Reports

Superconductivity of Metallic Aluminum Antimonide

Abstract. *The high-pressure metallic phase of aluminum antimonide is superconducting [critical temperature T_c ($P \sim 125$ kilobars) $= 2.8° \pm 0.2°K$]. This transition temperature is significantly lower than the transition temperature of metallic germanium under an equivalent high pressure. A similar result had been previously found for superconducting indium antimonide in comparison to tin.*

Aluminum antimonide transforms from the ordinary semiconducting phase to a metallic, "white tin" structure polymorph at approximately 125 kb at room temperature (*1*). The superconducting properties of the heavier Sb-compounds InSb and GaSb had been investigated recently (*2*). Some features of the superconducting properties of group IV elements Si and Ge (forced into the metallic state by application of high pressure) have been determined (*3*). On the basis of these measurements the following empirical relation seemed possible. Group IV elements Si, Ge, and Sn have transition temperatures which are, coarsely speaking, proportional to the inverse square root of their atomic mass. The superconducting properties of isostructural metallic versions of compounds of groups III-V may lend a further insight into this relation. If the relation is valid for these substances we may predict a monotonic increase in transition temperature in the sequence InSb, GaSb, and AlSb when going from heavier to lighter compounds. Quantitatively, if there is no other influence on transition temperature than mean atomic mass dependence, one would expect for AlSb nearly the same transition temperature as for metallic germanium (5.35°K) (*3*).

At the beginning of a study (*3*) of superconducting properties of compounds of groups III–V under high pressure, AlSb was examined. I now report results and compare them with measurements on InSb and GaSb made by others (*2*). The high-pressure cell and the experimental procedure has been described (*3*). Briefly, a powder sample of AlSb (*4*) was compressed in an electrical four-lead Bridgman-type pressure cell with a hydraulic press. This assembly makes possible the calibration of the internal pressure in that the dependence of the sample resistance on pressure can be observed, and well-established pressures at room temperature can be used as reference points on the high-pressure scale. In this report the drop in resistance associated with transition of semiconductor to metal, when AlSb is under pressure, is the reference indicating a pressure of about 125 kb, according to the data of Minomura, Drickamer, and Jamieson (*1*). Pressure is conserved for the low-temperature measurement by the fixed-clamp technique of Chester and Jones (*5*).

In the first type of measurement, pressure was applied at room temperature, and a typical plot of sample resistance against press load is shown in Fig. 1 (solid line). The sharp resistance drop of nearly three orders of magnitude indicates the semiconductor-to-metal transformation in the neighborhood of 125 kb. The resistance of sample tapers to about 100 milliohms, an indication [as in the case of other substances, Si, Ge (*3*), and Se (*6*)] that the sample is metallic. When the sample is cooled down to the temperature of liquid helium from point A (Fig. 1), under constant pressure only a slight decrease (10 percent) of electrical resistance with temperature was found. The same behavior was observed for all other samples. That means that the residual resistivity ratio $R(300°K)/R(4.2°K)$ was always near unity. Such a ratio of samples which were presumably completely in the metallic state (because pressure sometimes was far beyond the transition pressure) may be expected because of similar observations on metastable metallic InSb (*2*). A constant current of about 100 μa gave an easily measured voltage drop. Thus power dissipation in the high-pressure cell is kept near 10^{-9} watt. The width of the normal-to-superconducting transition (labeled A in Fig. 2) taken between 10 and 90 percent of normal resistance amounts to about 0.4°K. The transition is centered at 2.8°K. The sluggishness of the pressure-induced phase transformation at 300°K and a probably positive pressure coefficient dT_c/dp of AlSb may be responsible for the broadness of the transition. Both items, the poor residual resistivity ratio and the broadness of the observed superconducting transitions await further study.

In a second type of experiment, the cell was loaded to about 1.3 tons at room temperature, a pressure at which good contact seemed to be established between AlSb powder grains. The high-pressure apparatus was cooled, at constant pressure, in a bath of liquid air to 80°K. Resistance of the sample increases by two orders of magnitude, revealing that the sample is still semiconducting (Fig. 1). At 80°K the pressure was increased gradually, and resistance decreased, again with constant slope (Fig. 1). When 5.0 tons was reached resistance of the sample began to drop rapidly, indicating that transformation of the semiconductor to metal has set in. The high-pressure experiment was finished at point *B*, Fig. 1. This partially transformed sam-

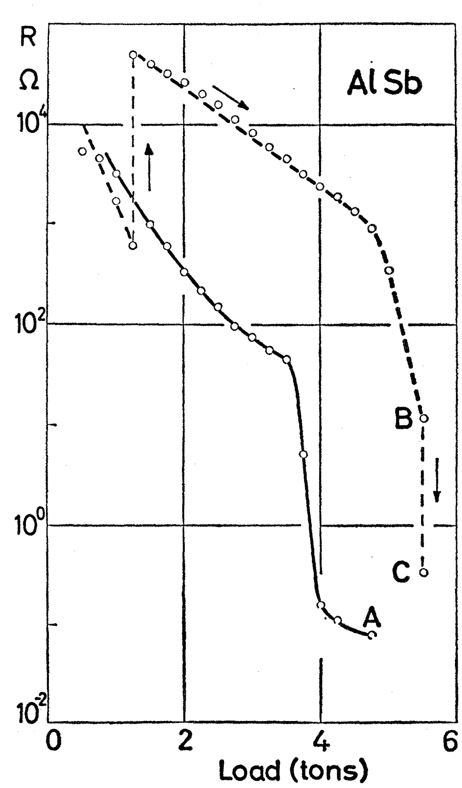

Fig. 1. Resistance plotted against load of AlSb for two different samples at 300° and 80°K.

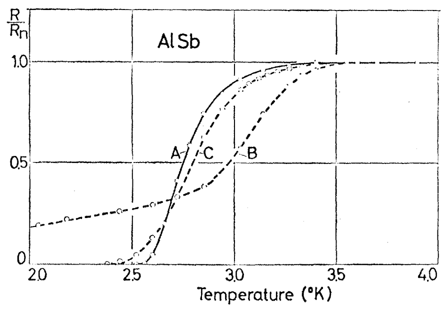

Fig. 2. Normal-to-superconducting transitions of AlSb samples. The letters correspond to the indicated points of Fig. 1.

ple became superconducting, with a very broad transition curve which had a long tail extending to lower temperatures (Fig. 2). Annealing this sample under constant pressure to about 100°C caused further transformation to the metallic state, as evidenced by an irreversible drop in resistance near room temperature which occurred during warming up (vertical dashed line in Fig. 1, ending in point *C*). The sample was again cooled under constant pressure, and as a result of annealing exhibited a much more sharp transition to the superconducting state at about 2.8°K (curve C, Fig. 2).

Previous results on InSb and GaSb (*2*) suggest that the high-pressure metallic phase of AlSb may be quenched at 80°K, if the pressure is cautiously removed at this low temperature. Several experiments completely failed because of blow outs of the interior of the pressure cell when the pressure was released. The use of an overall pyrophyllite-cell (*3*) seems a possible solution to this experimental problem apparently arising from a change in mechanical properties (such as internal friction) of cell materials with temperature. But no successful experiment has been carried out up to the present time.

Metallic AlSb is a superconductor with a critical temperature T_c ($P \simeq 125$ kb) equal to 2.8 ± 0.2°K. As expected from the simple mass rule this transition temperature is higher than that of InSb. For metastable metallic GaSb, values of T_c between 4.2 and 6.0°K under zero pressure are reported, depending on the kind of treatment by heat of the samples before they were quenched at 80°K to zero pressure. A comparison of transition temperatures seems to be reasonable at corresponding points of the isomorphous phase diagrams of these substances, for example, at their different equilibrium transition pressures between the semiconductor and metal stability fields. The pressure dependence of T_c of metallic GaSb and InSb has not yet been determined. A pressure which, in the case of GaSb, is about 70 kb below the equilibrium transition pressure may cause a remarkable shift in T_c. Therefore the reported values of T_c on GaSb cannot be compared with the T_c of AlSb, the latter studied under equilibrium pressure. This argument holds up for metastable InSb too, but the resulting shift in T_c will probably be much smaller because the transformation pressure for this substance is only about 20 kb.

Perhaps another difficulty arises from the fact that T_c values compared were determined by various methods. It seems to me that alternating-field induction methods, often preferred, are, in principle, resistance measurements with a different (that is circular) geometry. Therefore I do not believe that normal-to-superconducting transitions measured by a four-electrode technique differ essentially from results obtained by other methods.

New results have given some impetus to the idea that the superconducting transition temperatures of group IV elements and III-V compounds may be closely related to one another in a simple systematic way. A well-known high-pressure modification of tin has a transition temperature T_c ($P = 113$ kb) equal to 5.3°K (*3*). Minomura and co-workers (*7*) observed a pressure-induced phase transformation in InSb at about 80 kb which was accompanied by a small increase in resistance quite similar to that in the tin transition (*3*). This new high-pressure modification of InSb presumably has been quenched under the conditions of their experiments and exhibits a high critical temperature T_c ($P = 0$ kb) equal to 4.8°K, once again in analogy to the behavior of the high-pressure modification of pure tin which, indeed, has a higher critical temperature than the ordinary low-pressure modification (*3*).

This picture is, perhaps, an oversimplification of the situation because Kasper and Brandhorst (*8*) found an orthorhombic high-pressure phase near 30 kb for InSb in addition to the well-confirmed tetragonal high-pressure phase. The stability conditions of the various high-pressure modifications (there seem to exist at least three) are not known unambiguously at the present time. Therefore, the above-mentioned comparison of the behavior of Sn and InSb is tentative.

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Indium as an Impurity in Ancient Western Mexican Tin and Bronze Artifacts and in Local Tin Ore

Abstract. *The presence of indium in a nodule of cassiterite from the State of Guerrero increases the probability that ancient tin and bronze artifacts from Guerrero, which contain indium as an impurity, were made locally from metal extracted from local tin ore.*

At the 35th International Congress of Americanists in Mexico City in 1962, we presented evidence of tin smelting and the use of metallic tin in pre-Conquest Mexico, more specifically in the State of Guerrero (*1*). We noted that our analytical results for two, nearly pure, tin fragments of lip plugs found by D. F. Rubín de la Borbolla in 1957 at Teloloapán near Taxco were very unusual. One fragment containing 99.65 percent Sn had 0.12 percent In as an impurity. The other fragment contained 99.71 percent Sn with 0.09