

Semiconductor–metal transition in amorphous gallium antimonide at high pressure

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The mechanism for the pressure-induced semiconductor–metal transition has been studied in bulk samples of amorphous gallium antimonide. The test samples were synthesized by solid-phase amorphization of the high-pressure GaSb II crystalline modification. The transition of α -GaSb to the metallic state at $P \approx 3.5$ – 4.0 GPa is accompanied by a significant anomaly in the compressibility and by irreversible relaxation processes. It is concluded that the transition of α -GaSb to a metallic phase cannot be caused by a restructuring of the electron subsystem alone. It involves a change in the structure of the tetrahedral amorphous network and a transition of this network into a more compact state.

1. Amorphous tetrahedral semiconductors (Si, Ge, and III–V compounds) at high pressures have received much less study than several other classes of disordered solids, e.g., glassy chalcogenide semiconductors and oxide glasses. Until recently, the use of a variety of experimental methods has been held up by the lack of bulk samples of amorphous tetrahedral semiconductors. New opportunities have now been opened up by the development of methods for synthesizing bulk samples of certain of these semiconductors [GaSb (Ref. 1) and Si and Ge (Ref. 2)] by solid-phase amorphization of high-pressure phases. In this letter we are reporting a study of the mechanism for the semiconductor–metal transition in bulk α -GaSb samples at high pressure.

Structural studies of α -GaSb thin films³ have shown that over the pressure range 3–10 GPa the amorphous semiconductor undergoes a progressive transformation into a disordered, more closely packed phase with a short-range order characteristic of the crystalline modification GaSb II (a β -Sn structure with $z=6$). The metallization of amorphous films sets in below the pressure of the equilibrium GaSb I–GaSb II transition ($P_{tr}=6.2$ GPa; Ref. 4). An important distinguishing feature of the behavior of α -GaSb films is the absence of any crystallization process at pressures near the semiconductor–metal transition (at room temperature), in contrast with, for example, α -Ge (Ref. 3). It was suggested in Ref. 5 that a structural change in α -GaSb (in the pressure interval $P \sim 5.5$ – 6 GPa) is preceded (at $P \sim 3$ – 5 GPa) by an electronic nonmetal–metal transition of the Anderson type. Nevertheless, the mechanism for the semiconductor–metal transition in the case of α -GaSb remains unclear. We have studied the electrical conductivity of α -GaSb samples at various pressures and temperatures, the nature of the reversibility of the transition as the pressure is varied, and the compressibility of bulk samples. The results of this study allow some progress toward a resolution of this problem.

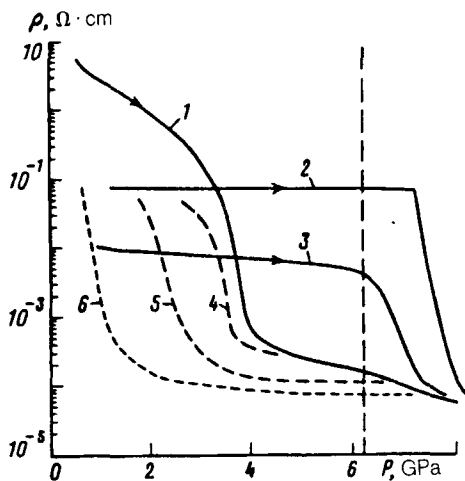


FIG. 1. Pressure dependence of the resistivity in the course of the semiconductor–metal transition. 1—Amorphous gallium antimonide; 2—GaSb single crystal; 3—polycrystalline GaSb sample. Curves of the inverse transitions (4–6) in GaSb are shown for various maximum loads. The vertical dashed line shows the pressure of the equilibrium GaSb I–GaSb II transition.

2. The high-pressure experiments were carried out under quasihydrostatic conditions in chambers of the Toroid type,⁶ calibrated on the basis of transitions in Bi (2.55, 2.7, and 7.7 GPa). The method for synthesizing the α -GaSb samples is described in Ref. 7. The absolute value of the resistivity of a sample was measured by the van der Pauw four-contact method. The compressibility was studied with the help of a resistive strain gauge, by the technique developed in Ref. 8, which we adapted here for quasihydrostatic conditions. In the experiments with NaCl containers, the strain-gauge technique yielded semiquantitative results: The compressibility was measured relatively accurately upon smooth variations in the sample volume V , while a large error was observed when V changed rapidly. Special calibration measurements were carried out on crystalline samples of GaSb and InSb. All measurements were carried out at room temperature. It was possible to heat or cool the samples slightly ($\sim 50^\circ\text{C}$); these temperature changes were measured by a Chromel–Alumel thermocouple. The phase composition of the α -GaSb samples before and after the high-pressure experiments was monitored by x-ray diffraction.

3. Figure 1 shows the resistivity ρ as a function of the pressure for bulk α -GaSb samples. Shown for comparison are data on $\rho(P)$ of crystalline gallium antimonide. The transition of α -GaSb to the metallic state is observed at $P_{\text{met}} \sim 3.5\text{--}4.0$ GPa. The characteristic values of the resistivity immediately after the completion of the semiconductor–metal transition are an order of magnitude higher than the values of ρ of the crystalline modification GaSb II. At $P \sim 4\text{--}7$ GPa, the α -GaSb samples are thus still in a highly disordered state, or they contain a substantial admixture of disordered phases. Important conclusions can be drawn from an analysis of the $\rho(P)$ curves for the inverse transitions, recorded at various maximum loads P_{max} (curves 4–6 in Fig. 1). We first note the hysteresis in the inverse metal–semiconductor transition as the pressure is lowered (curve 4). A hysteresis is atypical of a purely electronic mechanism for carrier delocalization.⁹ Second, the significant shift in the hysteresis of the inverse transition with increasing P_{max} (curves 5 and 6) indicates that the α -GaSb samples undergo a structural transformation in the pressure interval 4–8 GPa. This

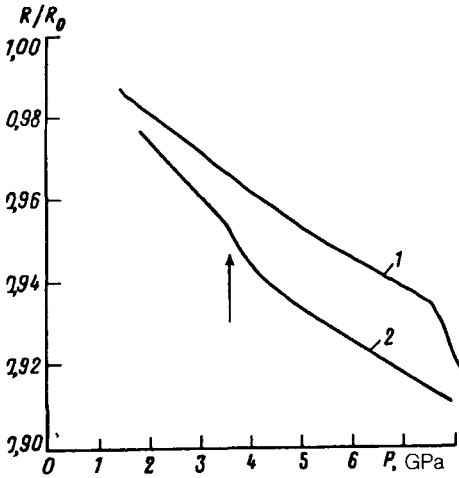


FIG. 2. Pressure dependence of the resistance of the strain gauge in the cases of (1) crystalline and (2) amorphous gallium antimonide. A decrease in R/R_0 corresponds to a decrease in the length of the strain gauge and thus a decrease in the linear dimensions of the sample. The bulk modulus is inversely proportional to the slope of the $R(P)$ curve in the course of a smooth, reversible change in volume. The arrow marks the anomaly in the compressibility of α -GaSb at the semiconductor-metal transition.

transformation can apparently include a compaction of porous regions with a low coordination number $Z \sim 4$ and a crystallization in the high-pressure GaSb II phase. After the pressure is removed, the samples remain amorphous.

We carried out the first direct study of the $V(P)$ dependence for the case of bulk α -GaSb samples. We found that in the vicinity of the semiconductor-metal transition (at $P \sim 3.5$ – 4.5 GPa) there is an anomaly in the compressibility, which is comparable in magnitude to (a bit lower than) the jump in volume in the course of the GaSb I–GaSb II phase transition (Fig. 2). It is thus clear that the metallization of α -GaSb is accompanied by a structural compaction of the amorphous semiconductor, which results in the formation of regions with a metallic conductivity. It can be seen in Fig. 2 that the bulk modulus of α -GaSb at 1.5–3 GPa is lower than that of the GaSb I single crystal. This result agrees qualitatively with calculations which have been carried out¹⁰ for a continuous random network.

The modification in structure is evidently accompanied by changes in the electron subsystem of the semiconductor, which lead to irreversible changes in the electrical conductivity. If the semiconductor-metal transition in α -GaSb is due to structural changes in an amorphous network, then at a fixed pressure in the region of the forward transition one could thus expect to see a relaxation decrease in ρ as time elapses. Such changes were indeed observed in α -GaSb. In our case, the test samples were heated slightly ($\Delta T \sim 20^\circ\text{C}$) at $P = \text{const}$. After they were returned to room temperature, the change in resistivity, $\Delta\rho$, was measured. Data on $\Delta\rho/\rho(P)$ are shown in Fig. 3. We clearly see the onset of relaxation processes at $P > 1$ GPa and a substantial intensification of these processes toward the semiconductor-metal transition ($P \sim 3$ GPa). In

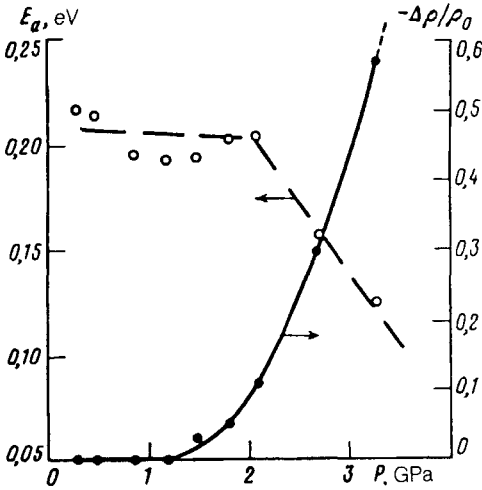


FIG. 3. Pressure dependence of the conductivity activation energy and of the amplitude of the relaxation change in the resistivity during temperature cycling (a heating by 20 °C followed by a return to room temperature at $P = \text{const}$).

the same pressure region we observe a sharp decrease in the activation energy (E_a) for the temperature dependence of the conductivity. Beyond this point, it becomes meaningless to determine E_a . We have thus found further arguments in favor of the “structural” model for the metallization of α -GaSb.

4. The microscopic mechanism for the substantial change in the behavior of the amorphous phase under pressure nonetheless remains unclear (Figs. 1 and 2). The amorphous tetrahedral network has the same short-range order as a diamond-like crystal lattice ($z=4$). The basic difference between the tetrahedral amorphous network and the crystal is the presence of fluctuations in the lengths of the bonds and in the angles between bonds. These fluctuations cause a local nonuniformity in the stresses and dynamic characteristics of the tetrahedral network at the atomic scale. Under pressure, these effects should result in a dispersion of the compressibility of various atomic configurations and in topological distortions of the amorphous network, in contrast with the uniform compression of a crystal lattice. Such distortions might be caused by either a smooth change in the geometry of the network or diffusive hops of atoms to new local minima. At a certain degree of local distortion of the tetrahedral coordination of the bonds, the sp^3 valence electrons should apparently undergo a delocalization, which would in turn change the specific atomic volume in the given part of the amorphous network.

Arguing in favor of this interpretation are data on the elevated compressibility and the appearance of relaxation processes at $P \sim 1$ GPa. These processes appear to correspond to a structural modification of the semiconductor. In the case of binary α -GaSb, we should furthermore not rule out a significant role of a chemical disorder, i.e., the presence of a significant number of Ga–Ga and Sb–Sb bonds.

In summary, these experimental data make it possible to rule out an interpretation of the semiconductor–metal transition in α -GaSb on the basis of a purely electronic mechanism. The data indicate a structural modification and a compaction of the amorphous network near the transition. However, a final resolution of this problem

will require direct structural studies at high pressure of both the intermediate-range and short-range order (by the EXAFS method, for example).

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