J.D. DUDLEY

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Melting and Polymorphism of Indium Antimonide at High Pressures *

THE change of electrical resistivity with pressure of indium antimonide has been studied by Keyes[1] up to 12,000 atmospheres and recently by Gebbie *et al.*[2], who extended measurements to 70,000 atmospheres. The resistivity measured at room temperature, according to them, shows an initial increase with pressure and drops several orders of magnitude at 30,000 atmospheres. This sharp drop in resistance was attributed by Gebbie *et al.* to melting, with the indium antimonide changing from a state of semiconduction in the crystal to metallic conduction in the liquid phase. A melting curve, based on the pressures giving a drop in resistivity at temperatures of 150°–800° K., was presented by them. The plotted points exhibit a wide scatter and the authors mention that the latent heat of melting calculated from the melting curve slope, namely 27 cal./gm., compares unfavourably with the experimentally determined value of 47·2 cal./gm. Hence it appeared to us that the melting curve of indium antimonide should be investigated again.

A piston-cylinder apparatus was used for generating high pressures. In this device, a tungsten carbide piston advances into a 'Carboloy' high-pressure chamber 0·5 in. in diameter and 2 in. long. The sample was sealed in a length of platinum tubing, $\frac{1}{2}$ in. × $\frac{1}{8}$ in., which was placed inside the talc-sheathed graphite furnace, which serves both for heating the sample and transmitting pressure to it. The absorption of latent heat accompanying melting was detected by differential thermal analysis. The sample temperature and the differential temperature were recorded simultaneously on a strip-chart recorder. The record of differential temperature analysis shows the latent heat accompanying melting as a break in the slope, or reversal of trend. Thus the melting point can be determined accurately. The high-pressure apparatus and the experimental techniques have been described in detail by Kennedy and Newton[3]. Semiconductor grade polycrystalline indium antimonide supplied by the Indium Corporation of America was used. Kennedy and Newton used platinum containers for the melting-point determination of both indium and antimony and have found platinum an inert container for both metals.

* Contribution No. 215, Institute of Geophysics, University of California, Los Angeles.

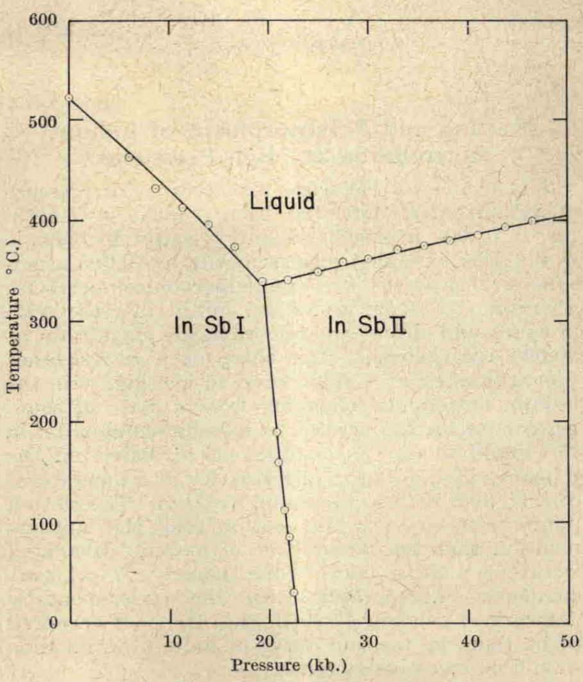

Fig. 1. Phase diagram of indium antimonide

Volume-change of transition was used to locate the lowest five points of Fig. 1, because of the small heat of transition and the advantage in accuracy in intersecting a phase-boundary at a high angle. Powdered indium antimonide was intimately mixed with silver chloride and the mix was compressed into a pellet of the shape and dimensions needed to fill the high-pressure chamber. A heating tape was wound on the steel supporting-ring of the 'Carboloy' core. In this way, a temperature of nearly 200° C. at the sample site could be reached. Ram pressure and piston displacement were recorded on an x–y recorder. Piston friction was eliminated by a piston rotation method[4] and wall-friction was reduced by a 0·001 in. lead-foil wrapping. A change of state is revealed by a break in the pressure versus displacement curve.

Fig. 1 shows the melting curve of indium antimonide obtained in the present investigation. It will be seen that the melting point goes down until a pressure of 19·4 kb. is reached and rises thereafter with increasing pressure. By inserting the initial value of the slope of this melting curve in the Clausius–Clapeyron equation and using the known volume contraction on melting ($\Delta V/V_{\text{solid}} = 0{\cdot}13$), the latent heat is calculated to be 49·0 cal./gm., which is in good agreement with the experimentally determined value of 47·2 cal./gm. To make doubly certain of the existence of melting above 300° C. at 40 kb., a special run was made in which a pure sample was compressed to 40 kb. at room temperature, and then heated. A thermal rest was encountered at 380° C., exactly as in the run on a sample of complicated pressure-temperature history.

Below 335° C., application of pressure transforms indium antimonide to another solid phase. We designate this new high-pressure form indium antimonide II, the normal form indium antimonide I. The solid–solid boundary was located by using the volumetric method briefly mentioned earlier. This boundary intersects the melting curve at 335° C. and 19·4 kb. The solid–solid transition has a large change in volume associated with it, and an estimate from measured displacement in transition gives $\Delta V/V \approx 20$ per cent, which is probably a minimum. It was found that a rise in temperature of 150° produced a great increase in the sharpness of the transition as recorded volumetrically. This is almost certainly due to higher transition velocity at higher temperature. The transition was so sluggish at room temperature that the pressure of transition could not be determined with nearly the precision at 80° C. This effect probably accounts for the very high-pressure values for drop in resistivity obtained by Gebbie *et al.* at 150° K.

It is well known that the intermetallic compounds formed among group III and V elements have properties resembling the corresponding members of the group IV elements. Indium and antimony occupy positions in the III and V group, sandwiching tin, which is the corresponding member of the fourth group IV. We may therefore expect indium antimonide to exhibit properties analogous to tin. Tin has two forms, grey tin and white tin, designated respectively α and β. White tin transforms to grey tin below 13° C. The latter has diamond structure and is a semiconductor while the former has a body-centred tetragonal lattice exhibiting metallic properties. The change-over from grey to white tin is accompanied by a large reduction in volume, amounting to 27 per cent. The transition in indium antimonide is strongly reminiscent of transformation from grey to white tin both in regard to the change from a state of semiconduction to metallic conduction and the large reduction in volume accompanying it. We believe from these considerations that the transformation which takes place in indium antimonide at high pressure is similar to the grey-white tin transition: indium antimonide I having zinc-blende structure corresponding to grey tin transforms to indium antimonide II having the structure of white tin.

A. Jayaraman
R. C. Newton
G. C. Kennedy

Institute of Geophysics,
University of California,
Los Angeles.

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