circles 1–4 indicate the conditions of these GGA simulations and the neutron diffraction experiments [20], respectively.

approximation gave excellent agreement with the experiment for both the stoichiometric GeTe and GeSe systems [6, 8], but notably failed in producing correct liquid Te structures, and Te is the major component of our system. After a new 5 ps equilibration process using a GGA approximation, we started to average the structural data. The four other simulations started from this point, with a rescaled simulation box, and at least a 7 ps thermalization/equilibration. The respective temperatures and densities of the simulations are indicated in figure 1.

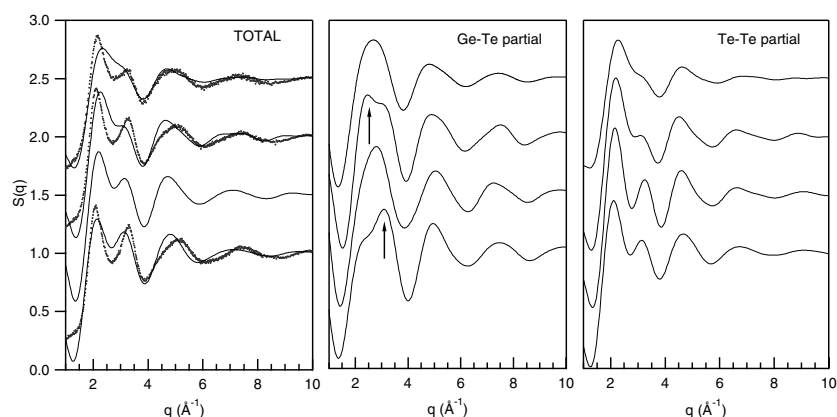
Besides the stability of the potential energy, the stability of the diffusion coefficient has been used as a criterion to determine that equilibrium has been reached. It is worth noticing that in such a glass-forming material, equilibration could take up to 10 ps, even when starting from a closely related configuration (i.e. same temperature and slightly different volume).

### 3. Results

The comparison between simulations (B–E) and the experimental (1–3) structure factors is given in figure 2 (left). Although the amplitudes of the peaks from the simulations are smaller than the experimental ones, the same evolution is observed with temperature and density. The differences between simulation and experiment are partly due to the temperature fluctuations of the small simulation box. The key feature in these spectra is the double-peak structure observed at lower temperature between 2 and 3 Å<sup>-1</sup> that evolves correctly into a single peak plus a shoulder on the right at high temperature. As seen on figure 2, central and right panels, this evolution is mostly due to a complete change in the morphology of the Ge–Te partial, which has a shoulder on the left at low temperature, and on the right at high temperature.

To gain a better understanding of the structural changes in Ge<sub>15</sub>Te<sub>85</sub>, we analyse in detail (see figure 3) the first coordination shells by calculating the contributions of the first-, second-, . . . , sixth-neighbour distances around a given atom. They correspond to the contributions of the different neighbours to  $r_{ij}^2 g_{ij}(r_{ij})$  and are normalized to unity.

Let us first consider the distributions of neighbours around Te atoms: the evolution is very continuous from simulation A to E. The further the neighbour, the broader the distribution and



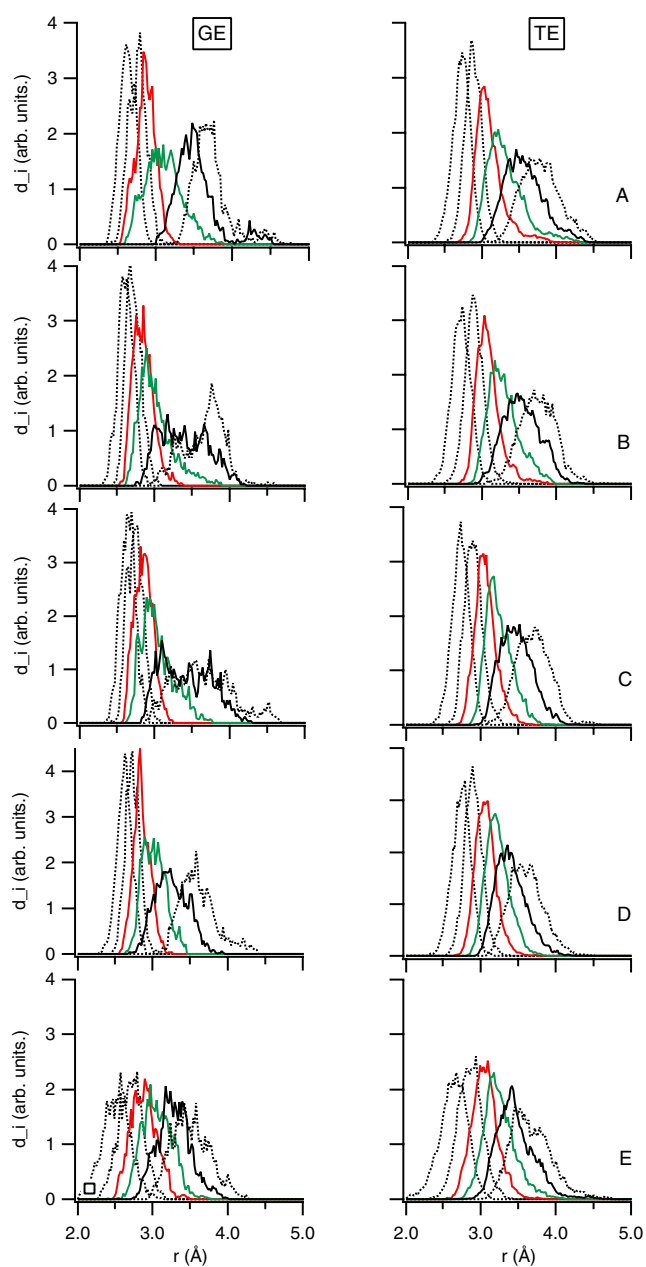
**Figure 2.** The total structure factor (left panel) for experiments 1–3 (symbols) and simulations B–E (curves), from bottom to top. Central and right panel: partial structure factors for simulations B–E, bottom to top.

there is no noticeable asymmetry. This is not the case for the distributions of Te atoms around Ge atoms. The distributions of the fourth, and even more so of the fifth and sixth neighbours change significantly, both in shape and position.

The average positions of the neighbours around Ge or Te atoms plotted in figure 4 show that the structural change in liquid  $\text{Ge}_{15}\text{Te}_{85}$  is due to a change in the local atomic ordering around Ge atoms. The bond angle distribution (not shown here) is very distinctly peaked around  $90^\circ$  for Te atoms and a little more scattered around Ge atoms: assuming  $90^\circ$  angles in all cases, we can sketch the evolution of the liquid structure by plotting the evolution of the distortion of the coordination octahedron around each atom (insets in figure 4). Going from simulation A to E, the Te coordination octahedron remains undistorted (the neighbour distribution around Te atoms in simulation E corresponds to a perfect octahedron of atoms vibrating around their equilibrium positions). Around Ge, the coordination is  $3 + 1 + 2$  in simulation A (low density, low temperature) and changes to  $4 + 1 + 1$ ,  $4 + 2$ ,  $5 + 1$  and finally 6 as the density is decreased and the temperature increased. This evolution is an almost exact counterpart of the  $\alpha$ - $\beta$  transition that occurs with increasing temperature in solid GeTe [8]. In that case, the coordination octahedron is distorted  $3 + 3'$  in the  $\alpha$ -phase due to the Peierls instability. As the temperature is increased, the undistorted coordination octahedron of the NaCl cubic phase becomes stable.

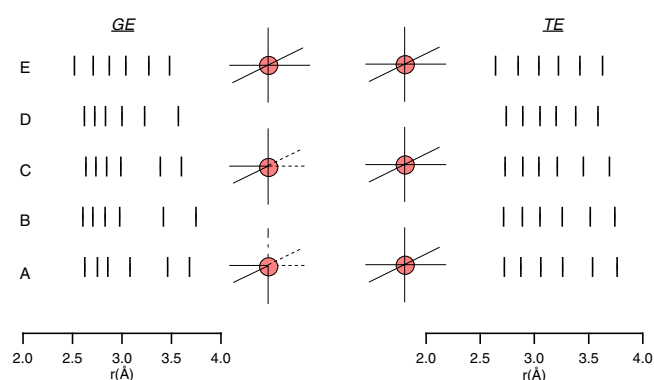
#### 4. Conclusions

In this paper, we have used first-principles molecular dynamics simulation to elucidate the microscopic structure of liquid  $\text{Ge}_{15}\text{Te}_{85}$ . Five simulations performed at different temperatures and densities have shown that the important anomalous change in thermodynamic quantities evidenced in the liquid is associated with a transition in the local environment of Ge atoms. Upon melting, the local Ge environment is analogous to the Peierls distortion observed in crystalline GeTe and GeSe at the current temperature and pressure. For those two compounds, the Peierls distortion vanishes at the  $\alpha$ - $\beta$  solid phase transition. In the eutectic liquid  $\text{Ge}_{15}\text{Te}_{85}$ , the structure is governed by the relative stability of two types of local order around Ge atoms: one is a distorted  $3 + 3$  phase (in fact, the simulation yields a  $3 + 1 + 2$  structure) stable just above  $T_m$ ; the other is a symmetric sixfold-coordinated Ge phase. As the temperature is increased,



**Figure 3.** Detailed contributions of the six first neighbours around a Ge atom to the partial  $g_{\text{GeTe}}(r)$  (left) and around a Te atom to  $g_{\text{TeTe}}(r)$  (right). Simulations A–E are represented from top to bottom.

the entropy causes the system to gradually transit from one type of local order to the other. This symmetry breaking followed by symmetry recovery at higher temperature is obviously related to the same Peierls distortion mechanism as drives the structures of stoichiometric GeTe and GeSe in both the solid and liquid states. The details of our calculations have also



**Figure 4.** Average neighbour positions obtained from the neighbour distributions of figure 3. Ge neighbours are plotted on the left, Te neighbours on the right.

emphasized that density is a key parameter for the liquid structure. This is not surprising since the Peierls distortion amplitude is particularly sensitive to volume, as observed in GeSe and GeTe upon melting. Further work is needed to evidence that the strong change in local order in liquid  $\text{Ge}_{15}\text{Te}_{85}$  is accompanied by a semiconductor-to-metal transition as in the case of liquid GeTe as well as to identify the role of charge transfers inside the liquid. Finally, we believe that this competition between two types of local order, one energetically, the other entropically favoured, makes  $\text{Ge}_{15}\text{Te}_{85}$  a model system in which to understand many of the recently evidenced LL' transitions in elemental liquid semiconductors as well as in undercooled water.

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JYR wishes to thank Drs Xavier Gonze and Giulia Galli and acknowledges support from the FNRS under the 'Charge de recherches' contract. This work was performed under the auspices of the US DOE at the university of California/LLNL under contract No W-7405-Eng-48.

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