Ab-initio study of amorphous germanium

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keywords: materials science, amorphous materials, molecular modeling, ab-initio, molecular dynamics, amorphous Ge

Abstract

We employ ab-initio molecular dynamics simulations to study the atomic structure of amorphous germanium. The preparation of an amorphous Ge numerical sample is performed by cooling down from the liquid phase. Calculated structural and thermal properties of the amorphous phase result in good agreement with experimental data. This is a necessary step for starting a complete characterization of the pressure effects on the amorphous germanium.

Introduction

Amorphous germanium (*a*-Ge) has been largely studied in the last decades using a variety of experimental and theoretical methods, being a material of outmost importance in basic science and applications in everyday life. Moreover the investigation of the structure of the condensed phases of germanium is of importance for fundamental science since it exhibits polymorfism in the solid state and pronounced changes in density and bonding upon melting and application of external pressure.

Germanium in its stable crystalline phase at ambient pressure, has a diamond structure (GeI) in which each atom is surrounded by four covalently bonded first neighbors in a tetrahedral formation. This phase of Ge has a very low density with respect to a close-packed structure and is semiconducting with an indirect gap of about 0.7 eV. Upon application of pressure, the tetrahedrally bonded network is broken and both the number of neighbors and the density increase. Around 11 GPa, a phase transition to the metallic β-Sn structure (GeII) occurs and even at higher pressures a hexagonal phase and a close-packed phase are found. Upon decompression, the crystalline stable structure is not always recovered, rather metastable crystalline phases are observed. The most common one is called ST12 (GeIII). It is based on tetrahedral structure with 12 atoms per unit cell arranged to form fivefold and sevenfold rings. Ge has higher density (about 10%) in this phase than in the underlying stable one Ref. [1]. It is based on tetrahedral structure with 12 atoms per unit cell arranged to form five-fold and seven-fold rings. As reported in Ref. [2], in case of rapid decompression, a cubic structure characterized by eight atoms per unit cell and called BC8 (or GeIV) is likely to occur [2,3]. This structure is not stable at room temperature but it transforms into the lonsdaleite structure (hexagonal with four atoms per unit cell) within a few hours.

At standard pressure the melting temperature of crystalline Ge is T_m= 1210 K. At the melting transition the tetrahedral network is disrupted and the average coordination number increases from 4 to about 7, which is still low compared to other liquid metals which typically have coordination numbers between 9 and 12. Liquid Ge is metallic and amorphous Ge is semi-conducting. Amorphous Ge is characterized by a continuous random network of distorted defective tetrahedra. Numerous experimental investigations of the density and bonding changes in different phases of germanium, using both x-ray [4] and neutron diffraction [5] techniques, are known in literature. Bond lengths do not differ more than 1% from the crystalline phase and bond angles show a modest spread of the order of 10 degrees about the ideal value of the crystalline counterpart.

Moreover *a*-Ge shows a complex behavior when an external pressure is applied, and scattered results are reported in literature. In particular, evidence for a sharp drop in resistivity and crystallization of thin *a*-Ge films was found at about 6 GPa [3,6].

The x-ray absorption spectroscopy (XAS) technique was used to study the evolution of the local structure at high pressures. Freund et al. [7] showed that *a*-Ge remains amorphous up to 8.9 GPa whereas more recent XAS measurements showed that *a*-Ge undergoes a phase transition at 8 Gpa, though remaining amorphous [8]. The glass transitions in Ge under pressure was also studied in recent works both experimentally [9,10] and through molecular dynamic simulations [11]. The combination of Raman and XAS spectroscopy measurements allowed to confirm that 8 GPa mark the onset of a polyamorphic transition in more homogeneous samples [12]. Moreover, Ref. [12] demonstrates that the actual transitions observed in a given sample depend on the initial morphology of the sample itself.

Polymorphism of amorphous Ge is reported to occur between the low-density amorphous (LDA) semiconductor and the high-density metallic amorphous (HDA) states. This intriguing phenomenon is linked to a proposed first-order density, entropy-driven phase transition in the supercooled liquid state. The LDA-HDA transition has been studied in details for thin film samples by x-ray absorption, extended x-ray-absorption fine structure (EXAFS), and Raman scattering methods [8,12,13]. Nevertheless, a detailed and unambiguous understanding of the complex phenomena taking place in *a*-Ge under pressure has been only recently published [13].

In the present paper, we report the study of the structural properties of *a*-Ge via ab-initio molecular dynamics in the framework of density functional theory. The atomic structure is characterized in terms of pair correlation functions, nearest neighbor analysis and neutron structure factor. The very good agreement with experimental results confirms that this amorphous system is a reliable starting point to study the pressure effects.

Computational details

Reliable amorphous structures of Ge are generated in the framework of first-principles molecular dynamics; the software employed is CPMD (Car-Parrinello Molecular Dynamics) [14,15]. The self consistent evolution of the electronic structure during the motion is described within density functional theory. A generalized gradient approximation (BLYP-GGA) is adopted for the exchange and correlation part of the total energy [16,17] and norm conserving pseudopotentials are used for the core-valence interactions. A Γ-point sampling for the supercell's Brillouin-zone integration, a reasonable choice for a 125-atom model, has been adopted. The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 60 Ry and an integration time step of 3 a.u. (0.072 fs) was used.

During the equilibration of the liquid and solid structures a Nosé thermostat was used to control the ion temperature [18,19,20]. The characteristic frequency for the thermostat was 1000 cm^{-1}, which lies close to the peak at 37 THz in the diamond phonon density of states. A second Nosé thermostat was used to control the fictitious electronic kinetic energy [21]. This thermostat prevented the electronic wave functions from drifting away from the instantaneous ground state (the Born-Oppenheimer surface), by removing excess fictitious kinetic energy. This drift is particularly severe for metals. In our simulation the liquid Ge sample possesses no band gap and hence the energy transfer rate is high. The characteristic frequency for the thermostat and the target kinetic energy was chosen according to the prescription in Ref. [21]. The Nosé thermostat on the electrons was used throughout the simulation and proved to be an effective way of keeping the electrons on the Born-Oppenheimer surface. During the equilibration of the liquid, the cooling of the liquid, and the temporal averaging of the solid, the deviation from the Born-Oppenheimer surface was never more than 0.01 eV/ion, and was often much less.

This set of parameters yields accurate and converged properties for the dimer Ge_2 as well as for Ge crystalline lattices, both diamond and β-Sn. Further legitimacy of our computational approach comes from the characterization of the amorphous structure described in the next section.

The amorphous structure has been obtained for a system consisting of N= 125 atoms in periodically repeated cubic cells of size L= 14.14 Å. The density is equal to the experimental value for a-Ge at T= 300 K: ϱ= 5.3 gr/cm^3 [22,23]. To ensure that our results are independent of the initial atomic configurations, they are chosen to be drastically different from the crystalline counterpart. Since it is expected that the amorphous structures have a high percentage of four-fold coordinated Ge atoms, the starting configuration has been generated by randomly placing the atoms in the simulation cell. This procedure designs a starting configuration with many defects and many atoms with coordination different from four. We further disordered the configuration by constant temperature and constant pressure MD equilibration at high temperature (T= 4000 K).

Results and discussion

During the high temperature simulations, atoms covered a distance as long as about 2 nm ensuring the final configuration retains no memory of the initial geometry. Then we gradually lowered it to T= 1278 K in 10 ps and performed an additional equilibration for additional 5 ps. The liquid configuration at T= 1278 K, just above the melting temperature, has been used as starting point for the quenching procedure. The amorphous Ge is attained by cooling to 300 K the liquid sample over 8 ps. Then this system was equilibrated for additional 8 ps to gain temporal averages. Two complementary simulations were performed to check the effect of quench-rate on the atomic structure. One used a slower cooling rate whereas in the other one the liquid was cooled instantly to 300 K. In all systems the main features of the amorphous Ge were all reproduced with minimal differences among them. This procedure is an essential check to produce a reliable amorphous atomic structure.

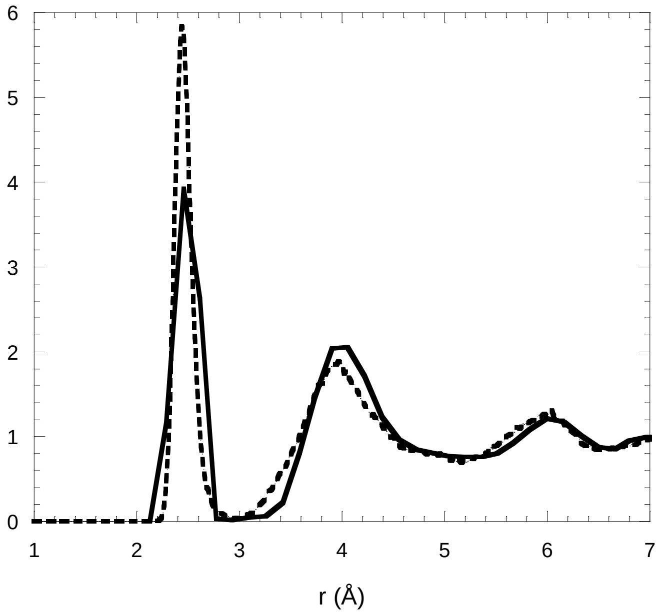

Figure 1*: Comparison between experimental (continuous line) and ab-initio prediction of the radial distribution function of amorphous germanium.*

To analyze the short-range order of the obtained amorphous phase we have calculated the total radial distribution function, reported in **Fig. 1**. The comparison with the experimental one reported in [23] confirms the reliability of our numerical model. It is interesting to note that our model well reproduces the position of the first peak at 2.44 Å even if more pronounced. The second peak is located at 3.97 in good agreement with experiments.

The calculation of the coordination, as the integral over the first peak of the radial function, confirms the picture of an amorphous system composed essentially by Ge atoms fourfold coordinated and a few threefold and fivefold coordinated. On the average each atom has 4.06 nearest neighbors: 90.5% of the atoms is four-fold coordinated, 1.8% is three-fold coordinated and 7.7% are five-fold coordinated.

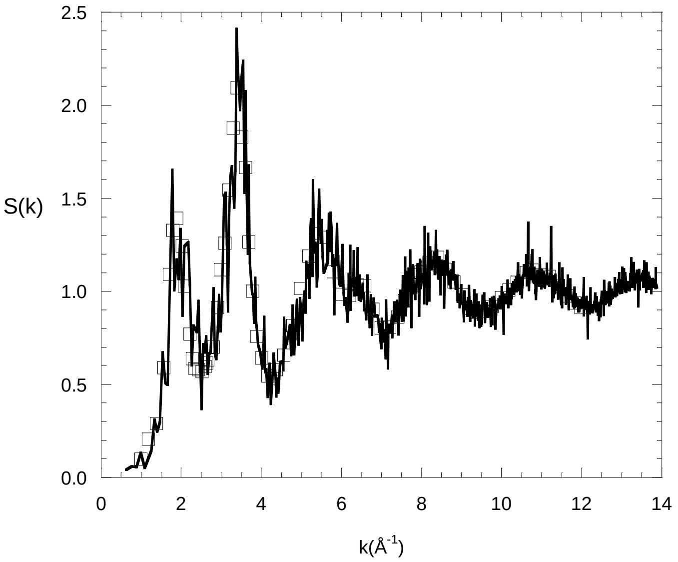

Figure 2: *Comparison between experimental (squares) and ab-initio prediction of the structure function S(k) of the amorphous germanium*

To verify the reliability of our approach also on longer length scales, we have computed the structure factor function. The calculated structure factor is shown in **Fig. 2** together with the neutron structure factor experimentally measured in Ref. [23]. The agreement is very good over the entire k range, the position of maxima and minima being accurately reproduced.

Conclusion

In this report our first goal has been to achieve a precise characterization of the atomic structure of amorphous Ge systems through a simulated sample. This amorphous sample, that we have demonstrated to be a reliable representation of a real amorphous phase, represents a good starting point for the study of pressure effects.

We have shown that our theoretical approach is able to accurately model all the main features of an amorphous system both in the short and long range scale. Moreover we are confident that this procedure can be successfully applied to produce and characterize the amorphous phase under pressure. This approach will allow to accurately study the relations between atomic scale intrinsic defects and the macroscopic structural and electronic properties.

Acknowledgments. The computing resources and the related technical support used for this work have been provided by CRESCO-ENEAGRID High Performance Computing infrastructure and its staff; see www.cresco.enea.it for information. CRESCO-ENEAGRID High Performance Computing infrastructure is funded by ENEA, the “Italian National Agency for New Technologies, Energy and Sustainable Economic Development” and by national and European research programs.

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