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New Phase Transformation in InSb at High Pressure and High Temperature

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A new phase transformation at high pressure and elevated temperature has been found in the InSb pressure–temperature phase diagram. This transformation to a new phase designated as InSb-III has been established by measurements of superconducting transition temperature (T_c) as a function of annealing temperature at several pressures and by x-ray determinations on the new phase, both retained at one atmosphere and at high pressure and temperature. The higher T_c for InSb-III ($T_c = 4.1° \pm 0.1°$K) and the x-ray results lead to the conclusion that InSb-III is a new phase different from the orthorhombic phase ($T_c = 3.5°$K).

INTRODUCTION

THE P–T phase diagram for InSb has been extensively studied.[1–3] It is generally agreed that the transformation at 23 kbar and 25°C is from the cubic, B3 (zinc blende) structure of InSb-I to the tetragonal, B7 (β-Sn) structure of InSb-II.[3–6] Since InSb-II can be retained[7] as a metastable phase at atmospheric pressure by cooling below 190°K, many of the properties of this phase have been investigated. These have included compressibility,[5] density,[3,5] resistivity,[5,8] and superconducting transition temperature.[9,10]

Various types of high-pressure apparatus have been used in the preparation of samples for these studies. Specimens of InSb-II, for retention as the metastable phase at one atmosphere, have been prepared generally in equipment which applied little internal shear to the sample. Therefore, annealing under pressure has been required[7] to completely transform all of the InSb-I phase which, if present, could act as nucleation sites for the re-transformation of InSb-II. On the other hand, x-ray studies under pressure have, with one exception,[6] been performed with Bridgman-anvil-type equipment which applies a large amount of shear to the specimen. Shear has been demonstrated to greatly accelerate transformations under pressure.[11] Therefore, in experiments in high-shear pressure equipment, transformations may appear at much lower pressures than are found in equipment with essentially hydrostatic pressure chambers. However, in experiments with small diameter Bridgman anvils, the actual pressure on the specimen is difficult to determine without an internal standard.

Some of the inconsistencies among the data on the structure and properties of the high-pressure phases of InSb probably result from the variations in experimental methods and also from the fact that most experimenters have studied a single property (e.g., x-ray structure) or a single variable (e.g., pressure). We have been attempting to resolve these inconsistencies by investigating the structures both of the retained phases and of the phases while under pressure at elevated temperatures. On the retained high-pressure phases, we have also studied the electrical resistivity and the superconducting transition temperature (T_c); a concurrent investigation has been concerned with thermodynamic properties.[12] Our work has not only helped to explain some of the data obtained earlier but has also shown the existence of a new high-pressure-high-temperature phase transformation for InSb. This transformation, to a phase designated as InSb-III, has been established by measurements of T_c as a function of annealing temperature at several pressures and by x-ray determinations on the new phase, both retained at one atmosphere and at high pressure and temperature. (The referee has called our attention to unpublished resistance data of Y. Kato, Hitachi Co., Tokyo, which indicate the occurrence of a phase transformation in the vicinity of the boundary between InSb-II and InSb-III established in the present study.)

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[1] A. Jayaraman, R. C. Newton, and G. C. Kennedy, Nature **191,** 1288 (1961).

[2] M. D. Banus, R. E. Hanneman, A. N. Mariano, E. P. Warekois, H. C. Gatos, and J. A. Kafalas, Appl. Phys. Letters **2,** 35 (1963).

[3] R. E. Hanneman, M. D. Banus, and H. C. Gatos, Phys. Chem. Solids **25,** 293 (1964).

[4] J. C. Jamieson, Science **139,** 845 (1963).

[5] A. J. Darnell and W. F. Libby, Phys. Rev. **135,** A1453 (1964).

[6] J. S. Kasper and H. Brandhorst, J. Chem. Phys. **41,** 3768 (1964).

[7] A. J. Darnell and W. F. Libby, Science **139,** 1301 (1963).

[8] M. D. Banus, Lynne B. Farrell, and A. J. Strauss, J. Appl. Phys. **36,** 2186 (1965).

[9] H. E. Bömmel, A. J. Darnell, W. F. Libby, and B. R. Tittman, Science **139,** 1301 (1963).

[10] S. Geller, D. B. McWhan, and G. W. Hull, Jr., Science **140,** 62 (1963).

[11] F. Dachille and R. Roy, *Modern Very High Pressure Techniques*, R. H. Wentorf, Jr., Ed. (Butterworth, New York, 1962), pp. 175–179.

[12] A. Jena, M. B. Bever, and M. D. Banus, Trans. AIME (in press).

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EXPERIMENTAL

Specimens of the high-pressure phases of InSb for retention at one atmosphere were prepared in a "belt-type" high-pressure chamber by the techniques previously described[8] with 0.6–0.8 g of Cominco semiconductor-grade InSb. The melting, annealing, and quenching temperatures were measured and controlled with chromel–alumel thermocouples, the hot-junction being within 0.5 mm of the specimen. The pressure of 37, 52, or 65 kbar was applied to the specimen at room temperature. For most specimens the cycle followed was: heat into the liquid region (400°–475°C depending on the pressure) for 1–2 h, quench to room temperature, and then heat to the desired annealing temperature for 20 h to 11 days depending on the pressure and temperature. After annealing, the specimens were cooled to ~125°K by passing liquid nitrogen through the jacket of the "belt" die before releasing the pressure. The specimens were subsequently handled and stored under liquid nitrogen to prevent retransformation of the metastable high-pressure phases.

The superconducting transition temperature (T_c) for all specimens was measured (usually within 24–48 h of their preparation) by the self-inductance technique.[13] The frequency change vs temperature curves are sharp for single phase specimens. An extended region of gradual change at either the start or the end of the curve was observed if a small amount of second phase was present. In a few cases, two distinct breaks in the curve suggested nearly equal quantities of two phases. The temperature at the midpoint in the fractional change of frequency was taken as T_c. Repeated measurements on the same specimen were reproducible to ± 0.02°K.

The resistivities of the freshly prepared samples were measured at 77°K in a spring loaded four-point probe using the van der Pauw technique.[14] The resistivity of the specimens varied from 1 to 7×10^{-5} Ω·cm without any correlation with the method of treatment or the resulting phase. Traces of impurities from the boron nitride pressure cell were probably responsible for the variation.

The retained phases were investigated at 120°–150°K by x-ray diffraction with a Norelco diffractometer equipped with a low-temperature stage. The samples were held in a copper specimen holder with a lead glass plate to absorb the diffraction from the copper (see Fig. 1). The temperature was measured with a copper–constantan thermocouple in contact with the sample. To avoid retransformation to InSb-I by deformation, an end of the cylindrical specimen or an internal cleaved surface was mounted in the specimen holder without any further treatment.

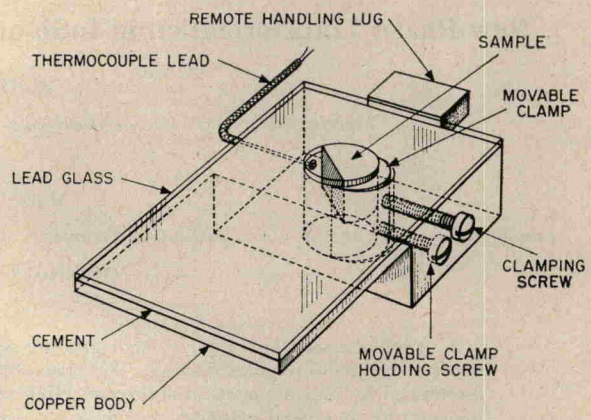

FIG. 1. Schematic diagram of the sample holder for the low-temperature stage for use with the Norelco diffractometer.

X-ray diffraction films were obtained at high pressures and temperatures in an M.R.C. high-pressure x-ray camera equipped with diamond anvils and a heater. In this unit the x-ray beam, collimated to 0.010 in., passes through the specimen parallel to the pressure axis and strikes the x-ray film at some set distance.

A 0.010-in.-diam specimen is located along the axis of a 0.080-in.-diam by 0.013-in.-high boron–epoxy sample cell. The pressure gradient across the portion of the sample intersected by the beam is minimized by the small diameter of the beam. This gradient is estimated to be from 20 to 50 kbar at an average pressure of 35 kbar and 40 to 80 kbar at 60 kbar average. In the experiments with this camera, the average pressure was increased by increments of about 5 kbar at room temperature (starting at 20 kbar) until the resulting pattern showed only the β-Sn-type structure. Beyond this, the pressure could be raised further at room temperature, or alternatively the temperature of the diamond anvils and sample could be raised to ~300°C. Exposures of at least 36–48 h were required for readable film patterns at high pressures and elevated temperatures. The sample chamber was swept with dry N_2 gas throughout the temperature run to prevent oxidation of the samples and heater.

RESULTS

The existence of the InSb-II–InSb-III transformation is demonstrated by the plot of the superconducting transition temperature (T_c) vs the annealing temperature at 37 and 52 kbar shown in Fig. 2. Only specimens with sharp, single transitions have been included in this figure. The abrupt change in T_c between specimens annealed at 300° and 315°C at 37 kbar shows that the transformation from InSb-II ($T_c=2.0\pm0.1$) to InSb-III ($T_c=4.1\pm0.1$) occurs at 308°±7°C at this pressure. At 52 kbar, the transformation temperature is 287°±12°C. The negative sign of dT/dP for this phase boundary is consistent

[13] T. B. Reed, H. C. Gatos, W. J. LaFleur, and J. T. Roddy, *Metallurgy of Advanced Electronic Materials*, G. E. Brock, Ed. (Interscience Publ. Inc., New York, 1963), p. 71.
[14] L. J. van der Pauw, Philips Res. Rept. **13**, 1 (1958).