

Local structural rearrangement in deeply undercooled liquid Ge probed by subsecond time-resolved x-ray-absorption spectroscopy

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(Received 1 March 2000)

The local structure in deeply undercooled Ge has been probed by time-resolved x-ray-absorption spectroscopy (XAS). By using a technique that allows us to collect full x-ray-absorption spectra in less than a second, snapshots of the electronic and local structure in the metallic phase of Ge were taken at temperatures much lower than had been possible with previous static XAS investigations. Upon a rapid freezing of the melt, and prior to the occurrence of the solidification transition, we observe a sharpening of the pair correlation function $g(r)$, and a slight shift of $g(r)$ towards smaller distances. We interpret this phenomenon in terms of increased stability of the covalent bonds that are continuously formed and destroyed in the liquid.

Many liquids can be cooled far below their equilibrium melting temperature T_m without solidification, giving origin to a metastable undercooled liquid phase. In the absence of any external driving forces, which trigger the so-called heterogeneous nucleation process, the equilibrium crystalline phase is reached through density fluctuations, which lead to the spontaneous formation of a crystalline nucleus (homogeneous nucleation).^{1,2}

The structure of this metastable phase, and the local rearrangements that lead to the nucleation mechanism, represent a fundamental topic in the understanding of microscopic atomic interactions. Computer simulations on simple Lennard-Jones liquids have evidenced the appearance, to some extent, of icosahedral ordering in deeply undercooled liquids.³ Very recently, an x-ray-absorption spectroscopy (XAS) experiment on undercooled liquid Pd (Ref. 4) attributed the structural changes occurring in the liquid phase from the equilibrium to the undercooled state to the increasing contribution of ordered structural units. Still, it is poorly understood if this metastable liquid phase can be identified as a frozen version of the equilibrium liquid above T_m , or if atomic configurations appear at very deep undercooling.

The equilibrium phase of liquid Ge (*l*-Ge) has several intriguing but poorly understood properties. Upon melting, Ge undergoes a semiconductor-to-metal transition, as evidenced by a jump in the conductivity by a factor of 11.⁵ At the same time, its density increases by $\sim 5\%$ and its structure goes from an open diamondlike lattice with coordination number equal to 4 to a more compact liquid structure characterized by a coordination number between 6 and 7. This is fairly unusual as most liquid metals are more closely packed with a coordination number ~ 12 . A very similar phenomenology is observed for Si.^{6,7}

The past accepted structural models for describing the short-range order in liquid Si (*l*-Si) and *l*-Ge either assume the presence of two kinds of atoms (fourfold coordinated semiconducting and highly coordinated metallic) or assume an isomorphism with the β -Sn or simple cubic structures (both sixfold coordinated and metallic). However, recent *ab*

initio molecular-dynamics (MD) simulations on both *l*-Si (Ref. 8) and *l*-Ge (Ref. 9) indicate that these models are unrealistic and suggest instead the presence of a broad, homogeneous distribution of local bonding configurations. Valence-electronic-charge densities have been modeled demonstrating the persistence of some covalent bonds in the melt. Unlike the case of the crystal, in the liquid the covalent bonds are continuously broken (and reformed) in response to atomic motion. As the majority of bonds are broken on average, this leads to fast diffusion and to metallic behavior of the melt.

Upon freezing from the melt, *l*-Ge can be cooled to a high degree. XAS on homogeneously dispersed micrometric droplets supported in a pellet of pressed inert matrix powder showed that it was possible to follow the structure of undercooled Ge down to $\Delta T_u = T_m - T \sim 260$ K.¹⁰ The large undercooling was achieved because of the low probability of nucleation events in μm size droplets.¹ Using an advanced data-analysis procedure,¹¹ the authors accurately determined the short-range side of the radial distribution function $g(r)$. They observed a regular trend in the sharpening of the first peak of the $g(r)$ upon decreasing the temperature of the undercooled liquid phase. These results match well with *ab initio* MD simulations⁹ that show that for small undercooling ΔT_u the first and second peaks in the $g(r)$ grow in amplitude and become more symmetric. The simulations also show that the average coordination number decreases down to below 5 and that tetrahedral angles become dominant in the bond-angle distributions.

At large ΔT_u , both thermodynamical calculations¹² and MD simulations⁹ suggest that structural relaxation should become too slow to allow local equilibration in experimental times, the consequence being the formation of an amorphous solid or a glass. But *l*-Ge cannot be quenched into a glassy state, even with the fastest cooling rates obtainable under laboratory conditions. As the temperature decreases, a reduced atomic mobility is achieved, covalent bonds that have once been formed survive, and the metal-semiconductor transition occurs rather quickly.

Various experimental techniques have been developed to study undercooled liquid properties. Drop-tube experiments have opened the possibility to study refractory metals.¹³ Electromagnetic levitation has been used to study thermo-physical properties of metallic liquid elements and alloys.¹⁴ A gas nozzle levitation apparatus has been developed to perform x-ray diffraction experiments on both metallic and insulating materials.¹⁵

In the past few years, XAS was shown to be a powerful tool to probe the local atomic arrangement in undercooled liquids.^{2,4,10} These investigations clearly pose severe experimental difficulties, due to the short lifetime of the metastable phase. Since XAS is a technique sensitive to both electronic and atomic degrees of freedom, the ability to collect complete x-ray absorption spectra on a subsecond time scale opens the possibility to record snapshots of the electronic and local structure in short-lived metastable phases of a number of systems. This has been made possible by the availability of high brilliance third-generation synchrotron-radiation sources, and by new developments for time-resolved x-ray absorption spectroscopy.^{16,17}

In this paper we present an investigation of the local structure of undercooled liquid Ge, by means of time-resolved XAS. We recorded a series of hundreds of x-ray absorption spectra during a rapid cooling of the melt, thus being able to follow the evolution of the electronic and local structure of the undercooled phase down to unprecedented low temperatures.

The Ge *K*-edge XAS measurements were performed at the European Synchrotron Radiation Facility, on beamline ID24,¹⁸ equipped with an undulator source and energy dispersive optics. A Si (111) curved crystal polychromator was used, yielding a total energy band pass of ~ 550 eV and a horizontal spot size of ~ 50 μm . Following a well-established protocol to produce samples suitable for XAS measurements,^{10,19} our samples were made of Ge micrometric powder pelleted together with BN powder in a 1:10 weight ratio. High-purity Ge lumps (up to 99.9995%) were ball-milled in an agatha mortar for 1 h. The resulting powder was then suspended in pure ethanol for several hours, and only the lighter particles still floating at the very top of the suspension tube were decanted by filtration of the ethanol. The particle size dispersion has been estimated to be similar to the one obtained with an identical procedure,²⁰ centered around a mean value of the order of 1 μm . From previous studies with complementary techniques BN has proved to be chemically inert with Ge even at high temperature, and to act very poorly as a catalytic trigger for the heterogeneous nucleation of undercooled Ge droplets.²⁰ To overcome the problems related to the strong small-angle scattering from the powder, which strongly affects the energy resolution when using position-sensitive detectors for parallel energy detection, spectra were recorded using sequential acquisition in the Turbo-XAS mode.¹⁷ A scanning slit of about 50 μm was placed downstream the polychromator, yielding a monochromatic photon flux on the sample of $\sim 10^9$ phot s^{-1} .

As in Ref. 10, our samples were heated to above the melting temperature in high vacuum using an electrically heated graphite crucible^{19,20} and subsequently cooled down. The temperature of the sample was monitored using a Chromel-Alumel thermocouple. Tracking the position of the edge,

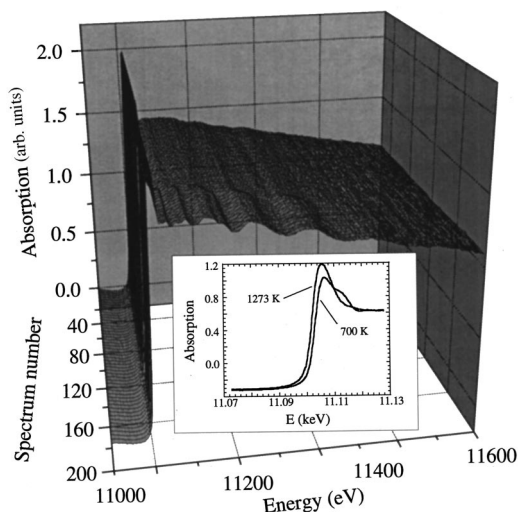


FIG. 1. Series of 200 XAS spectra recorded during a cooling cycle. The spectra were collected at intervals of 1.2 s and the total acquisition time/spectrum was 520 ms. A continuous trend from very smooth spectra characteristic of the liquid phase (the very first spectra at high temperature) to the more structured spectra typical of a crystalline state is clearly visible. Inset: the first (liquid Ge) and last (crystalline Ge) of a series of 500 spectra collected over the near-edge region.

which is physically connected with the density of states at Fermi level of the system, upon ramping the temperature it is possible to follow the temperature evolution of the electronic structure, e.g., the appearance of the gap at the onset of the metal-semiconductor transition. At the same time, we are able to collect the complete XAS spectrum, which provides us with the information about the local atomic arrangement. Therefore, we are able to follow the crystallization process both from the electronic and the structural point of view simultaneously.

Figure 1 shows a series of 200 XAS spectra recorded during a cooling cycle. The spectra were collected at 1.2 s intervals and the total acquisition time/spectrum was 520 ms. Another series of 500 scans, concerning a 60-eV energy range around the Ge *K*-edge absorption jump, were recorded at the same cooling rate, in order to have a finer mesh in the edge temperature evolution. These scans were again collected at intervals of 1.2 s and the total acquisition time/scan was 120 ms. The first (liquid Ge) and the last (crystalline Ge) spectra of this series are shown in the inset of Fig. 1. An energy shift of the absorption edge of about $\Delta E = 1.2 \pm 0.1$ eV is present between the spectra of the liquid and the solid sample. Moreover, the near-edge features are considerably different: in the solid phase the intensity of the absorption peak decreases by about 10% and its shape changes, as a bump appears on the high-energy side of the peak. All the observed modifications are found to be reversible upon heating the sample.

The upper panel of Fig. 2 shows the measured ΔE values as a function of temperature during a heating/cooling cycle at a constant rate $Q = 1.7$ K s^{-1} . During the heating ramp, the abrupt step in ΔE at $T = T_1$ is associated to the melting of the sample ($T_m = 1210$ K). The very rapid variation of ΔE with temperature indicates that melting occurs almost simultaneously for all the Ge micrometric grains. On the other hand,

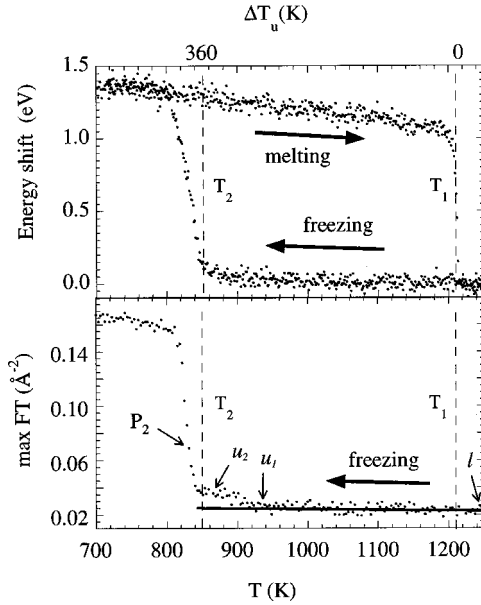


FIG. 2. Upper panel: Measured edge shift values (ΔE) as a function of temperature during a heating/cooling cycle. Lower panel: Maximum amplitude of the first peak in the Fourier transform $P_1(S)$ as a function of temperature. The arrows indicate the temperatures at which the prototypical spectra l , u_1 , and u_2 were recorded (see text for further details), and the temperature corresponding to the onset of peak P_2 (see Fig. 3).

upon freezing, a less abrupt step in ΔE is observed reflecting the statistical nature of the nucleation process on the large ensemble of droplets.² The energy shift starts around a temperature value $T_2 \sim 850$ K. As can be seen from Fig. 2 (upper panel), the temperature range during which the metastable undercooled liquid is probed is $\Delta T_u = T_1 - T_2 = 360 \pm 5$ K, which is 100 K larger than the maximum ΔT_u at which it was possible to collect a standard XAS spectrum.

Notwithstanding the overall similarity of the spectra shown in Fig. 1, a continuous trend from very smooth spectra characteristic of the liquid phase (the very first spectra at high temperature) to the more structured spectra typical of a crystalline state is clearly visible. A qualitative picture of the structural rearrangement, as a function of the temperature, can be obtained by a Fourier transform (FT) of the extracted x-ray absorption fine structure (XAFS) oscillations. Even though the local environment in the liquid phase can be correctly described only in terms of a radial distribution function, the evolution of the local structure upon crystallization is also apparent by comparing directly the FT of the XAFS oscillations. In solid Ge (*c*-Ge), the first two peaks of the FT correspond, respectively, to contributions from the 4 first-shell neighbors at $R_1 = 2.45$ Å and from the 12 second-shell neighbors at $R_2 = 4.00$ Å. In Fig. 3, we report the FT of the spectra collected during the cooling ramp. The FT relative to the liquid in its equilibrium state presents a weak structure S at a position similar to that of the first peak in its crystalline counterpart. As the temperature decreases below the melting point T_m the main features in the FT of the liquid remain apparently unchanged, until the onset of nucleation where two important modifications appear: a) the amplitude of S increases very rapidly and forms a well-defined peak P_1 and b) another peak P_2 corresponding to the second-neighbor

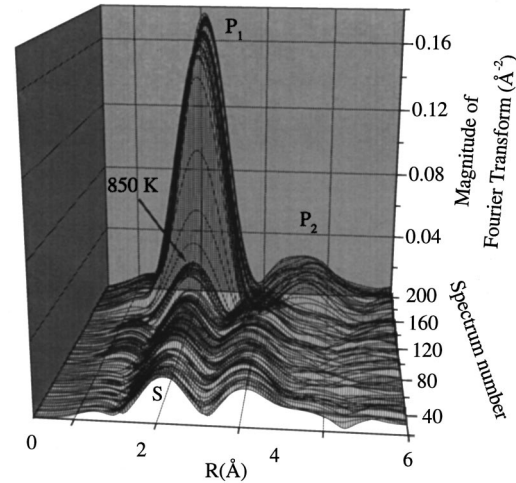


FIG. 3. Fourier transforms of the XAS spectra collected during the cooling ramp. The k -weighted spectra were Fourier transformed using a Gaussian window in the k range (3.0 – 11.2 Å⁻¹). The labels “ P_1 ” and “ P_2 ” indicate the positions of the peaks relative to the first and second coordination shell in crystalline Ge. Nucleation starts at temperatures close to $T = 850$ K. An increase of the intensity of the structure labeled “ S ” is evident prior to nucleation.

coordination shell rises. This latter reflects the detection by XAS of tetrahedral configurations, i.e., the formation of crystalline grains.

In order to compare the temperature dependence of the structure to that of the electronic state, the lower panel of Fig. 2 shows the variation of the amplitude of $P_1(S)$ as a function of T : the amplitude is very weak for $T > 850$ K and increases abruptly close to $T \sim 850$ K. A comparison with the upper panel shows that the crystallization and the metal-semiconductor transition occur simultaneously. This is not surprising.¹² However, a more careful comparison of the two panels sheds light on the details of the evolution of the electronic and structural transitions. As the temperature is lowered, the amplitude of P_1 increases linearly. Around $T \sim 900$ K a deviation from this linear behavior appears. At these temperatures, the sample is still in the metallic phase, as the ΔE behavior demonstrates. Moreover, nucleation has not been initiated yet as no substantial increase of tetrahedral configurations has occurred (the onset of formation of peak P_2 occurs at lower temperatures), and the sample has to be in the liquid state. We exclude that the observed deviation in the behavior of the local structure is due to a preliminary crystallization of a minority of particles, as this effect, however small it may be, should be accompanied by one of equivalent magnitude on the electronic structure. This is not the case, as shown in the upper panel of Fig. 2.

The observation of this small, but significant, trend in the local structure, may suggest the occurrence, at such low temperatures, of a slightly different average atomic arrangement. Liquid germanium has in fact recently been pointed out as a possible candidate for the observation of liquid polymorphism, like other liquids having an open molecular coordination environment at low pressure (Si, SiO₂, GeO₂, and H₂O).²¹ Such liquid-liquid phase transitions in pure isotropic substances are shown to most likely occur as metastable transitions in the undercooled liquid state. For this reason, their observation may be either obscured by crystal nucleation or

by the dramatic increase in structural relaxation time with the formation of a glass. The occurrence of a possible liquid polymorphism in deeply undercooled liquid Ge, anyhow, cannot be assessed in the current work, as it is foreseen to occur at higher pressure, but the promising results obtained with the present experimental technique should stimulate further studies.

To determine the structural evolution of undercooled *l*-Ge we chose to analyze four different prototypical spectra, respectively recorded in the equilibrium liquid phase (*l*) at $T = 1244$ K, in the undercooled phase (u_1) at $T = 935$ K and (u_2) at $T = 859$ K, and in the crystalline phase (*c*) at $T = 671$ K. The data analysis has been performed using an already published procedure^{4,10,11} that has proven to be extremely accurate in such systems. Care for the double-electron excitations has been taken, and the S_0^2 parameter has been kept equally fixed to 0.9 for all the spectra. The amplitude of the oscillations increases from *l* to u_2 , and a slight shift in the frequency appears. The corresponding reconstructed pair correlation functions $g(r)$ are plotted in Fig. 4. For comparison, also the model $g(r)$ from a neutron diffraction experiment (\diamond symbols)²² and the one for the solid *c* (dashed lines) are reported. Due to the noise level it is not possible to distinguish between the equilibrium liquid and the undercooled liquid u_1 . This is also apparent from Fig. 2 (lower panel), which clearly shows that the peak to peak dispersion in the data does not allow us to distinguish the amplitudes corresponding to points u_1 and *l*. Instead, the profile of the first peak of the $g(r)$ provided by the XAFS signal u_2 is evident: it is sharper and slightly shifted towards smaller distances, consistent with the qualitative observation of the FT trend (the amplitude at point u_2 is higher than at points u_1 and *l*).

The onset of a covalent network is definitively marked by the angular distribution, which becomes very sharp around a mean value of 109.47° . The present quality of our data does not allow us to shed any light on this issue. Nevertheless, our observations on the very first peak of the $g(r)$ are compatible with a slightly longer lifetime acquired by tetrahedral configurations due to the lower atomic mobility achieved upon cooling of the melt. This picture is consistent with a slightly

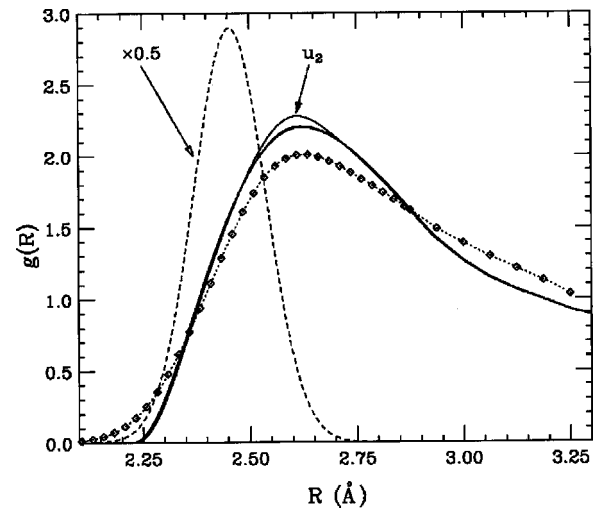


FIG. 4. Reconstructed pair correlation functions $g(r)$ relative to the crystalline phase (*c*) at $T = 671$ K (dashed lines—multiplied by 0.5 for better comparison), the neutron diffraction data (Ref. 22) (\diamond), the equilibrium liquid phase (*l*) at $T = 1244$ K, and the undercooled phase (u_2) at $T = 859$ K. The latter is sharper and slightly shifted towards smaller distances.

more open liquid structure and a decreased coordination number, as already supposed for undercooled *l*-Si.^{6,7}

In conclusion, we probed the structure of deeply undercooled liquid Ge, up to the onset of the metal-semiconductor (crystallization) transition. We find that the used experimental technique is an invaluable tool to shed light on the interplay of electronic and structural degrees of freedom.

Our observations are compatible with the possibility that at high ΔT_u tetrahedral configurations in undercooled liquid Ge are more probable, the melt still being in a metallic phase. The fact that this behavior is not seen for low ΔT_u suggests that it is intimately related to the lower atomic mobility present at such low temperatures in the liquid.

It is a pleasure to acknowledge useful discussions with A. Filipponi. The technical help of S. Pasternak and R. Weigel has been extremely useful during the experimental setup.

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