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PRESSURE-INDUCED TRANSFORMATIONS IN MOLECULAR CRYSTALS

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ABSTRACT

A review is given on the unique features of the Mössbauer spectroscopy (MS) which by virtue of the quadrupole interaction and the lattice dynamics allows one to characterize some structural properties in the pressure-induced amorphous state of molecular crystals. Experiments were performed in GeI₄, SnI₄ and SnBr₄ by means of ¹¹⁹Sn and ¹²⁹I MS with pressures to 35 GPa at cryogenic temperatures using diamond anvil cells.

1 - INTRODUCTION

Properties of molecular crystals under pressure have been the subject of extensive investigations since the early days of high-pressure studies of solids [1]. The introduction of diamond anvil cells (DAC) [2] as a hydrostatic pressure generator allowed the investigation of structural and electronic transformations of molecular crystals by optical methods and recently by synchrotron radiation to $P > 300$ GPa. The use of high-pressure Mössbauer spectroscopy (MS) to study *pressure-induced transformations* in molecular crystals was first applied by Pasternak et al. [3] for the case of diatomic molecular iodine using a DAC. The various transformations preceding the molecular dissociation into atomic iodine were clearly demonstrated via the various parameters of the quadrupolar interaction in ¹²⁹I₂. Thus for the first time, the unique spectroscopical features of MS as a *molecular spectrometer* in the atomic scale were established. In the present work we apply ¹²⁹I and ¹¹⁹Sn high-pressure MS to characterize the various aspects of pressure induced transformations of penta-atomic molecular crystals.

When certain penta-atomic molecular crystals of the form MHa_4 , where M and Ha stand for tetravalent metal ions of the IV column and the halides respectively, are compressed beyond a critical pressure P_c , the crystalline structure transforms into an **amorphous** (disordered) phase. The molecular crystals SnI₄, GeI₄ and SnBr₄ are examples in which this phenomenon occurs. The Sn and Ge tetra-iodides crystallize in a cubic lattice with point group $T_h^6 - Pa3$ and eight molecules per unit cell, whereas SnBr₄ is monoclinic, point group T_d and four molecules per unit cell. In the present paper we illustrate the various features of these transformations, emphasizing the uniqueness of the MS in determining molecular structure in a disordered phase, and correlate them with data obtained by other methods, namely, optical spectroscopy, X-ray diffraction and electrical transport.

2 - EXPERIMENTAL

All samples were prepared by vapor-metal reaction of the elements using spectroscopical pure materials and enriched ^{119}Sn and ^{129}I isotopes. A miniature Merrill-Bassett-type diamond-anvil cell (DAC) was employed for pressure studies. Anvils with culet flats of 700 μm were used, and a sample cavity was obtained by drilling a 300- μm hole in a $\text{Ta}_{90}\text{W}_{10}$ gasket pre-indented to 40-50 μm . The gasket also served as a collimator of the 23.87-keV and 27.8 keV radiation associated with the Mössbauer transitions in ^{119}Sn and ^{129}I , respectively. A commercial 1.5-mCi $\text{Ca}^{119\text{m}}\text{SnO}_3$ source was used at room temperature and ^{119}Sn MS measurements were conducted with DAC's absorbers at 70 - 120 K in conjunction with a 25- μm Pd filter. A $\text{Mg}_3^{129\text{m}}\text{TeO}_6$ source was used for ^{129}I measurements where source and absorber were held at the same temperature and operated in the 4-50 K range.

2.1 GeI_4 and SnI_4 .

Using X-ray diffraction (XRD) and Raman spectroscopy Fujii et al. [4] and Sugai [5] have shown that SnI_4 undergoes a continuous crystal - amorphous phase transition at $P_c = 13$ GPa,

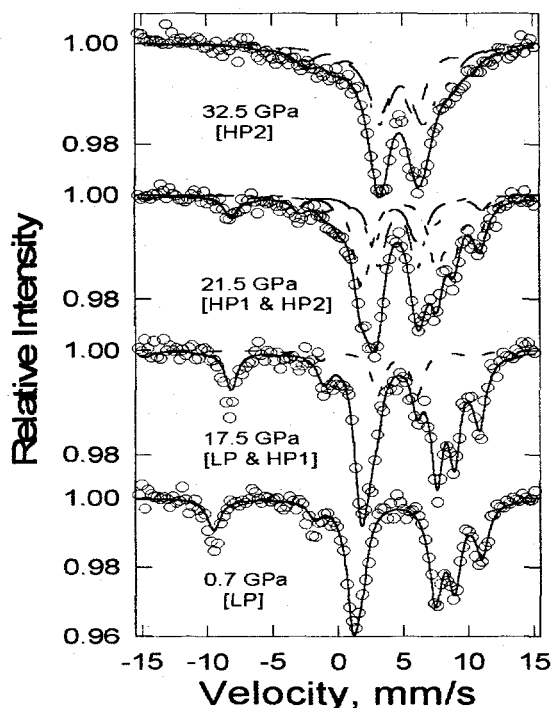


Fig. 1. Typical $\text{Ge}^{129}\text{I}_4$ spectra with increasing pressure. The solid line is the convolution of the various sub-spectra corresponding to different I-sites (see text)

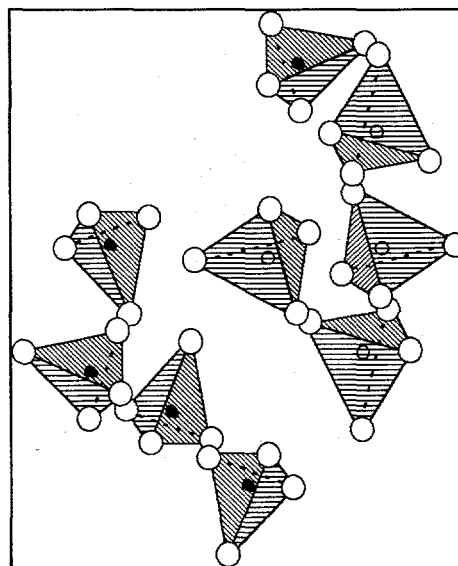


Fig. 2. The model suggested for the amorphous phase HP1 of SnI_4 at $P > 12$ GPa and as intermediate phase of GeI_4 ($14 < P < 22$ GPa). The phase is a disordered $(\text{MI}_4)_n$ metallic polymer.

reaching a complete amorphization at ~ 26 GPa. Upon decompression a large hysteresis is observed and the material crystallizes at ~ 4 GPa. A similar phenomena occurs in GeI_4 . XRD studies done in conjunction with ^{129}I MS (see Fig. 1) and X-ray absorption spectroscopy [6] have shown that $P_c(\text{GeI}_4) = 12$ GPa.

Concurrent with amorphization both compounds undergo an insulator - metal (IM) transition at $P = P_c$ [7]. First indications of crucial changes in the band-structure, suggesting an IM transition, were reported by Pasternak and Taylor [8] in their ^{119}Sn and ^{129}I MS studies of SnI_4 .

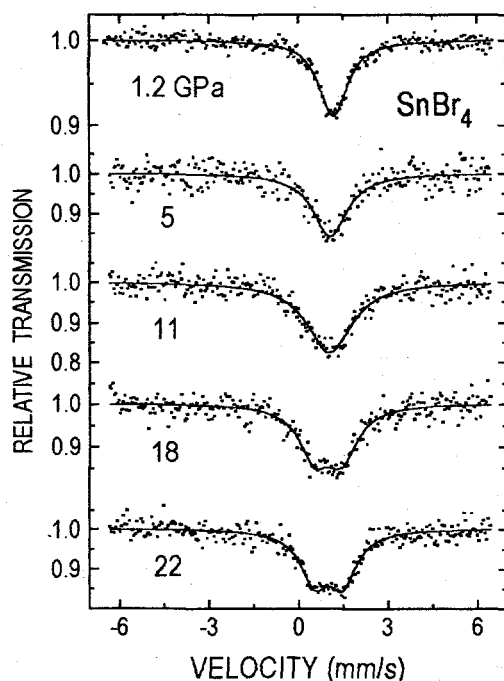
Once the amorphous/metallic state was formed, a new single line in ^{119}Sn was detected differing dramatically from that of the low-pressure phase. The IS value of 1.5 mm/s, characteristic of an insulating crystalline SnI_4 with a Sn^{4+} state, changed discontinuously to 3.7 mm/s indicative of a large increase in $\rho_s(0)$ of about 1s electron/atom. This was accounted for by the gap-closure, upon metallization, of the *valence* ($\text{I}-5s^25p^6$) - *conduction* ($\text{Sn}^{4+}-5s^05p^0$) bands.

Mössbauer spectroscopy in ^{129}I proved to be essential for determining the structure of the Ge and Sn iodides upon amorphization. At $P < P_c$ the single quadrupole split site with a **negative** e^2qQ and $\eta = 0$ is typical of a C_{3v} symmetry of the σ -bonded I to the central M ion. It is characteristic of the low pressure (LP) phase (see Fig. 1).

At $P > P_c$ a second spectral component appears, characterized by a **positive** and reduced value of e^2qQ and $\eta = 0.6$ indicative of the formation of π -bonding. This high pressure phase designated as HP1 is due to a strong I-I intermolecular overlap resulting in *molecular association*. In the case of SnI_4 HP1 and LP coexist up to 22 GPa, and HP1 dominates the amorphous phase up to 35 GPa, the highest pressure utilized. HP1 is modeled as disordered chains of $(\text{SnI}_4)_n$ where two out of four iodines are *intermolecular* bonded (see Fig. 2). In GeI_4 , the LP phase exists to 14 GPa, HP1 and coexists with LP in the 14 - 20 GPa pressure range. At 21 GPa a new phase is formed where all four iodines overlap intermolecularly forming a HP2 phase. This 3-D phase has not been observed in SnI_4 although it may appear at $P > 35$ GPa.

2.2 SnBr_4

The ^{119}Sn MS features of the amorphized SnBr_4 molecular crystal are distinctly different from the iodides. Previous Raman and reflectivity studies by Williams and Lee [9] have shown that to the highest pressure measured (25 GPa) there is no gap closure and SnBr_4 remains a *bona fide* insulator.



Upon amorphization at ~ 6 GPa one observes a concurrent onset of a quadrupole interaction, signaling the break of the T_d symmetry, and an abrupt increase of the absorption area, that is of the f -value [10]. In Fig. 3 we present a series of spectra with increasing pressure. Based on the MS and Raman results [11] we proposed a model [11] for the high pressure phase where dimers of $(\text{SnBr}_4)_2$ are the building blocks of the amorphous/insulator SnBr_4 . In Fig. 4 we present a model consistent with these spectroscopical findings.

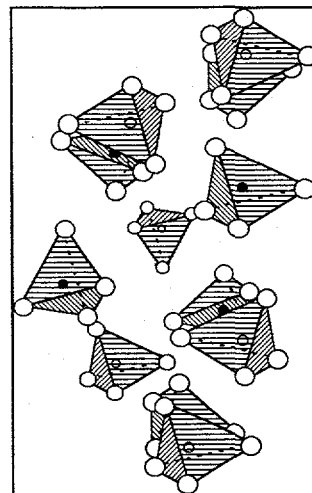
Fig. 3. Typical $^{119}\text{SnBr}_4$ spectra for various increasing pressure. Spectra for $P > 5$ GPa were fitted with a quadrupole splitting (see text).

3 - DISCUSSION and CONCLUSIONS.

In this paper we have shown that the MS by virtue of its unique spectroscopical features was essential for determining structural information of molecular crystals upon amorphization under pressure. Data from both MS and optical spectroscopy studies were combined to provide a realistic model for amorphous high pressure phase of Ge and Sn halides.

The information provided by the quadrupole interaction in ^{119}Sn and ^{129}I and by the recoil-free fraction via the pressure dependence of the absorption area shed new light on the mechanism of polymerization and charge delocalization in the cases of Ge and Sn iodide and on the formation of dimers in the high pressure phase of SnBr_4 .

Fig. 4 A model suggested for amorphous structure for SnBr_4 . The building blocks of this disordered phase is the $(\text{SnBr}_4)_2$ dimer.



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