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Mössbauer studies of pressure-induced amorphization in the molecular crystal SnBr₄

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Properties of the molecular structure and the Sn(IV) valence of the pressure-amorphized SnBr₄ molecular crystal were investigated by ¹¹⁹Sn Mössbauer spectroscopy. Studies were conducted at 80 K with pressures to 25 GPa, far beyond the amorphization onset at $P_c = 7-9$ GPa as determined by previous Raman studies. No valence change in the Sn(IV) central ion takes place as deduced from the isomer shift (IS) variation with pressure, in contrast to the analogous molecular crystal SnI₄ which undergoes amorphization and metallization under pressure. The IS value of 1.15(5) mm/s, with respect to a CaSnO₃ source at 300 K, remains practically constant over the whole pressure range, suggesting little variation in both the Sn-Br intramolecular distances and covalency within the amorphous and/or insulator pressure regime. A single line spectrum is characteristic of the Mössbauer data obtained in the 0–5 GPa range, indicating the preservation of fourfold symmetry of the SnBr₄ molecule in the crystal. Above 5 GPa, near P_c , a *quadruple interaction* takes place concurrent with a dramatic increase in the *recoil-free fraction* (f). The value of the quadrupole splitting reaches a maximum of 0.9 mm/s at $P \sim 15$ GPa and remains constant thereafter. By ~ 9 GPa the absorption area, which is proportional to f , increases by 30–40 % over the lowest pressure value and then remains constant at higher pressure. These results are consistent with the formation of a molecular species, e.g., a (SnBr₄)₂ dimer, lacking the T_d symmetry at the original Sn⁴⁺ site and having optical phonons *hard* enough not to be excited by the nuclear recoil process. Molecular association into (SnBr₄)₂ dimers, the building block of the high-pressure disordered state, also explains many of the experimental features of the Raman data. Upon decompression, Mössbauer (and Raman) data suggest that these dimers dissociate into monomers at ~ 5 GPa; however, a disordered structure of SnBr₄ persists as pressure is decreased further. Crystallization is fully recovered below 1 GPa. The nature of the pressure-induced amorphization of the insulator SnBr₄ is discussed in terms of the structural and valence properties of the analogous metallic SnI₄.

INTRODUCTION

When certain penta-atomic molecular crystals are compressed beyond a critical pressure P_c , the original crystalline structure transforms to an amorphous (disordered) phase. The molecular crystals SnI₄, GeI₄, and SnBr₄ are examples in which this phenomenon occurs. The onset of structural disorder has been characterized by a variety of experimental methods, viz., by Raman, Mössbauer, and x-ray absorption spectroscopies and by x-ray diffraction.^{1–3} In SnI₄ and GeI₄ the order-disorder transition is accompanied by metallization,⁴ in contrast to the case of SnBr₄, which shows a definite optical band gap to at least 20 GPa, 13 GPa above P_c .²

In both GeI₄ and SnI₄ the nature of the disorder and metallization was qualitatively assessed from an analysis of the quadrupole interaction in the highly resolved ¹²⁹I Mössbauer spectra. It was found that at $P > P_c$ the *inter-*

molecular iodine atoms overlap to form disordered polymeric chains, thus creating a path for electronic delocalization. Furthermore, ¹¹⁹Sn Mössbauer spectroscopy (MS) in SnI₄ led to the discovery of an unusual Sn(IV) valence state attributed to the amorphous and/or metallic phase.¹ This was deduced from the isomer shift (IS) value of the single-line spectrum which was distinctly higher than, and which had an opposite pressure dependence to, that of Sn(IV) in the crystalline phase. The mechanism driving the change of the Sn(IV) electronic ground state at $P > P_c$ could not be established unambiguously; it could have been the consequence of either metallization or amorphization, or both. Thus, MS pressure studies of ¹¹⁹SnBr₄, an analogous molecular crystal to SnI₄, provides the opportunity for an atomic-scale investigation of pressure-induced amorphization *exclusively* without interference from the effects of metallization. The outcome of such an investigation may help to elucidate the microscopic origin and driving force of the

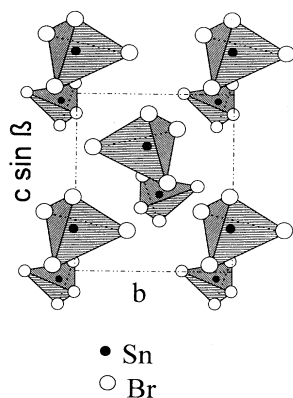


FIG. 1. A projection normal to the a axis of the monoclinic unit cell of SnBr_4 at ambient pressure and temperature (adapted from Ref. 5). This serves to emphasize the ordered arrangement of isolated molecules in the crystalline phase.

order-disorder transition. The main purpose of this work was to probe the site symmetry and valence of Sn and to monitor the SnBr_4 moiety as its crystal state is driven into an amorphous state upon application of external pressure.

At ambient pressure SnBr_4 is a transparent crystal. Its unit cell is monoclinic having four molecules per unit cell, yet the tetrahedral molecules of which it is comprised may well be described⁵ by the point group T_d . A schematic representation of SnBr_4 is shown as Fig. 1.

There has been only one set of high-pressure amorphization studies on SnBr_4 , involving both Raman and optical absorption spectroscopy (Williamson and Lee²). The relevant results can be summarized as follows: (1) New lattice modes appear at ~ 4 GPa, suggestive of a transition to a new crystalline structure composed of more than four SnBr_4 molecules per unit cell. (2) A splitting of the ν_1 "breathing" mode (symmetric stretch) occurs at 5 GPa that is interpreted as a coupling of the molecular subunits. Both the original unsplit ν_1 modes and the split ν_1 components (A_g modes) coexist in the range 5–13 GPa. This has been attributed to the coexistence of crystalline and amorphous phases that have a changing relative abundance with increasing pressure. (3) All lattice modes disappear at $P > 15$ GPa, signaling a complete transition to an amorphous phase. (4) The optical band gap in SnBr_4 closed monotonically with increasing pressure but remained finite at the highest pressure reached (20 GPa). (5) Raman data show substantial hysteresis effects upon decompression; features of the crystalline state reappear at $P < 1$ GPa. (6) Upon decompression, both the A_g and ν_1 modes are evident, down to 5 GPa; however, only the ν_1 mode is detected below 5 GPa.

EXPERIMENTAL

Tin-tetrabromide was synthesized by direct vapor (Br_2)-solid (Sn-metal) reaction in an evacuated glass tube at 350°C. Enriched ^{119}Sn isotope ($> 80\%$) was used and

Br_2 was obtained from the thermal dissociation of PdBr_2 . A miniature Merrill-Bassett-type diamond-anvil cell (DAC) was employed for pressure studies. Anvils with culet flats of 550 μm were used, and a sample cavity was obtained by drilling a 300- μm hole in a $\text{Ta}_{90}\text{W}_{10}$ gasket preindented to 40–50 μm . The gasket also served as a collimator of the 23.87-keV radiation associated with the Mössbauer transition.

The moisture-sensitive SnBr_4 was loaded in an inert atmosphere into the sample cavity without any additional pressure-transmitting medium. Grains of dry ruby chips were added into the cavity for pressure measurements through the ruby R_1 fluorescence line shift. Pressure gradients were typically 10% of the average pressure up to $P \sim 10$ GPa and less at higher pressure. The absorber was cooled to 80 K in a commercial flow cryostat modified for DAC-Mössbauer experiments. A $\text{Ca}^{119\text{m}}\text{SnO}_3$ source (~ 1.5 mCi) held at room temperature, a 25- μm critical-edge palladium filter, and a NaI(Tl) scintillation counter were used for the Mössbauer experiments in a conventional transmission geometry. The count rate through the DAC was ~ 10 c/s, and typically data for each pressure were accumulated for a period of 20–30 h. During the series of pressure measurements, special precautions were taken to keep the experimental settings and conditions constant. Mössbauer parameters have been extracted from theoretical fits by using Lorentzian line shapes and standard least-squares fitting programs.

RESULTS AND DISCUSSION

Representative Mössbauer spectra at various pressures during compression are shown in Fig. 2. Each spectrum at $P \leq 5$ GPa was fitted with a *single* absorption line. A nearly constant value of the IS ~ 1.2 mm/s, characteristic of Sn(IV), was obtained for the whole pressure range. At $P > 7$ GPa the MS absorption area increased rather markedly, and optimal fits were obtained by assuming a quadrupole interaction. The pressure dependence of the quadrupole splitting is shown in Fig. 3.

It is instructive to compare the pressure evolution of the $^{119}\text{SnBr}_4$ Mössbauer data with the previous pressure studies¹ of SnI_4 . A second Sn resonance site appeared at IS ~ 3.8 mm/s in the latter for $P \geq 9$ GPa, with an ever increasing abundance as the pressure was increased. This value of IS is quite different from typical values (centered at 1.1–1.5 mm/s) for tetravalent tin and is more typical of divalent tin at ambient pressure. Metallization in SnI_4 occurred at 12 GPa. Both crystalline and amorphous phases coexisted in the range 10–18 GPa, and the compound was exclusively amorphous for $P \geq 18$ GPa. Studies of ^{129}I MS on the same compound showed no evidence of a $\text{SnI}_4 \rightarrow \text{SnI}_2 + \text{I}_2$ molecular dissociation at the order-disorder transition. Another conclusion of that work was that molecular *association* of the SnI_4 tetrahedra occurred to form randomly oriented $(\text{SnI}_4)_n$ chains—constituting a new amorphous phase—starting at the onset of pressure-induced disorder at about 12 GPa. This polymerization process can account for the metallic behavior of SnI_4 under pressure by providing a pathway of elec-

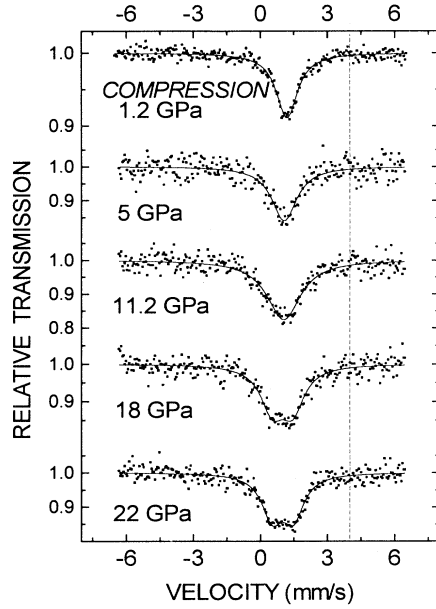


FIG. 2. A selection of ^{119}Sn Mössbauer spectra of SnBr_4 at 80 K measured at several pressures during compression. Solid lines are theoretical fits to the data. The vertical dotted line is located at a velocity typical of tin(II) compounds. In case of molecular dissociation into SnBr_2 , one would have observed an absorption line near this velocity (see text).

tron delocalization established along the -Sn-I-I-Sn- linkages of the chains. From the fact that no $^{129}\text{I}_2$ and $\text{Sn}^{129}\text{I}_2$ species were detected in the amorphous and/or metallic state, it was deduced that the high-pressure electronic state of tin remained tetravalent, and the resonance with IS at 3.8 mm/s was attributed to a new configuration of $5s5p-4p4d$ hybridization that results in an increase in the $5s$ electron density.

For SnBr_4 in the range 0–25 GPa the IS barely

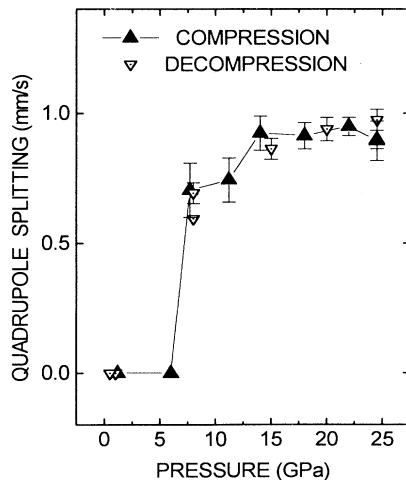


FIG. 3. Pressure evolution of the quadrupole splitting. Dotted or dashed lines are to guide the eye.

changes across the order-disorder transition. This indicates that the electronic state and valence of the tin atom are almost invariant over the measured pressure range. There is no additional signature characteristic of Sn(II) compounds,⁶ e.g., SnBr_2 from molecular dissociation or from the analog of the hybridized state¹ of ^{119}Sn in SnI_4 , at $\text{IS} \sim 4$ mm/s (see Fig. 2). Comparison of the pressure dependence of IS in SnBr_4 and SnI_4 suggests that in SnI_4 the site associated with the large IS is related to metallization, not amorphization. We proceed to examine the *molecular* properties of SnBr_4 as it amorphizes during pressurization and recrystallizes upon depressurization.

A. Compression

The quadrupole interaction in ^{119}Sn is a unique probe for detecting possible changes in the fourfold symmetry of the SnBr_4 molecule. Mössbauer spectra show no evidence of substantial line broadening with compression in the crystalline state, consistent with the Raman data on the behavior of the dominant ν_1 intramolecular breathing mode. For $P > 5$ GPa, a quadrupole interaction is evident (see Fig. 3), indicative of a breakdown of the symmetry of an ideal noninteracting SnBr_4 tetrahedron. Above this pressure, the Raman data showed two satellite peaks symmetric shifted by $\sim \pm 30$ cm^{-1} with respect to the ν_1 breathing mode. The onset of the two A_g modes may originate from a coupling of the molecular units and the associated splitting of the ν_1 modes may originate from a coupling of the molecular units and the associated splitting of the ν_1 mode. The formation of coupled SnBr_4 units by way of bridging bromide atoms could be a mechanism for destroying the fourfold symmetry around the Sn(IV) Mössbauer atom, and this would produce a quadrupole-split spectrum. A high-pressure phase having $(\text{SnBr}_4)_2$ dimers as the coupled units may account for both the observed splitting of the ν_1 Raman-active mode and the finite quadrupole interaction observed in Mössbauer spectra at $P > 5$ GPa. The pressure dependence of the Mössbauer resonance strength also provides experimental evidence for the formation of the dimers.

The absorption area of each Mössbauer spectrum is proportional to the Sn recoil-free fraction f in a first approximation. At the temperature of interest, $T \sim 80$ K, the Boltzmann population of *intramolecular* Sn-Br vibrational modes ($\nu_1 = 220$ cm^{-1}) is small and their influence on f may be ignored. The dominant influence on f in the ordered molecular crystal is from the acoustic and optical *intermolecular* soft phonon modes and the recoilfree fraction may be formulated as⁷

$$f = \exp \left\{ - \frac{3E_\gamma^2}{Mc^2k_B\theta_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1} dx \right] \right\}, \quad (1)$$

assuming a Debye model for the phonon spectrum, where θ_D is the effective Debye temperature, E_γ is the energy of the Mössbauer transition, M is an effective mass associated with the thermally excited motion of the Mössbauer atom, and all other symbols have their usual meaning. Thus, the effective mass M appropriate to Eq. (1) is pri-

marily that of a SnBr_4 aggregate having a monomer molecular weight of ~ 440 amu. The Raman data show lattice modes extending up to ~ 60 cm^{-1} in the low-pressure (< 5 GPa) crystalline phases. If this corresponds to the upper end of the total intermolecular frequency distribution function and if there is no marked distinction between acoustic and optical modes (because of the complexity of the unit cell), a Debye temperature of $\theta_D \sim 80$ K may be assumed.

The absorption area of the Mössbauer spectra undergoes a marked increase in the pressure range 5–15 GPa (see Fig. 4), the same region where Raman pressure studies have identified a progressive change to the amorphous state.² To explain the change in lattice dynamics evident in Fig. 4 we use in Eq. (1) the value $\theta_D \sim 80$ K—assuming that it remains almost constant across the order-disorder transition—and the approximation⁷

$$f = \exp \left[- \frac{3E_\gamma^2 T}{Mc^2 k_B \theta_D^2} \right], \quad (2)$$

which is valid for the temperature, $T \sim 80$ K, at which our measurements were performed $T > \theta_D/2$. By using the effective mass M of the SnBr_4 monomer we calculate $f \sim 0.5$ in the crystalline phase at $P < 5$ GPa. It follows from Eq. (2) that a twofold increase in $M(\text{SnBr}_4)$ will increase the recoilfree fraction to $f \sim 0.7$. This enhancement of $\sim 30\%$ in f upon dimerization is concordant with our experimental results.

Therefore, dimerization of the SnBr_4 molecular constituents of the low-pressure crystalline phase fully accounts for both the existence of a quadrupole splitting and an enhanced f value in the Mössbauer spectra. It is also noteworthy that when the presence of coupled molecular units first become evident in the Raman data at 200–300 cm^{-1} and $P \sim 7$ GPa, an additional low-intensity mode appears at ~ 150 cm^{-1} and persists to 25 GPa during

compression.² This mode could be attributed to the “breathing” mode specific to the $(\text{SnBr}_4)_2$ dimer in analogous fashion to the ν_1 symmetric stretch of the nearly isolated monomer of the crystalline phase. In SnI_4 the onset of a phase (metallization) of coupled molecular units occurs at ~ 10 GPa,^{1,4} yet no additional modes associated with the suggested molecular association could be identified in the Raman spectra of Sugai.⁸ However, opaqueness of the high-pressure metallic state of SnI_4 precludes the same quality of Raman data in this region when compared to the transparent SnBr_4 insulator.

B. Decompression

Upon decompression, the absorption area undergoes a significant reduction near $P = 8$ GPa approaching its low-pressure value upon further decompression to ~ 6 GPa, yet the relative change seems to be quite different to that measured during compression (see Fig. 4). Concomitantly, the quadrupole splitting undergoes a marked change to zero at $P < 8$ GPa; this is an indication that the linked molecules of the high-pressure phase decouple at low pressure. Previous decompression Raman data show evidence of a disordered structure consisting of uncoupled molecular units at $P \sim 5$ GPa. It should be noted that upon compression the structural change at 5–7 GPa is associated with an order-disorder transition, whereas upon decompression, the first structural transition is from a disordered network of dimers to a disordered configuration of nearly isolated monomers (i.e., molecules relatively weakly coupled by van der Waals forces). (See Fig. 5.) Consequently, the change in the lattice dynamics of the tin atom at the order-disorder transition upon compression may be different from the change at the structural transition when the sample is decompressed.

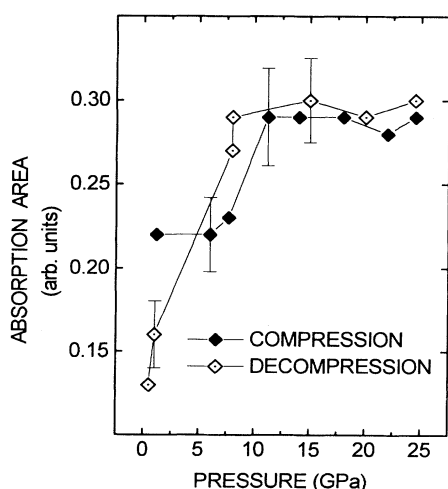


FIG. 4. Pressure evolution of the resonance absorption area. Dotted or dashed lines are to guide the eye.

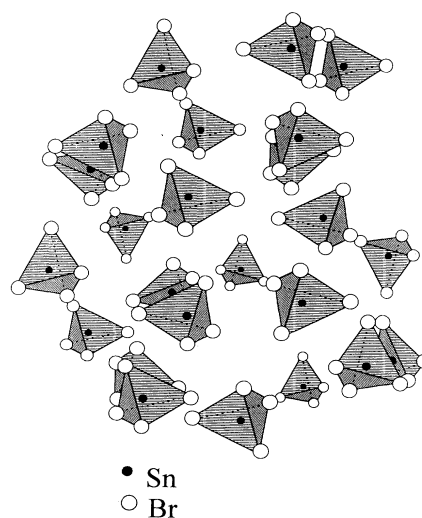


FIG. 5. Schematic representation of the disordered assembly of $(\text{SnBr}_4)_2$ dimers in the amorphous phase at high pressure. Three possible configurations of dimers are depicted with single, double, or triple intermolecular bromine bonding.

The significant reduction in the absorption area at $P < 8$ GPa upon decompression is consistent with the idea of a transition to a disordered assembly of SnBr_4 monomers. The Raman experiments show evidence of a complete recrystallization by 0.6 GPa.

CONCLUDING REMARKS

The present Mössbauer studies in conjunction with previous Raman data show evidence of a rich sequence of structural transitions as the molecular crystal SnBr_4 is compressed to 25 GPa and then progressively decompressed to ambient pressure. The Raman data have identified a crystallographic phase transition at ~ 4 GPa during compression. This is followed by a progressive crystalline-to-amorphous transition that is compressed at $P \sim 15$ GPa. The Mössbauer probe has proven to be indispensable in establishing the nature of the amorphous phase at high pressure and its subsequent behavior during decompression. There is compelling evidence from ^{119}Sn Mössbauer data that no molecular dissociation takes place when crystalline SnBr_4 is transformed into an amorphous state under compression. The behavior of the lattice dynamics and site symmetry of Sn in the SnBr_4 molecule suggests that the amorphous phase

is a disordered assembly of dimers. This configuration remains stable to ~ 5 GPa upon decompression. As pressure is reduced further the dimers decouple to form a disordered configuration of monomers stable to ~ 1 GPa. Raman data have shown that recovery of crystallization occurs somewhat below 1 GPa.

It should be emphasized that previous Raman studies show that the pressure evolution and behavior of intramolecular and intermolecular modes in SnBr_4 are quite similar to that of SnI_4 . But our Mössbauer data on SnBr_4 in conjunction with previous MS studies of SnI_4 suggest that the nature of the disordered phase at high pressure is completely different in the two cases. In SnI_4 the metallic amorphous phase has randomly oriented $(\text{SnI}_4)_n$ polymeric chains to provide a pathway for electron delocalization. In contrast, the insulating amorphous phase of SnBr_4 has $(\text{SnBr}_4)_2$ dimers as the principal constituent of a van der Waals solid.

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¹M. P. Pasternak and R. D. Taylor, *Phys. Rev. B* **37**, 8130 (1988).

²W. Williamson III and S. A. Lee, *Phys. Rev. B* **44**, 9853 (1991).

³M. P. Pasternak, R. D. Taylor, M. B. Kruger, R. Jeanloz, J. P. Itie, and A. Polian, *Phys. Rev. Lett.* **72**, 2733 (1994).

⁴A. L. Chen, P. Y. Yu, and M. P. Pasternak, *Phys. Rev. B* **44**,

2883 (1991).

⁵V. P. Brand and H. Sackmann, *Acta Crystallogr.* **16**, 446 (1963).

⁶P. A. Flinn, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), p. 593.

⁷R. Herber, J. Fischer, and Y. Hazony, *J. Chem. Phys.* **58**, 5185 (1973); S. Bukshpan and R. H. Herber, *ibid.* **46**, 3375 (1967).

⁸S. Sugai, *J. Phys. C* **18**, 799 (1985).