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Pressure-induced transformations and superconductivity of amorphous germanium

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The effect of pressure on amorphous Ge was probed by Raman spectroscopy combined with molecular-dynamics simulations. A large jump occurs in the principal peak position due to nearest-neighbor Ge-Ge vibrations at 11–12 GPa and 7–5.5 GPa, respectively, during increasing/decreasing pressure due to a polyamorphic transition occurring between the low-density amorphous semiconductor and a metallic high-density polyamorph (HDA). We measured the superconducting transition temperature (T_c) using magnetic susceptibility measurements in the diamond anvil cell and determined that T_c for the high-density HDA polyamorph was higher than that for the β-Sn structured Ge-II crystalline phase.

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The high-pressure behavior of the technologically important semiconducting elements Si and Ge has been investigated for more than three decades but major questions remain concerning the stable and metastable transformations among the crystalline and amorphous states. The diamond-structured crystalline materials transform into metallic β-Sn structured polymorphs (Si-II, Ge-II) above $P \sim 8-10$ GPa followed by a series of higher density phases formed at increased pressures.[1–5] Various metastable tetrahedrally bonded polymorphs occur during decompression[6–9] and low-density open-framework clathrate structures are produced at ambient P using chemical synthesis methods.[10–12] Within amorphous Si and Ge materials pressure-induced polyamorphism is reported to occur between the low-density amorphous (LDA) semiconductors and a high-density metallic amorphous (HDA) form. This unusual phenomenon is linked to a proposed first-order density- and entropy-driven phase transitions in the supercooled liquid state.[13–16] The LDA-HDA transition has been studied in detail for a-Si using Raman scattering and synchrotron x-ray diffraction experiments combined with electrical conductivity measurements and molecular dynamics (MD) simulations.[17,18] For a-Ge LDA-HDA polyamorphism was investigated previously for thin film samples by x-ray absorption, extended x-ray-absorption fine structure (EXAFS), and Raman scattering methods.[19–22] Here we report the polyamorphism observed in bulk samples of bulk a-Ge prepared by chemical synthesis techniques using Raman spectroscopy combined with MD simulation results along with *in situ* determination of the superconducting T_c of the metallic amorphous HDA state.

Shimomura *et al.*[23] reported a semiconductor-to-metal transition occurring in a-Si and Ge samples. A superconducting $T_c = 5.5$ K was reported for a-Ge at 7 GPa that decreased to 4.8 K by 10 GPa. During decompression the materials reverted to a semiconducting state and x-ray studies of recovered samples indicated amorphous materials. Aptekar[13] used a two-state thermodynamic model to predict a first-order phase transition occurring between low- and high-density liquid phases (LDL, HDL) for Si and Ge and predicted an LDL-HDL transition line along with spinodal boundaries extending into the supercooled liquid state and the solid amorphous regime. The two-state model was used to analyze polyamorphism in a-Si and a-Ge studied by experimental and theoretical techniques.[15,17,18,24–26] Recent work has focused on the polyamorphic behavior of a-Ge.[21,22,27] The pioneering high P conductivity experiments could not observe the state of the samples directly.[23] Later work using synchrotron x-ray diffraction in a large volume device showed that a-Ge samples became fully or partially crystallized above 6–7 GPa and that by 10 GPa metallic β-Sn structured Ge-II was the dominant phase.[9,28,29] During decompression the Ge sample reamorphized leading to recovery of LDA a-Ge material. Freund *et al.*[19] suggested that a-Ge samples preannealed during the course of the deposition processes were more stable. A sample studied in Ref. 19 was deposited on a kapton substrate held at 265 °C. The resulting a-Ge films were pressurized in a diamond anvil cell (DAC) and remained amorphous to $P \sim 8.9$ GPa. Subsequent XAS studies indicated that a first-orderlike transition occurs between the LDA and HDA forms of a-Ge at high pressure.[20–22] Samples prepared by vapor-deposition techniques could contain significant density variations that might affect the polyamorphism and phase transformation behavior.[22] Here we prepared homogeneous bulk a-Ge samples using a solid-state chemistry technique[30] and studied the LDA-HDA transition using Raman spectroscopy combined with MD simulations and we determined the superconducting transition temperature (T_c) for the HDA state.

Bulk a-Ge samples were produced from NaGe synthesized by reacting Na with powdered Ge in an autoclave followed by thermal treatment (10 days; $T = 150$ °C) with NH_4Cl (Ref. 30)

$$\mathrm{NaGe} + \mathrm{NH_4Cl} = \mathrm{NaCl} + \mathrm{NH_3(gas)} + \frac{1}{2}\mathrm{H_2(gas)} + \mathrm{Ge(amorphous\ solid)}.$$

The a-Ge samples were loaded into a mechanically driven symmetric DAC (Ref. 31) with NaCl as pressure-transmitting medium and ruby chips for P measurement.[32] Raman studies were carried out with 514.5 nm radiation

from an Ar^+ laser (5–10 mW) focused by a Mitutoyo 50SL objective.[33] Superconducting T_c's were measured using a nonmagnetic DAC made of NiCrAl alloy. Fragments of a-Ge ~ 30 μm in dimension were loaded inside a hole spark drilled in a NiMo gasket preindented to 50 μm. Methanol-ethanol 4:1 mixture was used as a pressure transmitting medium. The pressure in the cell was changed at room temperature. Superconducting transition was detected inductively using balanced pick-up coils and lock-in amplifier (Stanford Research 830).[34] For comparison, we also measured the pressure dependence of T_c for a Ge single crystal sample under the same conditions.

The MD studies used a Stillinger-Weber (SW) potential modified to reproduce the 300 K structure of a-Ge.[27,35,36] Simulations were performed along the 300 K isotherm on a system containing 999 atoms at constant T and P maintained using Nosé-Hoover thermostats and barostats.[37,38] The pressure was increased in $\Delta P \approx 0.3$ GPa steps with runs of ≈ 1 ns duration. The vibrational density of states [VDOS: $g(\omega)$] was extracted from 100 configurations at each P with a ≈ 10 ps time separation.[39] The Hessian (U is the total system energy for a given configuration $\{\mathbf{R}_N\}=\{\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N\}$)

$$H_{i\alpha,j\beta}=\frac{1}{m}\frac{\partial^2 U}{\partial r_{i\alpha}\,\partial r_{j\beta}}$$

was calculated numerically and diagonalized to produce the VDOS. Raman spectra [with $C(\omega)$ as the light-vibronic coupling coefficient]

$$R(\omega)=C(\omega)g(\omega)$$

were generated using a bond polarizability model.[39,40]

The ambient P Raman spectrum of a-Ge is dominated by a 280 cm^{-1} band close to the Raman peak of the crystalline semiconductor due to tetrahedral Ge-Ge stretching TO modes.[41,42] Raman spectra and peak positions recorded during a typical compression-decompression cycle are shown in Fig. 1. Above $P=8$ GPa broadening occurs due to distortion of the tetrahedral units as indicated by the MD studies (Fig. 2). Above 11.6 GPa the main band is replaced by a broad feature extending between 200–350 cm^{-1} indicating the presence of a polyamorphic transition into the HDA form with longer bond lengths and higher coordination.[21,22,25] Similar behavior was observed during our recent study for a-Si.[17] During decompression a large hysteresis is observed: the HDA polyamorph is retained to $P \sim 6.5$ GPa before it returns to the tetrahedral LDA semiconductor form [Fig. 1(c)]. A weak feature near the maximum of the HDA a-Ge spectrum near 200–250 cm^{-1} reveals the appearance of a small amount of crystalline β-tin structured Ge-II that is also formed within the sample at high P.[43]

In Fig. 2 we show Raman spectra calculated from MD simulations of the VDOS for a-Ge at high P. The simulated results reproduce the band observed experimentally at ~ 250 cm^{-1} but show an additional peak at lower frequency (~ 100 cm^{-1}). As P is increased the 250 cm^{-1} peak intensity decreases rapidly and above 8 GPa it is replaced by a broad weak feature at lower frequency, extending between 200–350 cm^{-1} consistent with the experimental observations. The inset to Fig. 2 shows the corresponding radial distribution functions. At low P characteristic peaks at 2.49 and 4.05 Å correspond to nearest- and next-neighbor Ge-Ge distances within the tetrahedrally bonded LDA structure. At $P > 10-12$ GPa a shoulder at ~ 3.40 Å becomes dominant due to near-90° bonded Ge-Ge-Ge triplets signaling a significant increase in 5-coordinate polyhedra (2% at $P=0$ GPa vs 54% at $P \sim 12.4$ GPa) (Fig. 2). Analysis of the MD configurations indicates that the Ge tetrahedra become distorted as P is increased and a large density jump to the HDA polyamor-

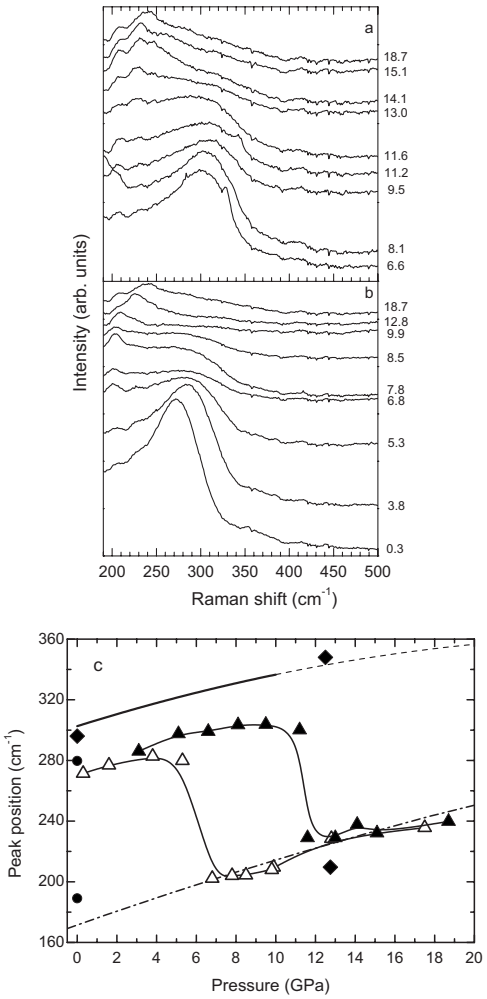

FIG. 1. Raman spectra of amorphous Ge during pressurization to 18.7 GPa followed by decompression. (a) Spectra obtained during increasing pressure. (b) Spectra obtained during decompression. (c) Positions of peak maxima as a function of pressure during compression and decompression. Solid triangles indicate positions measured during pressurization and open triangles indicate positions during decompression. Lines drawn through the data points are guides to the eye. The thick solid curve and dashed line indicate the pressure variation of the Raman active mode of crystalline diamond-structured Ge-I and its extrapolation to higher P. The dash-dot curve indicates the pressure variation of the TO mode of the metallic β-Sn structured Ge-II phase (Ref. 43). The positions of maxima in the vibrational density of states for LDA and HDA polyamorphic forms obtained from *ab initio* calculations (Ref. 25) are indicated by solid diamonds. Circles denote peak positions recorded for a-Ge samples prepared by vapor deposition (Ref. 41).

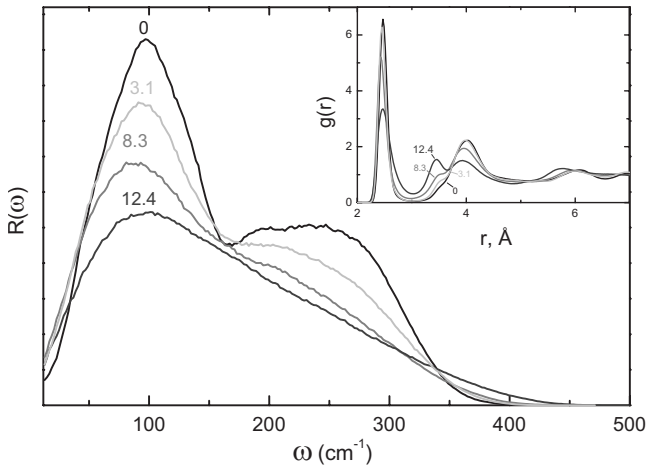

FIG. 2. Raman spectra $R(\omega)$ calculated from MD simulations using a Stillinger-Weber potential and bond polarizability model averaged over 100 configurations at each P. Spectra are shown during a compression cycle, digits indicate corresponding pressure values (in GPa). The inset shows the corresponding radial distribution functions g(r).

phic state occurs as 5-coordinate clusters appear in the structure. This interpretation is consistent with EXAFS results and is analogous to the behavior of a-Si at high P.[17,18,20]

The pressure-induced transition of a-Ge sample into the metallic HDA state was also monitored by ac magnetic susceptibility measurements of the superconducting transition during several compression-decompression runs carried out to between 3–26 GPa (Fig. 3). The onset point of the superconducting transition T_c was determined as the intersection of tangents drawn to the experimental $\chi(T)$ curves both in the normal state and during the step change in the susceptibility associated with the superconducting transition [Fig. 3(a)].

No superconductivity was observed at low P as expected for the semiconducting LDA polyamorph. The initial T_c value recorded for HDA at $P=9$ GPa occurred at ~6 K, close to that observed for crystalline Ge-II. The HDA T_c value increased until it achieved a maximum near $P\sim 12$ GPa and then decreased to $T_c=3.4$ K by 26 GPa [Fig. 3(c)]. The T_c of single-crystalline Ge was measured using the same method during decompression from 13 GPa down to 7.6 GPa. The T_c value for the crystalline sample is 3.4 K lower than that for the HDA polymorph of amorphous Ge at 13 GPa [Fig. 3(c)]. Previous data obtained for crystalline samples also indicated that the T_c for HDA a-Ge remained ~1.0–1.5 K higher than for crystalline Ge-II during the pressurization cycle between 11–21 GPa (Ref. 44) [Fig. 3(c)]. The previous data were obtained by electrical resistivity measurements under nonhydrostatic conditions.[44–46] As was emphasized in Ref. 46 pressurizing crystalline Ge at liquid helium temperature results in pronounced enhancement of the T_c if compared with runs in which the pressure is changed at room temperature as was done here. This is due to the sensitivity of T_c for the Ge-II phase formed at high pressure to structural imperfections as well crystallite size and strain relaxation. The observed enhancement of T_c for the amorphous state relative to a corresponding crystalline material as observed in our experiment has been noted previously to occur for metallic thin films and it is attributed to effects of structural disorder.[47] In the $\chi(T)$ data two superconducting transitions are observed at $P=12.3$ GPa [Figs. 3(a) and 3(b)]. The lower T_c value corresponds to crystalline Ge-II material present within the sample that is formed during compression along with the LDA-HDA transition; the higher T_c value is clearly due to the HDA polyamorph. During decompression the $\chi(T)$ curves indicated that a higher proportion of crystalline material was present between 10.5–7 GPa. The width of the transition was observed to be sharper and the T_c value was lowered indicating that the

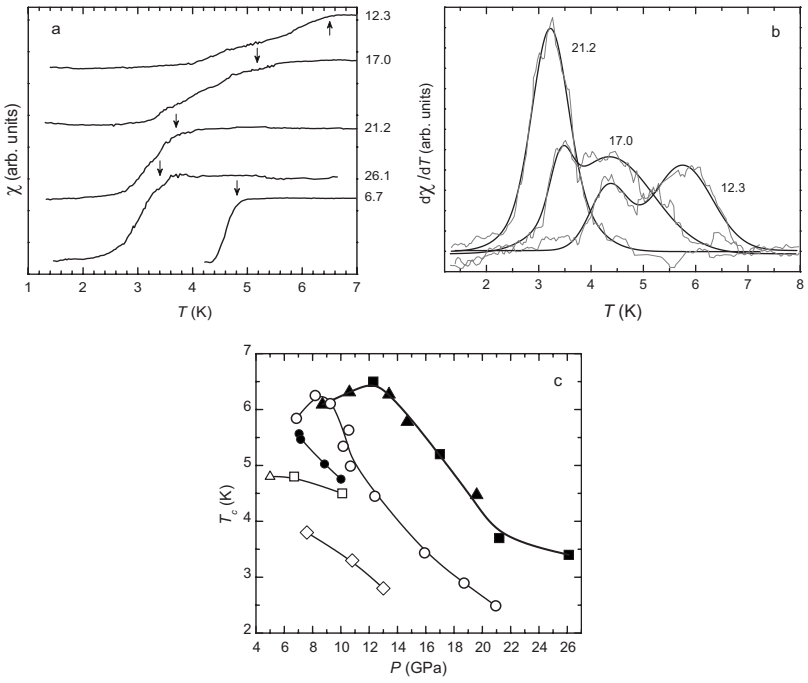

FIG. 3. (a) ac magnetic susceptibility (χ) versus temperature measurements for a-Ge in the DAC at different pressures. The curves at 12.3, 17.0, 21.2, and 26.1 GPa were measured on increasing pressure and that at 6.7 GPa on releasing pressure in the same cycle. (b) First derivative of $\chi(T)$ dependences clearly demonstrating the presence of two superconducting transitions due to HDA a-Ge polyamorph and to the presence of crystalline β-Sn structured Ge material appearing within the sample. (c) T_c onset values determined from the magnetic susceptibility data. Solid squares and triangles represent data obtained during increasing pressure and open squares and triangles represent decompression data. Open diamonds denote the T_c values obtained for Ge single crystals in the present paper upon decreasing pressure. Solid circles are the onsets of the superconducting transition of amorphous Ge presented in Ref. 23 for increasing pressure. Open circles represent T_c points for c-Ge above 10.1 GPa for increasing pressure while the points below 10 GPa are for releasing pressure (Ref. 44).

signal was now dominated by contributions from the crystalline phase [Figs. 3(a) and 3(c)].

Our results demonstrate that an LDA-HDA polyamorphic transition occurs between semiconducting and metallic forms of a-Ge as a function of pressure. The HDA form contains atoms in higher average coordination than the tetrahedrally bonded LDA polyamorph.[21,22] During compression the LDA-HDA transformation occurs at $P \sim 8-12$ GPa. During decompression the reverse transformation occurs between $P \sim 5.5-6.5$ GPa indicating substantial hysteresis for the first-orderlike transition as observed previously for a-Si at slightly higher P.[15,17] We expect that the polyamorphic LDA-HDA transformation in a-Ge is linked to a density-driven liquid-liquid (LDL-HDL) phase transition that is predicted to occur in the supercooled liquid state.[13,25]

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