Metallization and amorphization of the molecular crystals SnI_4 and GeI_4 under pressure

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The insulator-to-metal transition in SnI_4 and GeI_4 was studied as a function of pressure up to 25 GPA by measuring the temperature dependence of the sample resistance inside a diamond-anvil cell. Both materials were found to metallize at well-defined pressures. A model proposed by Pasternak and Taylor in which the tetrahedral iodide molecules are linked to form conducting chains was found to explain both the metallization and amorphization of these molecular crystals.

Pressure-induced metallization of molecular crystals has been the subject of extensive investigations for over fifty years.[1-4] On the other hand, pressure-induced amorphization has attracted much attention only recently.[5-7] To our knowledge, the only molecular crystal that has been shown to undergo both amorphization and metallization under high pressure is SnI_4.[2,6] Thus potentially SnI_4 provides an interesting case for studying these two pressure-induced phenomena. SnI_4 crystallizes in a cubic lattice consisting of tetrahedral SnI_4 molecules[6,8] attracted to each other by weak van der Waal forces. At ambient pressure the crystal is an insulator. In 1963 Rigglemann and Drickamer found that the resistance of SnI_4 decreased by several orders of magnitude under pressure.[2] More recently, Fujii, Kowaka, and Onodera[6] showed by x-ray diffraction that SnI_4 gradually transformed into an amorphous phase between 10 and 20 GPa and also confirmed the electrical measurements of Rigglemann and Drickamer. They noticed that the pressure coefficient of the electrical resistance of SnI_4 changed abruptly around 10 GPa. Although Rigglemann and Drickamer and Fujii, Kowaka, and Onodera both suggested that SnI_4 became metallic at high pressure, neither group determined the exact value of the metallization pressure. Contradictory conclusions on the metallization mechanism in SnI_4 have been obtained from pressure-dependent Raman study and from Mössbauer spectroscopy (MS). Sugai concluded from Raman scattering[9] that SnI_4 molecules dimerized under pressure implying that electrons are still localized in the molecules while Pasternak and Taylor[10] (to be abbreviated as PT) concluded from MS that SnI_4 molecules polymerized to form conducting chains. Thus a number of important questions on the metallization of SnI_4 at high pressure remained unanswered. One question is whether the high-pressure amorphous phase of SnI_4 is metallic or not.

If SnI_4 does become metallic, what is the transition pressure and the metallization mechanism? Furthermore, does amorphization play any role in the metallization process?

In this contribution we present pressure- and temperature-dependent resistance measurements on SnI_4 and isostructural GeI_4. From the temperature dependence of the resistance we determine unambiguously that both materials become metallic under pressure. While SnI_4 transforms gradually from the crystalline phase to the amorphous phase over a pressure range of several GPa, both materials exhibit a relatively sharp insulator-to-metal transition. By comparing our resistance data to the MS data, we conclude that metallization occurs in both SnI_4 and GeI_4 via the formation of I—I bonds which joins the tetrahedral molecular units together to form conducting chains. The same polymerization process is also responsible for the gradual amorphization of SnI_4 observed by Fujii, Kowaka, and Onodera. By applying percolation theory to this model, the pressure dependence of resistance in both materials is explained.

Resistances were measured inside a diamond anvil cell using the technique developed by Erskine, Yu, and Martinez[11] which used $CaSO_4$ powder as the pressure medium. However, we used a true four-probe rather than a quasi-four-probe method to measure the resistance. Polycrystalline samples of SnI_4 and GeI_4 were obtained commercially from Alfa Products. Typical sample sizes were approximately $50 \times 50 \times 10$ μm^3; pressure inhomogeneities were $\pm 5\%$. The resistances were measured at room temperature as a function of pressure with pressure increments of about 1 GPa and as a function of temperature for a number of pressures. Because the pressure inside the cell increased on cooling between room temperature and 80 K, the temperature dependence of the resistance was measured between 4 and 80 K only. All mea-
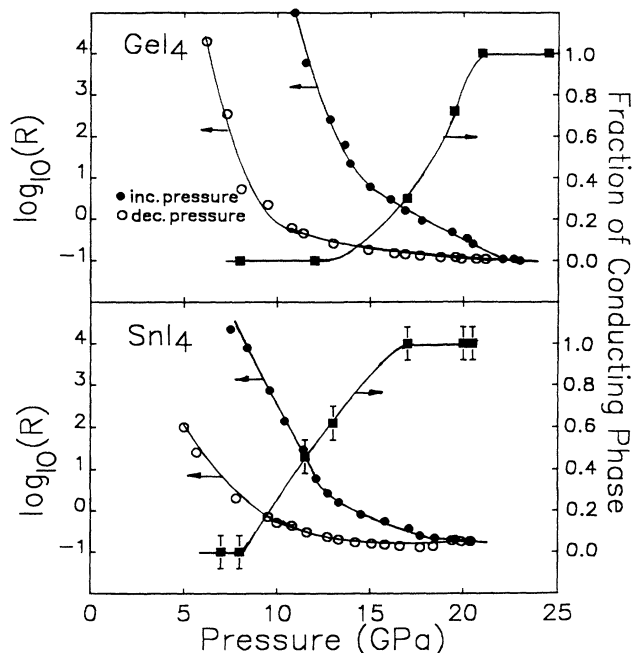
FIG. 1. Logarithm of the resistance of GeI_4 and SnI_4 as a function of both increasing (solid circles) and decreasing (open circles) pressure. Lines through data points are guides for the eye. The changes in slope with increasing pressure occur at 15 and 22 GPa for GeI_4 and 12 and 18 GPa for SnI_4. The fraction of conducting phase (FCP) is a measure of the number of iodine atoms involved in intermolecular bonding as deduced from Refs. 10 and 12 for increasing pressure (see text). FCP is plotted to illustrate the relationship between the decrease in resistance of the iodides and the bonding fraction. The pressure uncertainty of the data is ±5%. Unit of resistance is measured in ohms.

surements were repeated several times and the results found to be completely reproducible.

The room-temperature resistances of GeI_4 and SnI_4 are plotted as a function of pressure in Fig. 1. The results in both samples are qualitatively very similar. The logarithm of the resistance first decreases rapidly (at a rate of ≈ 1 GPa^{-1}) with increasing pressure; then at a well-defined pressure the slope decreases suddenly to a value of about 0.2 GPa^{-1} and finally at a higher pressure the resistance levels off. For GeI_4 the first change in slope occurs at 15±1 GPa while the resistance started to level at 22±1 GPa. In SnI_4 the corresponding changes occur at 12±1 and 18±1 GPa, respectively. Our data on SnI_4 agree qualitatively well with that of Fujii, Kowaka, and Onodera. However, our value of the pressure at which the slope changes suddenly is approximately 2 GPa higher than that reported by Fujii, Kowaka, and Onodera.[6] This difference is within the combined uncertainty of the two experiments. We found 5–7 GPa hysteresis in the pressure dependence of resistance in both materials. For decreasing pressure we find that the resistance increases smoothly with no sudden change in slope.

Figures 2 and 3 show the temperature dependence of the resistance for SnI_4 and GeI_4 for several pressures. The Arrhenius plots facilitate the determination of the
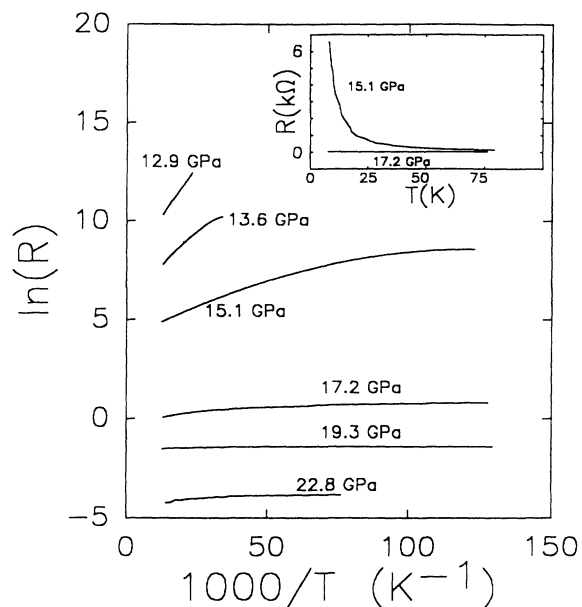

FIG. 2. Arrhenius plots of resistance in ohms of GeI_4 vs temperature for various pressures. The inset is a linear plot of resistance vs temperature. It shows that at 15.1 GPa the resistance diverges at $T=0$ K while at 17.2 GPa the resistance extrapolates to a finite value. This indicates that metallization of GeI_4 occurs around 16±1 GPa.

carrier activation energy. The insulator-to-metal transition can be defined as the pressure at which the activation energy vanishes. The Arrhenius plots are not perfectly straight lines because of pressure homogeneity in our cell which resulted in a distribution of activation energies. Instead we found that a more sensitive way to determine
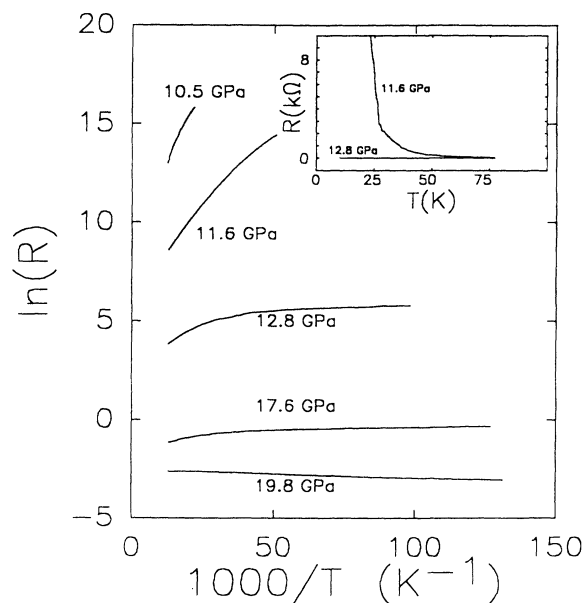

FIG. 3. Arrhenius plot of resistance of SnI_4 similar to Fig. 2. As in Fig. 2, the plot of resistance vs temperature in the inset shows that SnI_4 metallizes at 12±1 GPa.

the metallization pressure is to plot the resistance directly as a function of temperature and define a metal as a state with a finite resistance as the temperature is extrapolated to 0 K. The insets in Figs. 2 and 3 show the resistance versus temperature curves for pressures just below and above the metallization pressures in both iodides. From these curves we conclude that both GeI_4 and SnI_4 become metallic under pressure and their metallization pressures are 16 ± 1 and 12 ± 1 GPa, respectively. If we neglect the slight curvature of the Arrhenius plots we find that the activation energies for conduction in both iodides decrease with pressure at the rate of approximately -5 meV/GPa. Thus the pressure inhomogeneity resulted in a variation of about 10 meV in the activation energy. Extrapolating the activation energies to zero yields metallization pressures in both materials in agreement with the values deduced from the resistance versus temperature curves.

An analysis of the data reveals that a pressure-induced band overlap model does not offer a satisfactory explanation of the metallization. In such a model the conductivity is proportional to the product of the carrier density n and the carrier mobility μ. Assuming that the mobility does not change drastically with pressure P, the resistivity ρ would be inversely proportional to n which depends exponentially on the activation energy E according to the expression $\exp(-E/k_BT)$ where k_B is the Boltzmann constant. Assuming that the activation energy depends on the pressure linearly, $E(P)=E_0+\alpha P$ where α is the pressure coefficient of E, then $d\ln(\rho)/dP=\alpha/k_BT$. Applying this expression to the data in Fig. 1 in the insulating phase resulted in $\alpha\approx-50$ meV/GPa for both materials. This is a rather large pressure coefficient for the band gap of a molecular solid even considering the large compressibility of such molecular crystals. This value of α is not consistent with the value of about -5 meV/GPa obtained directly from the Arrhenius plots. This model also cannot explain why the changes in the slope of the $\log_{10}(R)$ vs P curves, which occur at 12 and 18 GPa, are almost coincident with the onset and completion of the amorphization process. It also is not clear why the resistance of the sample in the metallic state continues to decrease with pressure but levels off when the sample becomes completely amorphous.

Alternatively, our resistance results can be understood qualitatively based on the model proposed by PT to explain their MS results.[10] MS results in SnI_4 suggested that intermolecular I—I bonding started to form above 8 GPa. The percentage of iodine atoms involved in forming the I—I bonds increases approximately linearly with pressure from 0% to 50% for P varying between 8 and 17 GPa. MS study on GeI_4 revealed similar behavior between 13 and 21 GPa.[12] Based on the MS results, PT suggested that the formation of the I—I bonds between the tetrahedral SnI_4 molecules causes the molecules to tilt and resulted in the gradual amorphization of the crystal. The formation of the I—I bonds also links the SnI_4 molecules to create polymeric chains. If these polymeric chains are conducting, this model explains the strong decrease in the resistance of SnI_4 in the pressure range of 8–18 GPa and also the leveling off of the resistance
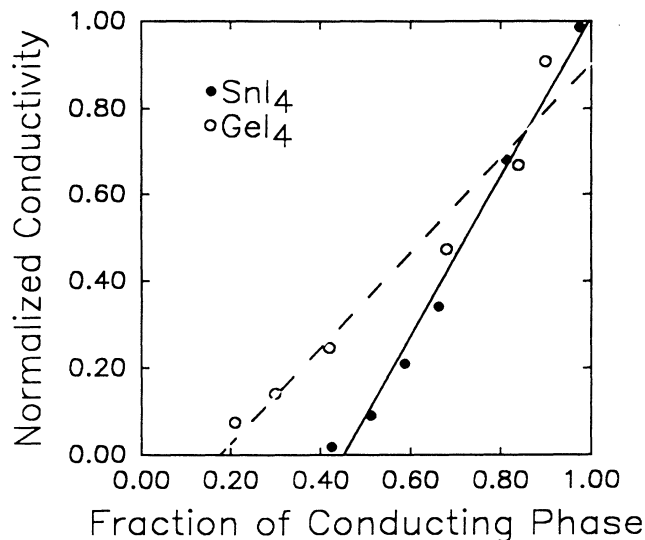

FIG. 4. Conductivity of GeI_4 and SnI_4 vs fraction of conducting phase (FCP) (see text) showing the approximately linear behavior above the critical FCP. Lines are least-squares fits to the data. Extrapolation yields critical FCP of approximately 0.4 and 0.2 for SnI_4 and GeI_4, respectively. The conductivity is normalized to the conductivity at maximum FCP. Pressure is translated into FCP using data from Ref. 10 and 12 (also shown in Fig. 1).

beyond 18 GPa where the fraction of iodine atoms forming I—I bonds saturates.

The pressure dependence of resistance in both iodides can be analyzed quantitatively by applying percolation theory to the polymeric chain model of PT. The SnI_4 molecules are the lattice sites in a percolation problem while the conducting paths between the sites are provided by the formation of the I—I bond. In the ideal percolation case the conductivity should remain zero until a critical fraction of the sites is joined by conducting paths. The critical fraction depends on the specific geometry of the problem, but is generally between 0.2 and 0.3 for the three-dimensional networks.[13] When the fraction of conducting paths formed is much higher than the critical fraction, percolation theory predicts that the conductivity increases approximately linearly with the fraction of conducting bonds.[13] (Only very near the critical fraction is the conductivity described by the so-called critical exponent.) The fraction of conducting paths linking the sites in our case can be deduced from the MS data. According to the MS data[10] the fraction of iodine atoms involved in forming I—I bonds increases almost linearly with pressure between 8 and 17 GPa for SnI_4. Above 17 GPa the fraction of iodine atoms in I—I bonds reached the saturation value of 0.50. We will define the fraction of iodine atoms that are in I—I bonds normalized by the saturation value as the fraction of conducting phase[14] (FCP) and plot its pressure dependence in Fig. 1. Thus within this model, the critical fraction can be determined from the MS data by reading off FCP at the metallization pressure (P_m). Using this definition we determined the critical FCP to be about 0.2 and 0.4 for GeI_4 and SnI_4, re-

spectively. In Fig. 4 we have replotted the conductivity of both SnI_4 and GeI_4 as a function of the FCP instead of pressure. The conductivity has been normalized to the value of the conductivity achieved when the maximum bonding fraction is reached. In both cases the conductivity increases approximately linearly with FCP. Considering the uncertainties in the experiments, we conclude that the experimental results are in good agreement with percolation theory. Percolation theory also explains why metallization occurs at a pressure (12 GPa) that is higher than the pressure at which amorphization begins (10 GPa) since a critical fraction of the material has to be in the conducting phase before a continuous conducting pathway traverses the entire sample. Once the system is metallic, further increase in the conducting phase decreases the resistance more slowly. The resistance finally levels off at 18 GPa as all the molecules are linked by conducting I—I bonds.

In the case of GeI_4 there is no x-ray diffraction data to provide information on pressure-dependent structural changes, but a comparison of the resistance data with the MS data also supports the polymerization model. Thus we predict that GeI_4 will begin to amorphize around 13 GPa and become completely amorphous by 21 GPa.

The polymerization model also explains qualitatively the hysteresis in the pressure dependence of the resistance in both iodides. We expect that the reversion to the insulating state upon decompression should coincide with the breakup of the intermolecular bonding measured by MS. MS measured a precipitous decrease in the number of intermolecular bonds at approximately 3 GPa in SnI_4. On decompression we found that the resistance increased rapidly between 7 and 5 GPa. However, the resistance data for decreasing pressure were not as reproducible as the data for increasing pressures and the pressure was also not as homogeneous. Considering these experimental difficulties there is still fairly good agreement between the x-ray, MS, and electrical resistance data on decompression in SnI_4.

We have determined, by temperature- and pressure-dependent resistance measurements the metallization pressure of GeI_4 and SnI_4. By correlating features in the pressure-dependent resistance data with the MS results we conclude that SnI_4 transforms under pressure into a metallic, intermolecularly bonded amorphous solid. The electrical properties of this metallic state are explained satisfactorily with percolation theory.

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[14]The interpretation of the data of GeI_4 (see Ref. 12 for details) is complicated by the emergence of another type of intermolecular I—I bond (denoted by PT as $I_{b\sigma}$) above 21 GPa. The I—I bonds that form in SnI_4 (denoted as $I_{b\pi}$ by PT) also form in GeI_4 between 13 and 21 GPa. For GeI_4 we define the number of I—$I_{b\pi}$ bonds normalized to the saturation value of I—$I_{b\pi}$ as the fraction of conducting phase (FCP).