The electrical and phase properties of Hg$_3$Te$_3$–In$_2$Te$_3$ alloys to high pressures

G D PITT†, J H McCARTNEY†, J LEES† and D A WRIGHT‡
† Standard Telecommunication Laboratories Ltd, London Road, Harlow, Essex
‡ Department of Applied Physics and Electronics, University of Durham, South Road, Durham

MS received 26 January 1972

Abstract. Hall-effect and resistance measurements on single-crystal alloys of Hg$_3$Te$_3$ with In$_2$Te$_3$ indicate the types of conduction and the related band structures for both atmospheric pressure and high-pressure phases of the system. The addition of In$_2$Te$_3$ to Hg$_3$Te$_3$ gives a zero bandgap at 7±2 mol% In$_2$Te$_3$. Electrons in the high-pressure cinnabar (HgS) form of Hg$_3$Te$_3$ occupy off-centre, heavy effective mass minima, with a mobility near 10 cm$^2$ V$^{-1}$ s$^{-1}$. The variation with pressure of the electrical properties of the ordered adamantine vacancy structure found at 37.5% In$_2$Te$_3$ can be fitted by a simple two-band model. The presence of an impurity level above the lowest minimum is inferred. A new rock-salt phase has been discovered above 42 kbar and 46 kbar for the 37.5% and 50% alloys respectively. Low-temperature measurements indicate that the phase is metallic: it is possibly superconducting at low temperatures.

1. Introduction

The electrical and phase properties of the Hg$_3$Te$_3$–In$_2$Te$_3$ alloy system at atmospheric pressure have been discussed previously by Spencer (1964), Giriat (1964), Lewis and Wright (1966), and Wright and Dahake (1968): these papers will be referred to as I, II, III and IV. The examination of ordered zinc-blende structures incorporating vacancies in the superlattice are of basic physical interest, but the alloy system is also worthy of study in view of the possible use of such narrow band materials as infrared detectors (cf HgTe–CdTe alloys) and thermoelectric devices (I).

It is now accepted that Hg$_3$Te$_3$ is a semimetal and has an inverted InSb structure following the original model for α-Sn of Groves and Paul (1963). The Γ$_6$ band lies below the T$_5$ band by about 0.16 eV at atmospheric pressure and 300 K. The addition of In$_2$Te$_3$ causes the bands to close, and for 4–7% molecular In$_2$Te$_3$ there is zero gap (I, IV). Similarly the application of pressure and reduction of the lattice parameter can cause the bands to change in energy. In materials with zinc-blende or diamond structures, a distinct pattern for the pressure coefficients of bands at certain critical points has emerged (Paul 1961). Thus optical and electrical pressure measurements can help to identify the bands involved in the conduction process.

It was found (I) that as further In$_2$Te$_3$ was added, the band gap increased with a disordered (α) structure to about 20% In$_2$Te$_3$. The electron mobility remained high, 20 000–5000 cm$^2$ V$^{-1}$ s$^{-1}$, and the electron effective mass was estimated to increase to about 0.04 $m_0$ (IV), implying that the same band was involved through the range. An
ordered adamantine ($\beta$) phase was found near 37.5\% $\text{In}_2\text{Te}_3$, the structure of which has since been solved by McCartney (1971). The electron mobility fell to near 400 cm$^2$ V$^{-1}$ s$^{-1}$, and the effective mass rose to 0.07 $m_0$, leading to the speculation that a new band was dominating the conduction (IV). Near 50\% $\text{In}_2\text{Te}_3$ another zinc-blende phase occurred with an order–disorder transition at 595 K (Maynell et al. 1970), an energy gap near 0.75 eV, and mobility $\mu_e \sim 50$ cm$^2$ V$^{-1}$ s$^{-1}$. At higher compositions a defect chalcopyrite ordered structure is centred at 75\% $\text{In}_2\text{Te}_3$ (II) with an energy gap of 0.95 eV. A detailed phase diagram after Ray and Spencer (1968) is shown in figure 1.

More recent unpublished work at Durham has given the results shown in figures 2 and 3. The minimum in effective mass in figure 2 suggests that the zero bandgap occurs near 7\% $\text{In}_2\text{Te}_3$.

![Figure 1: Temperature-composition diagram for the Hg$_2$Te$_3$-In$_2$Te$_3$ pseudo-binary system (after Spencer and Ray 1968).](image)

![Figure 2: Plots of electron effective mass against percentage $\text{In}_2\text{Te}_3$ in Hg$_2$Te$_3$ at 100 K: $\times$ $n = 3 \times 10^{18}$ cm$^{-3}$; $\circ$ $3 \times 10^{17}$; $\square$ $10^{17}$. Data taken from Wright and Dahake (1968).](image)

A program to study crystals of the alloy system under hydrostatic and quasi-hydrostatic pressures was begun in the hope that we might obtain more information about the band structure. Both electrical and high-pressure x-ray measurements were made, but this paper is confined to the electrical results. A number of new high-pressure phases were observed, and Hall and resistance measurements have been interpreted in terms of the conduction state, band structure and the effect of impurity states in the
new phases. A detailed discussion of the high-pressure-phase crystal structures is given elsewhere (McCartney 1971); these results allow us to make comparisons of the type of conduction for materials of similar crystal structure.

Figure 3. Plot of effective mass at 100 K against carrier density for different compositions (figures denote % In$_2$Te$_3$). Data taken from Wright and Dahake (1968).

2. Experimental techniques and crystal samples

Three types of high-pressure equipment were used. Simple two-probe resistance measurements were initially made up to 60 kbar in the tetrahedral apparatus. The single crystals were immersed in epoxy resin at the centre of an MgO epoxy-loaded tetrahedron (Lees and McCartney 1968). Hall measurements to 60 kbar were made using an opposed anvil apparatus, with the crystal again supported in epoxy resin (Pitt 1968). These techniques allow single-crystal measurements to much higher pressures than previously obtained, but below 25 kbar piezoresistance measurements have revealed that the stress is nonhydrostatic. This makes the interpretation of results difficult if off-centre minima are involved in the conduction process. This gap was partially filled by hydrostatic measurements to 18 kbar, using a piston and cylinder Hall apparatus (Pitt and Gunn 1970).

Low-temperature measurements to 100 K at high pressures were made using a cooling collar about the opposed and tetrahedral anvil and blowing liquid nitrogen through the coils by nitrogen gas. A chromel–alumel thermocouple placed in close proximity to the sample in epoxy was used to monitor temperature.

A variation on the manganin gauge technique of Giardini and Samara (1965) was used to observe the phase transition pressure of a number of samples. The crystal, with a coil of three turns of manganin wire about it, was potted in epoxy. The resistance of the manganin wire was then observed continuously as the pressure increased, and at a phase transition the decrease in volume caused the manganin to be subjected to a small shear stress, so that a well-defined kink in the resistance curves was observed.

The crystal growth and sample preparation have already been discussed in detail (I, IV). The atmospheric pressure electrical parameters of the alloys have also been given (IV), and the same crystals were used in the present work.

3. Resistivity and Hall measurements

3.1. The Hg$_3$Te$_3$ and 4% In$_2$Te$_3$ alloy

These results have been partially discussed elsewhere (Pitt and Lees 1969). Hall-effect measurements to 60 kbar on the 4% alloy are shown in figure 4. The results for pure
The electrical and phase properties of $Hg_3Te_3-In_2Te_3$ alloys

Figure 4. Normalized resistivity $\rho/\rho_0$ and Hall constant $R_H/R_{HO}$ for the $Hg_3Te_3-4\%$ $In_2Te_3$ alloy as functions of pressure.

Figure 5. Normalized Hall mobility $\mu_H/\mu_{HO}$ as a function of pressure for the $Hg_3Te_3-4\%$ $In_2Te_3$ alloy.
Hg$_3$Te$_3$ are similar, and show a large increase in resistivity near 14 kbar of about four orders of magnitude to a maximum, followed by a more gradual decrease at higher pressures. The rapid resistivity increase is attributed to the zinc-blende/cinnabar (HgS structure) phase transition. The positions of the atoms in the high-pressure phase have been determined by McCartney (1971). In the zinc-blende phase below 14 kbar for the 4\% alloy a definite decrease in mobility was observed beyond 3 kbar (figure 5), while in HgTe the mobility was almost constant to 11 kbar and decreased at higher pressures. More accurate Hall measurements on HgTe–CdTe alloys by Otmezguine et al (1970) and Hg$_3$Te$_3$–Ga$_2$Te$_3$ alloys by Morrissy et al (1972) show that the maximum in the mobility is a good indicator of the proximity of zero gap. We conclude from the onset of our mobility decrease that for the 4\% alloy a negative gap still exists, and that band cross-over (inversion) occurs at 7 ± 2\% provided the pressure coefficient in the alloy remains the same as in Hg$_3$Te$_3$. Unfortunately no more crystal samples remained of the alloy to permit a more accurate determination of zero gap composition using hydrostatic techniques. This is excellent confirmation, however, of the new analysis of the previous data presented in figure 2.

Hall measurements on the cinnabar structure phase for both Hg$_3$Te$_3$ and the 4\% In$_2$Te$_3$ alloy revealed mobilities close to the value of 10 cm$^2$ V$^{-1}$ s$^{-1}$ measured by Tabak and Roberts (1968) on HgS. Further resistivity measurements on Hg$_3$Te$_3$ crystals of different size showed large piezoresistive effects, giving varying resistivity–pressure curves. The discrepancies tended to disappear at higher pressures as the conditions became more hydrostatic. Similar results were found in the original work on Si (Lees and McCartney 1968): these indicated that, as with Si, the occupied band in the cinnabar structure Hg$_3$Te$_3$ is not at the centre of the Brillouin zone. This would agree with the optical data of Zallen (1967) on HgS, and, taken with the agreement in mobilities for both materials, is strong support for the suggestion that the same heavy effective mass, off-centre band is occupied in both compounds.

![Figure 6. Activation energy $E_i$, derived from $\rho = \rho_0 \exp (-E_i/kT)$, for Hg$_3$Te$_3$ as a function of pressure in the cinnabar phase.](image-url)
The electrical and phase properties of $\text{Hg}_3\text{Te}_5$-$\text{In}_2\text{Te}_3$ alloys

Resistivity measurements to low temperatures were made at different pressures in the high-pressure phase of $\text{Hg}_3\text{Te}_5$, and an activation energy of 0.34 eV was found when the energies were extrapolated to atmospheric pressure (figure 6). Andrews (1969) found a similar activation energy of 0.50 eV in the cinnabar form of $\text{HgSe}$. The optical gap is 2.0 eV in $\text{HgS}$, determined by Zallen (1967). It has generally been found that the energy gap increases with the ionicity of the compound, and hence we must consider the possibility that we are observing the band-band activation energy ($E_g \sim 0.68$ eV) in $\text{Hg}_3\text{Te}_5$ rather than an impurity level. The activation energy decreases at $-2.2 \times 10^{-3}$ eV kbar$^{-1}$, which is more characteristic of a state situated away from the zone centre in a diamond or zinc-blende material (Paul 1961).

3.2. 8% and 15% alloys

Only manganin coil experiments were carried out on these crystals. Results showed that as more $\text{In}_2\text{Te}_3$ is added to $\text{Hg}_3\text{Te}_5$ the cinnabar phase transition moved to higher pressures. It was confirmed by high-pressure x ray analysis that the 15% alloy had the cinnabar structure.

3.3. The 37.5% alloy

Two different crystals of this alloy composition were studied. Crystals A and B had mobilities of 300 and 420 cm$^2$ V$^{-1}$ s$^{-1}$ respectively at room temperature. Initially simple two-probe measurements were made on A in the tetrahedral apparatus to 50 kbar (figure 7) with considerable variation in results. This was not surprising, since no attempt was made to keep the size of the crystal uniform and on the larger variation runs cracking was observed. A general pattern emerged, however: namely, a gentle rise in resistance to a maximum near 20 kbar, followed by a steepening decrease to near 41 kbar where the resistance suddenly dropped to an extremely low value. Bridgman-anvil Hall measurements to 20 kbar were also attempted on A (figure 8), but the material broke at higher pressures. The large scatter of results perhaps reflects the inhomogeneity of the material and the influence of nonhydrostatic stress. Both the Hall constant and resistivity had increased by 15 kbar indicating carrier loss.

Crystal B was studied by Hall effect under hydrostatic conditions, and normalized measurements from two slices of the same ingot are shown in figure 9. The results are at first sight in disagreement with those obtained for A. The Hall constant $R_H$ passed through a maximum and returned by about 16 kbar to near the original value. The resistivity eventually rose to a value near $\rho/\rho_0 \sim 3$ and showed signs of levelling off by 20 kbar. The Hall mobility $\mu_H (=R_H/\rho)$ also decreased and showed signs of levelling off near 18 kbar.

It was decided to attempt an explanation for the results obtained on crystal B under hydrostatic conditions and then see if the model still held for crystal A. The curves in figure 9 for crystal B are reminiscent of those observed in GaAs (Pitt and Lees 1970) and Ge (Fletcher and Pitt 1971) under pressure, where electrons have transferred from one state to another. The maximum in the Hall constant indicates the coexistence of two types of carrier with different mobilities. A theoretical fit of the curves in figure 9 must be complicated because our knowledge of the band structure in such a vacancy-ordered compound is extremely vague, unlike that in the III–V or group IV compounds where analogies can be drawn for a particular minimum from different compounds.

The unit cell in the 37.5% alloy has been found to have eight times the volume of that
Figure 7. Normalized two-contact resistance variations (---) on crystal A of Hg$_2$Te$_3$-37.5\% In$_2$Te$_3$ to high pressures using the tetrahedral anvils. A theoretical fit (-----) using a two-band model is shown. Curves (a), (b) and (c) represent three runs on samples of varying size and orientation. It is suggested that for curves (b) and (c) the stress system in the vicinity of the crystal was such that the higher lying minima were split.

Figure 8. Normalized Hall constant $R_H/R_{HO}$, resistivity $\rho/\rho_0$, and mobility $\mu_H/\mu_{HO}$ results on crystal A of Hg$_2$Te$_3$-37.5\% In$_2$Te$_3$ to high pressures.
The electrical and phase properties of Hg$_3$Te$_3$–In$_2$Te$_3$ alloys

for simple Hg$_3$Te$_3$ from x ray measurements (McCartney 1971). The reduced Brillouin zone will thus be an eighth of the size for Hg$_3$Te$_3$, and the number of bands will be increased. A typical band structure calculation might be carried out by considering the gradual addition of In to Hg$_3$Te$_3$ and then calculating the effect of the potentials on the cation sites. Then the ordered vacancy should be included, which would give rise to an additional periodic potential. It is likely that the effect of the vacancy will not be negligible since McCartney found that the symmetry of the Te atoms was reduced and

![Figure 9. Normalized Hall mobility $\mu_H/\mu_{H0}$, Hall constant $R_H/R_{H0}$, and resistivity $\rho/\rho_0$ for crystal B of Hg$_3$Te$_3$–37.5% In$_2$Te$_3$ to high pressures using the hydrostatic Hall apparatus. A theoretical fit using a two-band model is shown for the mobility.](image)

the positions of Te atoms near the vacancies (B1 sites) were displaced from their ideal position by $0.31 \pm 0.03$ Å. Also one of the cation sites (A3) was displaced by $0.27 \pm 0.03$ Å. Thus any band structure calculation, while not impossible since the positions of the atoms and vacancies are known, would be an extremely lengthy procedure. We can perhaps make some estimate of the band positions by drawing an analogy with the chalcopyrite band structure where the Brillouin zone is halved. In this case, bands at the edge of the old zinc-blende zone (i.e L (111) or X (100) points) are ‘folded back’ and provide minima at the $\Gamma$ point (Goryunova et al 1970). For example, in ZnSiP$_2$, it is thought that electrons occupy a minimum at the $\Gamma$ point of the zone, which is similar to the minima in the point X of the original zinc-blende Brillouin zone. The problem in our case is considerably more complex, and the ‘folding back’ procedure to give the reduced Brillouin zone will
give rise to several new extrema at the centre of the zone which can have L and X characteristics.

The effective mass of 0.070 \( m_0 \) found in IV for the 37.5\% alloy is typical of a band at the centre of the Brillouin zone with a low density of states. In \( \text{Hg}_3\text{Te}_3 \) the \( \Gamma_6 \) minimum has a pressure coefficient near \( +12 \times 10^{-3} \text{ eV kbar}^{-1} \) (Camphausen et al 1971) away from the valence band. We have used these two initial values as a starting point and assumed the electrons have transferred to a new state with a small negative pressure coefficient of \( 5 \times 10^{-4} \text{ eV kbar}^{-1} \). This assumption is reasonable, since typical band structure calculations (eg Katsuki and Kunimune 1971) show that all accessible bands in \( \text{Hg}_3\text{Te}_3 \), apart from the \( L_6 \) or \( \Gamma_6 \) bands, have zero or small negative pressure coefficients.

The mobility ratio was taken as constant (ie \( \mu_X/\mu_T=3 \)), which is the ratio obtained experimentally, and \( \mu_X \) is the mobility of the higher lying minimum. It is possible that the mobility in the \( \Gamma \) lower minimum will decrease by perhaps 15\% by 20 kbar depending on the dominant scattering mechanism (cf Pitt and Lees 1970 for the case of GaAs), but for this calculation, where there are so many uncertainties, to assume a constant mobility is a reasonable first approximation.

We use the charge-balance equation

\[
N_D - N_A = n_T + n_X + n_d
\]  

(1)

where \( N_D \) and \( N_A \) are the number of donors and acceptors respectively, and the number of electrons in the \( \Gamma \) minimum is

\[
n_T = N_T F_{1/2} \left( \frac{E_i - E_T}{kT} \right)
\]

(2)

\( N_T \) being the standard density-of-states expression \( (\propto m^{*3/2}) \) and \( F_{1/2} \) the Fermi integral of order \( \frac{1}{2} \). \( n_d \) is the number of electrons on donor sites:

\[
n_d = \sum_i \frac{N_D}{1 + (1/g_i) \exp \left[ \left( \epsilon_i - E_i \right)/kT \right]}
\]

(3)

where \( \epsilon_i \) is the activation energy of the impurity level corresponding to the \( i \)th state and \( g_i \) is the degeneracy. For crystal B it was assumed that all electrons were ionized below each minimum since \( R_H/R_{HO} \) returned to unity by 18 kbar; that is, \( n_d = 0 \).

We fitted the Hall mobility

\[
\mu_H = \mu_T \left( \frac{(\mu_X/\mu_T)^2 + n_T/n_X}{\mu_X/\mu_T + n_T/n_X} \right)
\]

(4)

after first adjusting the Fermi level \( E_i \) in equation (1) and varying the sub-energy gap between the minima. The theoretical mobility curve plotted in figure 9 was obtained for a sub-band gap \( \Delta E \) of 0.15 eV and an effective mass ratio of \( m_X^*/m_T^* = 5.7 \). The fit is quite reasonable considering the uncertainties involved, and shows that a simple two-band model can be used. If \( m_T^* \) is 0.07 \( m_0 \) (IV), then \( m_X^* \approx 0.40 m_0 \). This is a density-of-states effective mass, and is higher than might be expected for a \( \Gamma \) state, but similar to that found for a typical L state (cf 0.54 \( m_0 \) for Ge) in compounds with a zinc-blende or diamond structure. Other paired values of \( m_X^* \) and \( \Delta E \) give reasonable fits—for instance, \( m_X^* = 0.21 m_0, \Delta E = 0.13 \text{ eV} \). Thus we allow for considerable error in our effective mass estimate for the higher state and take \( m_X^* = 0.30 \pm 0.10 m_0 \), while the sub-band gap is \( 0.14 \pm 0.02 \text{ eV} \). The main inference is that the higher minimum probably has L or X characteristics when referring to the original \( \text{Hg}_3\text{Te}_3 \) zinc-blende Brillouin zone.
The electrical and phase properties of $\text{Hg}_3\text{Te}_2-\text{In}_2\text{Te}_3$ alloys

An L or X higher lying state would also help to explain the different results obtained on three samples from ingot A. These are shown in figure 7 as curves (a), (b) and (c). The degeneracy of the off-centre minima is generally removed by a deviation from hydrostatic stress. This leads to piezoresistive effects which depend on the size, shape and orientation of the crystal (Lees and McCartney 1968). We applied the two-band model to crystal A and obtained the theoretical curve shown in figure 7, where we have included an impurity level 0.03 eV above the $I'$ minimum with a zero pressure coefficient. Thus we included equation (3) in equation (1) and then adjusted the Fermi level to obtain $m_T^*$ and $m_X^*$. These were then substituted in the resistivity equation

$$r(P) = \frac{n_T(0) \mu_T(0) + n_X(0) \mu_X(0)}{n_T(P) \mu_T(P) + n_X(P) \mu_X(P)}$$

Again a reasonable fit was obtained, particularly for curve (a) with the resistance levelling off near 20 kbar. The further decrease in resistance could be explained by the movement of the band at $5 \times 10^{-4}$ eV kbar$^{-1}$ towards the stationary impurity level, with the further ionization of carriers. The fits for curves (b) and (c) in figure 7 were not good, but could be improved if we assumed a deeper impurity level or that in these cases the crystal orientation was such that under the nonhydrostatic stress the degeneracy of the higher level was split. This splitting will still occur even if the minimum lies at the centre of the zone after the 'folding back' procedure to form the highly reduced Brillouin zone in the ordered alloy, provided it comes originally from an L or X point. The important result in terms of the suggested two-band model is that in all cases the resistance reaches a maximum by 20 kbar when transfer is complete.

Deep nonhydrogenic impurity levels that exist above the lowest conduction band have now been observed in several zinc-blende II–VI and III–V compounds. It is still uncertain whether the dominant contribution to the impurity wavefunction comes from the valence or conduction bands. For example, in the case of a vacancy in silicon, Callaway and Hughes (1967) calculate that the major contribution to the impurity level would come from the valence band, and it is conceivable that such a level could exist above the conduction band. Paul (1968) has also observed these 'resonance states' from pressure measurements and concludes, particularly in GaSb, that they are largely controlled by the movement of the conduction band. A more recent study on CdTe (Iseler et al 1971) has again illustrated the existence of these levels, and they are considered to be caused by halogen impurities associated with the conduction band. To fit our model, we require a very low pressure coefficient for the impurity level which could be characteristic of either the valence or conduction band. Our tentative band structure for the 37.5% alloy is summarized schematically in figure 10.

The resistance data in figure 5 showed a sudden large drop at 42 ± 2 kbar. This type of variation strongly suggested the presence of a phase transition, and this was confirmed by McCartney (1971) who found a new rock-salt-structure phase. Further four-probe Bridgman-anvil measurements in the rock-salt phase gave a resistivity at 55 kbar, $\rho(55)$, of $10^{-4}$ Ω cm and a minimum number of carriers of $3 \times 10^{22}$ cm$^{-3}$ (ie more than 0.3 carriers per atom). A low-temperature measurement in the new phase showed a linear decrease in resistivity towards 100 K (figure 11). The apparent metallic nature of the new phase leads us to speculate that it might be superconducting at very low temperatures (1–2 K) since this behaviour is known in a number of rock-salt compounds—such as SnAs and InTe at 2 K. Geller and Hull (1964) have suggested that the rock-salt $\text{In}_{1-x}\text{Te}$ compounds will also be superconducting, but the presence of $\text{Hg}_3\text{Te}_3$ in our
Figure 10. Tentative two-conduction-band model for Hg$_3$Te$_2$-37.5\% In$_2$Te$_3$. Energy is shown as a function of $k$, but the higher minimum could be at the centre of the reduced zone, and originate from an L or X state when referred to the original Hg$_3$Te$_2$ zinc-blende Brillouin zone.

Figure 11. Four-contact resistivity measurements to 100 K at 55 kbar for the rock-salt-structure phase of the Hg$_3$Te$_2$-37.5\% In$_2$Te$_3$ alloy: measured as a voltage at constant current.
compound will probably have an interesting diluting effect and could lower the transition temperature to an extremely low value.

3.4. 50% alloy

The two-probe resistance measurements were similar to those for the 37.5% alloy, except that the maximum occurred nearer 30 kbar, followed by an ever steepening decrease with the phase transition taking place near 46 ± 2 kbar. No analysis of the results was made, since no material was left for the more comprehensive hydrostatic Hall measurements or for studying the probable influence of compensation effects (IV). The high-pressure phase was again shown to have a rock-salt structure (McCartney 1971), and the final resistance was near that for the 37.5% alloy. It would be interesting to look for superconductivity in both alloys to observe how the presence of Hg₃Te₃ affects the transition.

In both alloys prior to the transition, the resistance decrease steepened. This is attributed to a sudden increase in hole concentration, similar to that observed prior to the similar transitions in InAs (Adler 1969, Pitt and Vyas 1972b) and InSb (Narita and Masaki 1970). The transition from zinc-blende to rock-salt structure is reconstructive, and will involve breaking bonds. The apparent increase in p type carriers would suggest that these dangling bonds are providing acceptors before the transition proceeds to completion. Adler (1969) found the effect to be more pronounced for polycrystalline InAs, and Narita and Masaki (1970) showed that InSb changed from n type to p type just before the transition near 25 kbar, and were able to carry out a low-temperature measurement without the transition proceeding further. This implies that we are not seeing the beginnings of the heterogeneous nucleation of the new phase.

4. Conclusions

We have described electrical measurements to high pressure on crystals in the Hg₃Te₃–In₂Te₃ system, with particular emphasis on the high-pressure phases in Hg₃Te₃ and the 37.5 and 50% alloys. The cinnabar structure form of Hg₃Te₃ above 20 kbar has electrical characteristics similar to those of HgS. Results indicate that electrons occupy heavy effective mass off-centre minima. Band cross-over from the inverted to the true

![Figure 12. Plots of transition pressures against (a) alloy composition and (b) optical energy gap: • manganin coil; ○ resistance; x x ray diffraction.](image-url)
InSb-type band structure in zinc-blende \( \text{Hg}_3\text{Te}_3 \) is estimated to occur at \( 7 \pm 2 \text{ mol}\% \text{In}_2\text{Te}_3 \).

The addition of higher concentrations of \( \text{In}_2\text{Te}_3 \) moved the transition to higher pressures. Figure 12(a) is a plot of transition pressure against composition. The transitions for the 37·5 and 50 \% alloys were to rock-salt structures which appeared to have metallic characteristics. It is suggested that both might be superconductors at low temperatures. In figure 12(b) the transition pressure is plotted as a function of optical energy gap (measured by Spencer 1964). We find that, regardless of the type of transition concerned, the pressure increases with energy gap, agreeing with the empirical relation to be found in III–IV compounds (Jamieson 1963). A greater degree of ionicity gives both higher band gaps and requires a higher pressure to encourage the transition. Prior to the transition, a decrease in resistance is attributed to a sudden increase in hole concentration.

Hall and resistivity measurements on the ordered zinc-blende 37·5 \% alloy have been analysed in terms of a simple two-band model. A tentative conduction-band structure has been proposed, giving a band 0·14 ± 0·02 eV higher in energy above the lowest central minimum. This minimum could be either away from or at the centre of the reduced Brillouin zone of the ordered vacancy alloy. It has an effective mass near 0·30 ± 0·10 \( m_0 \), which is more comparable with the \( X_1 \) and \( L_1 \) minima found at the zone edge in other zinc-blende compounds. It is possible that deviations from ohmic behaviour might occur at high electric fields due to transfer of electrons to the higher lying minima. The mobility ratio suggested by our results, however, indicates that a transferred-electron device comparable in efficiency with GaAs is not likely. Room-temperature measurements on bar samples (1 \( \times \) 0·1 \( \times \) 0·1 mm\(^3\)) to 10 kV cm\(^{-1}\) revealed no negative differential conductivity.

Acknowledgments

We thank Professor C H L Goodman and Dr D Jones for helpful discussions, and Dr G A Saunders of Durham University for supplying some crystals.

References

Jamieson JC 1963 Science, NY 139 845–7
The electrical and phase properties of Hg$_3$Te$_5$–In$_2$Te$_3$ alloys

Morrissy J H, Pitt G D and Vyas M K R 1972 Proc. 11th Int. Conf. on the Physics of Semiconductors, Warsaw submitted for publication
—— 1968 Proc. 9th Int. Conf. on the Physics of Semiconductors, Moscow (Leningrad: Nauka) pp 16–26
Pitt G D and Gunn D A 1970 High Temp. high Press. 2 547–52
Pitt G D and Vyas M K R 1972 submitted for publication
Spencer P M 1964 Br. J. appl. Phys. 15 625–32