Effect of pressure on the electrical resistivity of indium sulphide

Indium sulphide (InS) is a III–VI compound semiconductor and crystallizes in the orthorhombic structure with a space group $D_{2h}^{12}(P_{mnn})$. The lattice parameters at room temperature and atmospheric pressure are: $a = 3.944$ Å, $b = 4.447$ Å and $c = 10.648$ Å [1, 2]. The crystal structure comprises an ethane-like S_3InInS_3 atomic arrangement; the S_3InInS_3 groups are mutually linked by sharing S corners and form a three-dimensional network. Compared to other III–VI compound semiconductors, InS has attracted relatively little attention. Part of the reason for this can be attributed to the difficulties of crystal growth and sample preparation. The semiconducting properties of InS have been the subject of recent studies by Hamakawa and co-workers [3, 4]. These authors report the electrical resistivity, the Hall effect and optical measurements in the temperature range 77 to 300 K.

In this paper the results of electrical resistivity measurements made on melt grown InS crystals at high pressures (up to 70 kbar; 1 kbar = 0.1 GPa) are reported. These measurements have been performed in a Bridgman type opposed anvil apparatus with a clamping arrangement. The clamping arrangement was used for making resistivity measurements as a function of temperature (100 to 300 K) at fixed high pressures.

The InS crystals used in the present study were grown from In melt in a manner similar to that described by Nishino and Hamakawa [4] and Harsy [5]. Briefly, the contents (99.999% pure S and In in the ratio 1 : 4.5 by weight) were sealed in a quartz ampoule at about 10^{-5} torr. To prevent volatalization of sulphur, one end of the ampoule was kept in a liquid nitrogen bath during sealing. The sealed ampoule was then lowered into a vertical furnace and growth was accomplished by keeping the contents molten at about 900° C for a few hours and then allowing it to solidify by cooling at the rate of about 25° C h^{-1}. The reddish coloured InS crystals thus grown were separated from excess In using the leaching procedure described by Nishino and Hamakawa [4]. The leached out crystals were in platelet form. Back-reflection Laue photographs revealed sharp undistorted spots characteristic of good quality single crystals. Debey–Scherrer powder photographs obtained for different samples could all be indexed on the basis of an orthorhombic unit cell and the lattice parameters were in general agreement with those previously reported [2]. These X-ray studies rule out the presence of any sulphide other than InS in the samples studied.

For electrical resistivity measurements, platelet crystal samples (about 1 mm × 0.7 mm × 0.05 mm) were used. Standard four probe resistivity measurements were carried out using a Keithley constant current source (Model No. 225) and a d.c. null detector (Model No. 155). The measurements at high pressures were carried out in a Bridgman type tungsten carbide (3% cobalt binder) opposed anvil apparatus with a 4 mm tip and a 12° tapering angle. A 100 ton hydraulic press, fitted with a Heise pressure gauge (0 to 1000 psi) with 1 psi resolution for measuring the oil pressure, was used to generate the pressure between the anvils. The anvil apparatus was pressure calibrated using the well known phase transformations of bismuth and ytterbium [6, 7]. Resistivity measurements were also made as a function of temperature (100 to 300 K) at fixed high pressures by using the pressure clamping arrangement of the anvil apparatus. For all the high pressure measurements, the crystal sample was embedded in a steatite pressure transmitting medium with a heat treated pyrophyllite gasket surrounding it. Details of the sample assembly, clamping arrangement, corrections for pressure relaxation at low temperatures and the cryostat used for the low temperature measurements are given elsewhere [8].

The normalized electrical resistivity is plotted in Fig. 1 as a function of pressure. Fig. 2 gives the normalized resistivity plots as a function of temperature at fixed high pressures. These plots represent the results of several independent runs made on different samples. The room temperature resistivity values differed somewhat from sample to sample. However, all the samples studied displayed similar pressure and temperature dependences.

From Fig. 1 it is seen that up to about 15 kbar the resistivity remains practically unchanged. Above 15 kbar there is a steep increase in the resistivity with pressure and this variation continues right up to 70 kbar. From Fig. 2 it is noted that while the resistivities at 35.6 and 28 kbar

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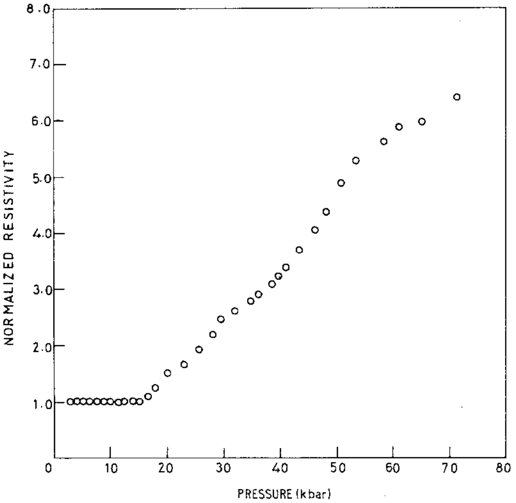

Figure 1 Normalized resistivity of InS as a function of pressure at room temperature.

show strong temperature dependences, with the variations much more pronounced at 35.6 kbar than at 28 kbar, the resistivity at 7.6 kbar is almost independent of temperature.

The sample to sample differences of the room temperature resistivity values suggest the possibility of impurity dominated resistivity. Previously, Nishino and Hamakawa [4] found n-type extrinsic behaviour in as-grown InS crystals. The room temperature carrier concentration was high (about $10^{18}\,\text{cm}^{-3}$) and did not vary much with temperature. In fact, below about 100 K the carrier concentration was independent of temperature. In the range 100 to 300 K the concentration showed a slight increase with temperature and from this Nishino and Hamakawa calculated a donor ionization energy of about 5 to 7 meV, a value which is very small compared to the optical band gap of about 2 eV. Our earlier [9] low temperature measurements corroborate this. The n-type extrinsic behaviour in as-grown InS crystals is most likely to be due to non-stoichiometry.

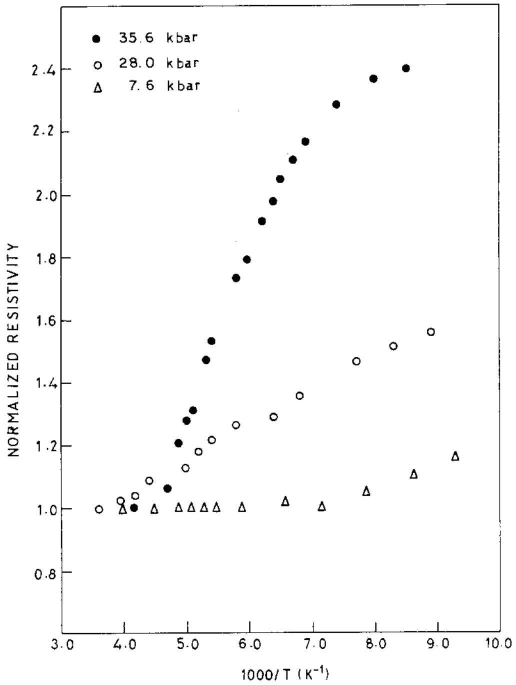

Figure 2 Temperature dependence of normalized resistivity of InS at different high pressures.

The observed resistivity changes with pressure can be understood in terms of the changes in the donor ionization energy E_i. For an n-type extrinsic semiconductor (with $N_A = 0$, $p \ll n$) the carrier concentration, n, is given by [10]

$$n = (N_D A_n/2)^{1/2}(kT)^{3/4}\,e^{-E_i/kT} \qquad (1)$$

where

$$A_n = 2(m_n/2\pi h^2)^{3/2} \qquad (2)$$

and the resistivity ρ is given by

$$\rho = (n\underline{e}\mu_n)^{-1}. \qquad (3)$$

N_D is donor density, N_A is acceptor density, k is Boltzmann's constant, T is absolute temperature, m_n is the density-of-states effective mass of electrons, h is Planck's constant, $\underline{e}$ is electronic charge and μ_n is electron mobility.

When all the donors are ionized, the number of carriers is determined solely by the concentration of impurities and is independent of pressure and temperature. Effects of pressure on resistivity then arise from effects of pressure on mobility (see Paul [11] for a general review). Now, referring to Fig. 1, it is plausible that up to about 15 kbar the donors are all essentially ionized. Further, since in this range resistivity remains practically constant it implies that mobility does not change much with pressure. Above 15 kbar, the donor deionization sets in and E_i increases with pressure and contributes to the rapid rise in resistivity. Further support for these arguments comes from the temperature dependence of resistivity at fixed high pressures (Fig. 2).

Finally, the rapid rise in resistivity above 15 kbar is apparently not associated with any pressure induced structural transformation. No new phase could be detected from high pressure X-ray diffraction measurements carried out at the National Aeronautical Laboratory, Bangalore, using a tungsten carbide anvil cell and a two film cassette [12].

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Stress relaxation in KCl single crystals

The Li–Gupta [1, 2] method of analysing stress relaxation data has had considerable success with bcc metals and many ionic crystals. The dislocation velocity–stress exponent, m^*, given in the empirical formula

$$\dot{\epsilon} = B\sigma_f^{m^*} \quad (1)$$

has been determined quite easily by this method. (In Equation 1, $\dot{\epsilon}$ is the strain rate, σ_f is the effective stress and B is a constant.) However, it is now clear that there are many materials with which Li–Gupta analysis breaks down [3]. KCl single crystal is one such material. Previously, we measured the stress relaxation of KCl single crystals and obtained the m^* values by this method [4], but the results obtained gave $m^* = \pm\infty$ at room temperature and negative values at temperatures higher than 150° C. (For instance, $m^* = -2.72$ at 450° C.) These are physically insignificant values. A similar result has been obtained by Ohring *et al.* [5] who measured the relaxation of decay current in deformed KCl single crystal.

On the other hand, the analytical method developed by Hart [6] has had remarkable success in analysing the stress relaxation of many metals and alkali halides. For instance, Lerner *et al.* [7] have analysed the stress relaxation of KI, LiF, NaCl and NaF single crystals according to Hart's theory. However, to the authors' knowledge, results for KCl have not been reported using this method. The purpose of this letter is to carry out, and report on the results, of the stress relaxation analysis of KCl single crystal by Hart's theory and to consider the reason why Li–Gupta analysis failed with this material.

First, the phenomenological model proposed by

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