C. NEW PHASE TRANSFORMATION IN InSb AT HIGH PRESSURES AND TEMPERATURES

The high-pressure phase of InSb with β-Sn structure, InSb(II), can be retained at atmospheric pressure by cooling to below 180°K before removing the pressure. This phase has a superconducting transition temperature of 2.1°K. In recent solution calorimetry experiments* at atmospheric pressure, undertaken to measure the heat of transformation of InSb(II) to the atmospheric pressure form InSb(I), it was found that the quantity of heat evolved on solution in molten tin was significantly different for samples annealed close to liquidus temperature than for those annealed at lower temperatures. Furthermore, the higher temperature samples had x-ray diffraction patterns at 170°K and atmospheric pressure inconsistent with the β-Sn structure, and their superconducting transition temperature T_c was 4.0° to 4.1°K. These observations suggested the possibility of a new high-pressure phase transformation in InSb at elevated temperatures. The existence of such a transformation, to a phase which we have designated as InSb(III), has been confirmed by measurements of T_c as a function of annealing temperature.

The samples to be measured were annealed in a belt-type high-pressure unit. Some were held at 450°C, above the liquidus, for an hour prior to annealing at lower temperature, while the rest were not melted before annealing. After annealing, the belt unit was cooled to about 130°K before the pressure was released, in order to retain the high-pressure phase. One series of samples was prepared at 37 kbar by annealing for 20 hours, a period found to be long enough to establish equilibrium at all the temperatures investigated. The T_c values, which were measured by a self-inductance technique, are plotted against annealing temperature in Fig. III-5. The abrupt change in T_c between 300° and 315°C shows that at 37 kbar the transformation from InSb(II) to InSb(III) occurs at 308° ± 7°C.

A second series of samples was annealed at 52 kbar. To establish equilibrium at this pressure, it was necessary to anneal for 40 to 100 hours, depending on temperature. Until equilibrium was reached, the samples exhibited two superconducting transitions. The plot obtained for T_c vs annealing temperature establishes the transformation temperature at 387° ± 12°C for 52 kbar. Therefore, the slope dT/dp is negative for the phase boundary between InSb(II) and InSb(III).

Kasper and Brandhorst[7] have reported that a phase with orthorhombic structure is the stable phase of InSb above 30 kbar at room temperature. Additional data supporting this conclusion have been obtained by McWhan and Marezio.[8] On the basis of the data so far available, it is not possible to decide whether or not InSb(III) and the orthorhombic phase are the same. There is some evidence, however, that the two phases are different. Thus, it appears that InSb(III) would be stable at room temperature only at pressures appreciably greater than 52 kbar, rather than at about 30 kbar. In addition, preliminary x-ray data for InSb(III) are inconsistent with the orthorhombic structure, and the scattered T_c values for the orthorhombic phase reported by McWhan and Marezio[8] are generally lower than the value of 4.1°K observed for InSb(III).

The existence of InSb(III) apparently explains a discrepancy in T_c data reported earlier for the high-pressure InSb-Sn system. According to our measurements,[9] T_c abruptly increases

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