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Abstract

Full Text

Chemistry

E. G. Ponyatovskii and G. I. Peresada

On Phase Transformations of Indium Antimonide at High Hydrostatic Pressures

(Presented by Academician G. V. Kurdyumov, December 22, 1961)

Indium antimonide —InSb —belongs to the group of intermetallic compounds (GaSb, InAs, GaAs, etc.) that possess semiconductor properties and play a major role in modern technology. Compounds of this group have a ZnS-type structure with coordination number 4. Their melting is accompanied by an increase in density. Consequently, all such compounds should have phase diagrams of the water phase-diagram type, with a decrease in the melting temperature as pressure is increased. At high hydrostatic pressures one may expect transformations of these compounds into new modifications possessing more densely packed structures and metallic conductivity, which makes these compounds especially interesting objects for investigations at high pressures.

Gabbi, Smith, and others (1) investigated the phase diagram of InSb at pressures up to 70,000 kg/cm^2 by measuring electrical resistance. According to their data, InSb has a P—T diagram analogous to the phase diagram of Ge (2). As in the case of Ge, the melting temperature of InSb decreases over the entire investigated interval, from 523° at atmospheric pressure to −170° at a pressure of about 45,000 kg/cm^2. No phase transformations in the solid state were observed. The study of the phase diagram in (1) was carried out under quasihydrostatic pressure conditions, using as the pressure-transmitting medium the solid phase —pyrophyllite.

We have carried out an investigation of the phase transformations of InSb under conditions of true hydrostatic pressure in order to verify the results of (1). The investigation was performed on single-crystal and polycrystalline samples of semiconductor-purity InSb* by methods of differential thermal analysis and electrical-resistance measurement, analogous to those used by us earlier in studying the P—T diagrams of bismuth, thallium, and cerium (3–5). High pressure was produced in a multiplier with a force of 400 tons. Isopentane served as the pressure-transmitting medium. Temperatures up to 600° were obtained with the aid of a nichrome heater introduced into the high-pressure vessel. The pressure was measured with a manganin manometer calibrated against the polymorphic transformations of bismuth; the temperature—by a chromel—copel thermocouple.

Fig. 1. Phase diagram of InSb

Figure 1: Fig. 1. Phase diagram of InSb

As a result of the investigation, more than one hundred experimental points were obtained, on the basis of which the phase diagram of InSb shown in Fig. 1 was constructed; in this figure, to characterize the scatter of the data, some of the experimental points* are plotted. The melting curve of the InSb modification stable at atmospheric pressure (we shall call it the α-phase) is slightly concave toward the pressure axis. Its initial slope with respect to the pressure axis is

$$(dT/dp)_{p=1\ \text{atm}} = 9.0 \cdot 10^{-3}\ \text{deg/kg} \cdot \text{cm}^{-2}.$$

Assume the volume effect of melting of α-InSb at atmospheric pressure to be equal to 13% (^{6}); then from the Clapeyron equation we obtain the heat effect of melting of α-InSb equal to 46.5 cal/g, which is in good agreement with the result of a calorimetric measurement of this quantity, 47.2 cal/g (^{7}).

The coordinates of the triple point α-β-liq: 348° and 18,300 kg/cm^2. The average slope of the melting line of β-InSb to the pressure axis is $3.3 \cdot 10^{-3}$ deg/kg $\cdot$ cm^{-2}. The data obtained in the present work, in the form of a P–T diagram of InSb, differ greatly from the results published by Gebbie, Smith, et al. (^{1}).

Fig. 1. Phase diagram of InSb

It is probable that the curve of the $\alpha \to \beta$ transformation in the solid state was taken by these authors as a continuation of the melting curve, while the melting curve of β-InSb was not observed because of the relatively small jump in resistance upon melting of the β phase. The phase transformation of InSb is accompanied by a sharp change in the electrical resistance of the specimen and proceeds with resistance hysteresis, which increases as the temperature is lowered.

Figure 2 shows the curve of the dependence of the electrical resistance of α-InSb (a single-crystal specimen) on pressure, which has an exponential character and is well described by the equation:

$$R = A \exp(P/B),$$

where P is the pressure, $A \simeq R_0$, i.e., the resistance of the specimen at normal pressure; B is a constant characteristic of the given material. This equation is satisfied both in the case of single-crystal and polycrystalline specimens. For the single-crystal specimens used by us, $B = 3400$ kg/cm^2. As a result of the

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* Principal characteristics: $n = 1 \div 2 \cdot 10^4$ cm^{-3}, μ = 300,000—400,000 cm^2/V $\cdot$ sec, R_x = 30,000—50,000 cm^3 coul^{-1}, ρ = 0.07—0.10 $\Omega \cdot$ cm.

Fig. 2. Dependence of the electrical resistance of α-InSb on pressure

Figure 2: Fig. 2. Dependence of the electrical resistance of α-InSb on pressure

transformation, the resistance of the specimen decreases by more than three orders of magnitude. The resistance of the specimen in the β state was of the same order as the resistance of the lead-in wires; therefore it was not possible to make an accurate measurement of the specific electrical resistance of β-InSb.

Fig. 2. Dependence of the electrical resistance of α-InSb on pressure

Both the direct and reverse transformations of InSb at temperatures close to the triple point proceed practically instantaneously. With decreasing temperature the rate of transformation decreases, and below 100° one can observe an isothermal transformation proceeding over many minutes or hours (depending on the position of the isotherm relative to the equilibrium line of the α and β phases). Figure 3 gives the temperature dependence of the rate of the $\alpha \to \beta$ transformation at a pressure of 24,500 kg/cm^2, constructed by taking resistance–time isotherms during the first heating of a single-crystal specimen. In calculating the transformation rate it was conventionally assumed that the amount of the β phase formed is proportional to the change in the electrical resistance of the specimen. At room temperature spontaneous $\alpha \to \beta$ transformation does not begin up to a pressure of 28,000 kg $\cdot$ cm^{-2}, which greatly exceeds the pressure of the $\alpha \to \beta$ transformation at 20° according to the data of Jayaraman et al. (23 000 kg/cm^2). Such a difference can be explained by the activating influence of plastic deformation, which is unavoidable when pressure is created in the solid phase.

To elucidate the kinetics of the reverse transformation at room temperature, the electrical resistance of an InSb specimen in the β-state was measured during a gradual decrease of pressure, with 20-minute holds after every 1000 kg/cm^2. The reverse transformation $\beta \to \alpha$ began at a pressure of about 13 500 kg/cm^2, with an incubation period of several minutes; at the beginning the process proceeded with an increasing rate in time. Lowering the pressure increased the rate of transformation. As the untransformed volume decreased, the transformation rate gradually fell. But even after holding at a pressure of 5700 kg/cm^2 for twenty-four hours, the electrical resistance of the specimen continued to increase, which indicated that the $\beta \to \alpha$ transformation was incomplete. As a result of one or several $\alpha \to \beta \to \alpha$ cycles, the initially single-crystalline specimen cracked and crumbled into a fine powder, as a result of which the electrical circuit was broken.

[*] After completion of the present investigation and preparation of the article for press, a paper by Jayaraman, Newton, and Kennedy (8) on the P–T diagram of InSb appeared. The positions of the equilibrium lines obtained in the present work are in good agreement with the data of Jayaraman et al. (8).

Fig. 3. Temperature dependence of the rate of the $\alpha \to \beta$ transformation of InSb at a pressure of 24 500 kg/cm^2

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Fig. 3. Temperature dependence of the rate of the $\alpha \to \beta$ transformation of InSb at a pressure of 24 500 kg/cm^2.

On the X-ray diffraction pattern taken from a specimen that had undergone the $\alpha \to \beta \to \alpha$ transformation, continuous Debye rings corresponding to the α-phase are visible; no traces of the β-phase were observed.

The strong dependence of the rate of the $\alpha \to \beta$ transformation of InSb on temperature makes it possible to hope for supercooling of the β-modification and for investigation of its structure at atmospheric pressure.

Thus, we have constructed the phase diagram of InSb in the pressure range 1–28 000 kg/cm^2. It has been shown that the melting temperature of InSb decreases with pressure up to a triple point with coordinates 348° and 18 300 kg/cm^2, above which InSb crystallizes in another modification (β-InSb). The melting temperature of the new β-InSb modification increases with increasing pressure. Some kinetic characteristics of the polymorphic transformation of InSb have been studied. It has been shown that this transformation proceeds with considerable hysteresis and is accompanied by a change in electrical resistance by more than three orders of magnitude. The transformation of InSb is crystallographically irreversible; as a result of its occurrence, a single-crystalline specimen crumbles into small fragments. The dependence of the rate of transformation of InSb on temperature and pressure has also been investigated.

Central Scientific-Research Institute of Ferrous Metallurgy

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