Pressure Induced Amorphization of GeI_4 Molecular Crystals

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X-ray, Mössbauer spectroscopy, and extended x-ray absorption fine structure studies provide an atomic-scale description of the pressure-amorphized GeI_4. At $P > 12$ GPa a gradual onset of structural disorder accompanied by a molecular-association process is observed. An amorphized state concurring with the transformation of the molecular crystal into a metallic glass stabilizes at 25 GPa. It is accomplished by a gradual growth of a disordered $(GeI_4)_n$ polymer, a phase characterized by enhanced Ge-I bond lengths and charge delocalization. Both phenomena are consistent with a $I_{5p} \rightarrow Ge_{4s4p}$ charge-transfer band closure.

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There is now increasing experimental evidence that the topology of structural disorder induced by hydrostatic pressure is distinctly different from that of classical amorphous glasses produced by rapid cooling from the melt. Pressure induced amorphization has been observed for over ten years. Recently, with an increasing number of studies employing a variety of experimental methods and the implementation of promising theoretical models, it is being realized that the mechanism of pressure induced amorphization is an entirely new phenomenon in the solid state [1-12]. Examples of unusual properties not encountered in conventional amorphous materials are (i) the recovery in many cases of the crystalline state upon decompression; (ii) the memory effect, in which a single crystal undergoing a pressure induced amorphization recovers its original translational and orientational properties upon decompression (e.g., $AlPO_4$) [13], and (iii) retention of the original Néel temperature in the amorphous phase (e.g., $FeSiO_4$) [14].

It is obvious that unraveling the nature of the disorder at an atomic scale is essential for elucidating the mechanism of pressure induced amorphization. The amorphization is determined by the complete loss of x-ray diffraction patterns and loss or weakening of optical vibrational frequencies related to the long range translational modes. The usefulness of optical spectroscopy for structural studies of the amorphized state is especially impaired, particularly when the sample is opaque, e.g., due to metallization. In the present studies, we combined for the first time the methods of x-ray diffraction (XRD), Mössbauer spectroscopy (MS), and x-ray absorption spectroscopy (XAS) to obtain detailed structural and valence information of a pressure amorphized material. We focus on GeI_4, a cubic molecular crystal containing eight molecules per unit cell and employ suitable probes for XAS (Ge K edge) and MS (27.8 keV level in ^{129}I) studies. Whereas the XRD measurements were applied to determine the onset, abundance and, upon decompression, loss of the amorphous state, Ge XAS was applied to probe the Ge-I interatomic distances and MS was used as a molecular probe of bonding changes associated with the amorphization. As will be shown, the combination of these spectroscopic methods, due to their complementarity, provide unique information regarding the disordered state.

We performed XRD both on compression to 63 GPa and on decompression using a Mao-Bell-type diamond cell with no pressure medium other than the sample. We employed the ruby fluorescence technique for pressure calibration, and mixed fine-grained Au along with the polycrystalline sample in order to calibrate the x-ray diffraction intensities [7,13]. On increasing pressure, the x-ray pattern of the GeI_4 degrades at about 12(3) GPa. At 25 GPa, a broad diffraction peak typical of a diffraction halo in glasses is clearly observed near the [222] line (Fig. 1). The relative intensity of this halo increases with pressure, such that no remnants of the crystalline phase are observed above 33 GPa. Upon decompression the crystalline diffraction pattern of GeI_4 reappears at $P < 3$ GPa.

X-ray absorption spectroscopy on the Ge K edge was carried out to 30 GPa at the energy dispersive XAS station of LURE (DCI Orsay). A Block-Pieramini-type diamond cell [15] was used without any pressure medium, and pressures were calibrated with the ruby-fluorescence method. Details of the XAS experimental procedures and data analysis are given elsewhere [16,17]. To avoid the diamond Bragg peaks, the energy range was set above 300 eV. Spectra recorded at low pressures were used for determining the phase shift and the backscattering amplitude, so that the pressure dependence of the nearest-neighbor Ge-I distance could be determined from the radial distribution function. Upon increasing pressure to 16 GPa, the Ge-I distance decreases uniformly [Fig. 2(a)]. However, information on next nearest neighbors is lost close to 15 GPa, and we observe beating between two or

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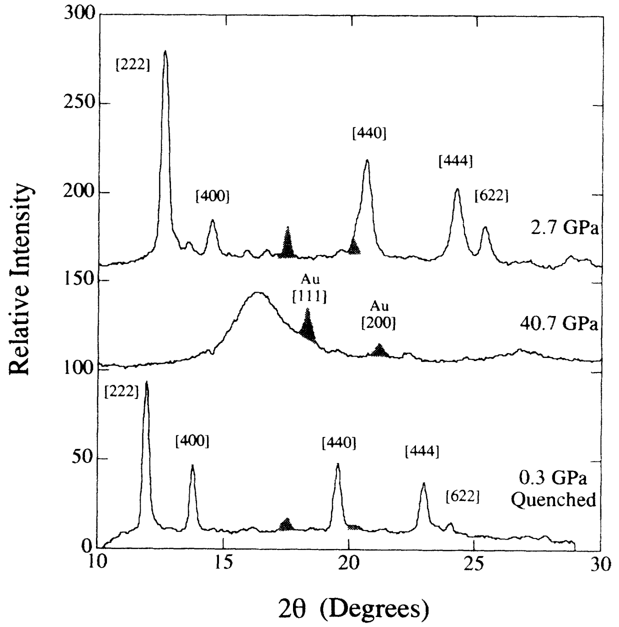

FIG. 1. X-ray diffraction patterns of the crystalline (upper) and amorphous (mid) phases of GeI_4. The lower part shows the pattern of the crystalline phase following decompression. The shaded lines correspond to Au patterns, used for intensity calibration.

more Ge-I distances over the 16-25 GPa pressure range; phenomena consistent with a transition into a disordered state (as manifested by the XRD data). The data cannot be modeled in terms of a uniform nearest-neighbor distance, and the values shown between 16 and 25 GPa in Fig. 2(a) are the averages. At $P \geq 25$ GPa, the beating ceases and a single interatomic distance is again observed, but is increased by about 0.18 Å with respect to the value below 16 GPa.

Samples of GeI_4 enriched with ^{129}I were used for Mössbauer spectroscopy. They were synthesized by the vapor-solid reaction of molecular iodine and Ge in an evacuated glass tube at 400 °C. An approximately 25-μm thickness of sample was placed in a 350-μm cavity drilled in a prepressed $Ta_{90}W_{10}$ gasket and loaded into a modified Merrill-Bassett cell with Ar as a pressure medium. Typical spectra recorded at 75 K with a $Mg_3{}^{129m}TeO_6$ point source at various pressures are shown in Fig. 3. Experimental details pertinent to high pressure MS are given elsewhere [18]. The spectra were fitted assuming a pure quadrupole spin Hamiltonian H affecting the excited ($I^* = \frac{5}{2}$) and ground states ($I = \frac{7}{2}$) nuclear levels, namely,

$$H = \frac{e^2qQ}{4I(2I-1)}[3\hat{I}_z^2 - I^2 + \tfrac{1}{2}\eta(\hat{I}_+^2 - \hat{I}_-^2)] , \qquad (1)$$

where $eq = eV_{zz}$ is the principal axis of the electric field gradient (EFG), e^2qQ is the quadrupole coupling, $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter, and $\hat{I}_z^2$, $\hat{I}_+^2, \hat{I}_-^2$ are spin operators. The free variables in the fitting program were the isomer shift (IS), line width, magnitude, and sign of e^2qQ, η, and the total area under the absorption spectra (intensity). In the molecular crystalline phase all four iodines of the GeI_4 molecule are identical, and display MS spectra with $e^2qQ = -47$ mm/s and $\eta = 0$. These values are typical of axial-symmetric $5p_z$ bonding where eV_{zz} is along the Ge-I bond, and the corresponding spectrum is designated as LP. The IS increases monotonically in the 0-14 GPa pressure range (Fig. 2) suggesting reduced intra- and intermolecular distances. The axial symmetry is preserved, however, with e^2qQ and η remaining unchanged.

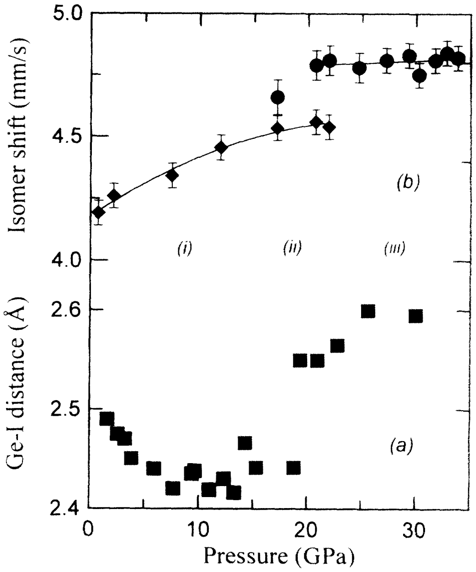

FIG. 2. (a) Ge-I interatomic distances as a function of increasing pressure. The pressure regions corresponding to the pure molecular-crystal phase, the intermediate range where both crystalline and amorphous phases coexist, and to the pure amorphous phase are indicated as (i), (ii), and (iii). In the (ii) range, the Ge-I distances are the average derived from the Ge K edge XAS data. (b) The ^{129}I IS data. The solid diamond and circle symbols correspond to the LP and HP phases, respectively. Notice the coinciding decrease of the Ge-I distance with increase in IS in the (i) region, the coexistence of two values of IS in the intermediate (ii) phase, and the discontinuous increase in IS in the phase (iii). The solid line is to guide the eye. Values of IS are with respect to $Mg_3{}^{129m}TeO_6$ at 70 K.

At $P > 14$ GPa, a second spectral component designated as HP1 appears and grows with intensity with increasing pressure. The fit of HP1 yields a positive e^2qQ [$+22(1)$ mm/s], a discontinuous large asymmetry parameter ($\eta = 0.8$), and a discontinuous increase in the isomer shift [see Fig. 2(b)]. At ~20 GPa the intensities of LP and HP1 components become equal. Then a third spectral component (HP2) appears at $P > 21$ GPa, convolved with LP and HP1. For HP2 we obtain $e^2qQ = -23(1)$ mm/s, $\eta = 0.3(1)$ and the same IS as in HP1. Ultimately, only the HP1 and HP2 components are

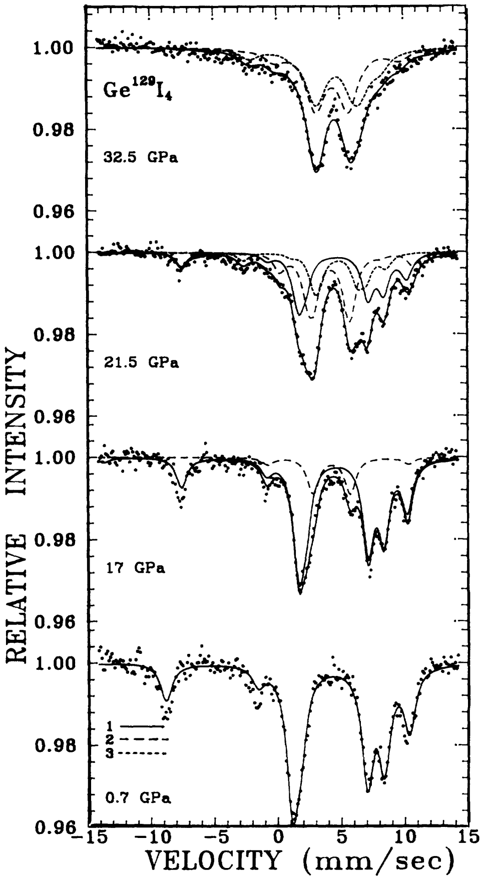

FIG. 3. Typical ^{129}I Mössbauer spectra measured at several pressures. The bold line through the experimental points is a theoretical fit assuming a pure quadrupole hyperfine interaction comprised of the LP subspectra (1), the HP1 subspectra (2), and the HP2 subspectra (3).

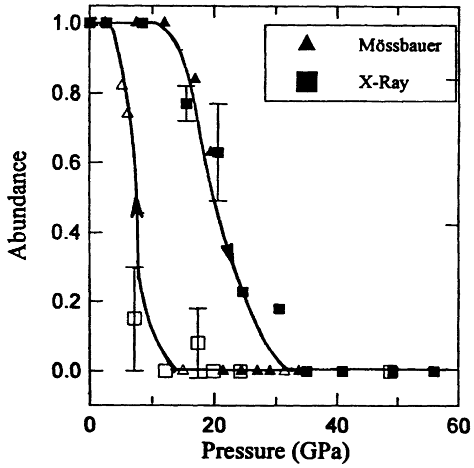

FIG. 4. The hysteresis of the crystalline → amorphous → crystalline cycle as recorded by XRD (□) and MS studies (△). The shaded and open symbols correspond to abundances upon compression and decompression, respectively. The solid line is to guide the eye.

present, with equal intensities, at 25–35 GPa, the highest pressure of our MS study. Upon decompression, at about 15 GPa the LP component reappears convolved with the HP1 and HP2 spectra and finally, at $P < 3$ GPa, the single LP spectral component becomes dominant.

We distinguish between three pressure ranges: (i) the pure crystalline phase at 0–15 GPa, (ii) the mixed phase in the 15–25 GPa range, and (iii) the pure amorphous phase at $P > 25$ GPa. The presence of the single-phase molecular crystal in phase (i) is manifested by the LP Mössbauer spectrum and the well defined XRD and XAS patterns. In this pressure range the Ge-I distance decreases gradually [Fig. 2(a)], consistent with the gradual increase in the IS. In the mixed phase region (ii), we interpret the appearance of the HP1 spectrum as the onset of intermolecular association; the formation of intermolecular -Ge—I—I—Ge- chains involving the iodine $5p_x5p_y$ orbitals (π bonding) [19]. Such a process leads to a flip in the eV_{zz} orientation, which becomes perpendicular to the Ge-I bond, and breaking of the C_{3v} symmetry. This is evident from the change in sign and magnitude of eV_{zz} and the large η value. In this mixed phase we also witness the beating of two or more Ge-I distances and the loss of next-nearest-neighbor information (as measured by XAS), and the coexistence of x-ray diffraction lines and a halo pattern in the XRD data. It is noteworthy that in the isomorphous compound SnI_4, two out of four iodines remain single-bonded and the other two exhibit strong intermolecular overlap to at least 32 GPa [20]. This disordered polymeric phase is present in the (ii) phase of GeI_4, but only over a limited pressure range (< 10 GPa). In general, the high-pressure phase of GeI_4 differs distinctly from that of SnI_4 in the appearance of HP2 at 21 GPa and the complete disappearance of the LP component at $P > 25$ GPa. We interpret the HP2 component as the last stage in the complete loss of the van der Waals character of GeI_4, and the onset of a pure covalent/metallic phase.

The intensity ratio LP/(LP+HP1+HP2) derived from the MS spectra is proportional to the relative abundance of the molecular phase [21]. In Fig. 4 we plot the relative abundances of the molecular crystalline phase, comparing the results from MS and XRD methods. As can be seen, the transition into the pure amorphous phase at $P > 25$ GPa based on XRD coincides very well with the complete polymerization inferred from the MS.

Unique information concerning changes in the iodine $5p$ valence band can be derived from the IS. In general, the IS is proportional to the s-electron density at the nucleus. Chemical bonding of the iodides involves primarily the outer $5p$ valence shell, with $5s^2 6p^{6-h_p}$ configuration, where h_p is the number of p holes. The relationship of the IS (h_p) with respect to a $Mg_3{}^{129m}TeO_6$ source in the $1 \geq h_p \geq 0$ range is well established [22], namely,

$$\mathrm{IS} = 1.50 h_p + 3.58\ \mathrm{mm/s}\,. \tag{2}$$

The abrupt increase in IS both in the HP1 and HP2 components is explained as due to the depletion of p electrons, about $0.2e^-$ per I, in the iodine valence band. This charge-transfer process,

$$I_{5p} \xrightarrow{e^-} \mathrm{Ge}_{4s4p}\,,$$

can explain the metallization of $\mathrm{GeI_4}$ in the amorphous phase [23]. In this phase the intermolecular van der Waals interaction is replaced by a metallic/covalent bond with increased Ge-I distances. The simultaneous transition to a metallic and amorphous phase is also observed in the analogous $\mathrm{SnI_4}$ [23]. The question then arises whether the occurrence of metallization and amorphization are correlated in the AB_4 molecular crystals. Apparently not necessarily; recent high pressure optical [24] and ^{119}Sn Mössbauer [25] studies in the analogous $\mathrm{SnBr_4}$ definitely show that the amorphous state reached at around 14 GPa is not accompanied by metallization.

In conclusion, our study documents for the first time the detailed process of structural and bonding evolution of a molecular crystal as it is being amorphized. So far, of all molecular crystals studied under high pressure (with the possible exception sulfur, a pseudomolecular crystal [11,12]), the only ones to show pressure induced amorphization are of the AB_4 pentatomic molecular crystals, where A and B are the IV-row cations and halides, respectively. It seems that the high pressure structural disordering of these crystals is a consequence of the onset of strong intermolecular overlap via the halide ions, resulting in orientational and translational disorder. As a result of the large energy separation between the outer p and s valence bands of the halides, in contrast to the oxides and chalcogenides, intermolecular bonding of the -A-B-A-B-A- type cannot take place. Such configurations might lead to increases in cation coordination numbers upon increasing density, as observed in the pressure amorphized oxides and chalcogenides. Our experiments do not resolve the Ge coordination number unambiguously, however, but do prove that molecular dissociation ($\mathrm{GeI_4 \rightarrow GeI_2 + I_2}$) does not take place under the conditions we have investigated.

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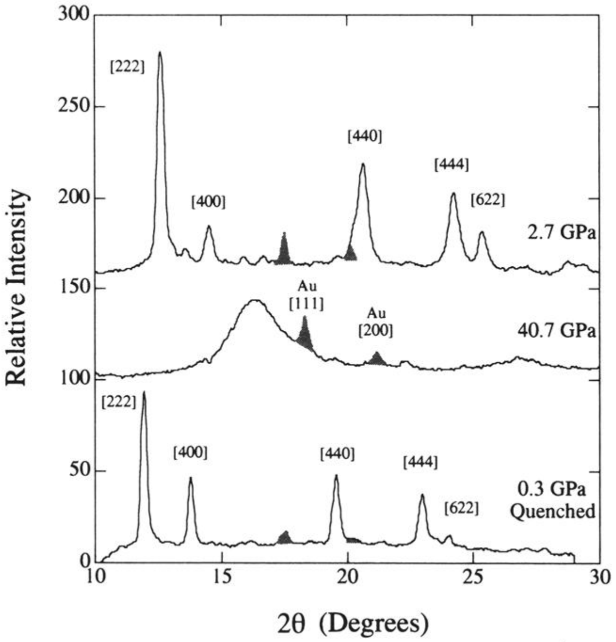

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