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The Growth and Electrical Properties of Single Crystal Cd_3As_2 Platelets

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Single crystal platelets of Cd_3As_2 having carrier concentrations less than 10^{24} m^{-3} have been grown from the vapour in the presence of argon gas and excess cadmium vapour. It is shown that the resistivity and Hall data is consistent with a band model in which there is a direct band-gap at $k = 0$ of approximately 0.38 eV and an indirect zero band-gap. It is suggested that the large electron carrier concentrations usually present in Cd_3As_2 result from anti-structure disorder.

1. Introduction

Although its melting point is 721°C, Cd_3As_2 undergoes a phase change at 578°C [1, 2] or possibly at the higher temperature of 615°C [3], with a consequent expansion as the material cools. Therefore by growing from the vapour phase at a temperature below the solid-solid phase transformation temperature, it is possible to avoid cracking of the crystals on cooling. Growth from the vapour has been reported by a number of authors [4-7], and in particular Silvey *et al* [8] have grown crystals in a hydrogen gas flow. In the present investigation growth has been by vapour transport in an inert gas (argon).

2. Growth of Cd_3As_2 Crystals

Growth was carried out within a silica tube of diameter 2.2 cm which was surrounded by a three-zone furnace of length 1 m. The temperature profile for the furnace is shown in fig. 1. The central zone was held at a temperature just below the phase-change temperature of Cd_3As_2 and an initial charge of Cd_3As_2 was placed in a silica boat at this point. The Cd_3As_2 charge had been obtained by heating stoichiometric quantities of 6N cadmium and 5N arsenic (supplied by Koch-Light Laboratories Ltd) to approximately 850°C for a few hours in a sealed evacuated silica tube and then rapidly cooling. In the first zone of the furnace was placed a silica boat containing cadmium and this zone was heated to just below 321°C, the melting point of cadmium. No heat was supplied to the third zone so that a steady decrease in temperature occurred through the zone. The silica tube was initially flushed out with argon gas and during the heating a steady flow of argon was passed through it.

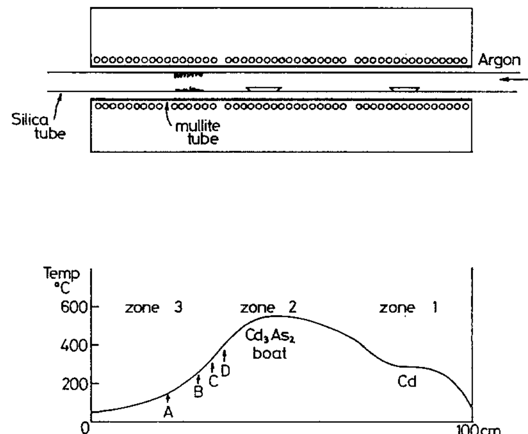

Figure 1 Temperature profile of the furnace.

During the approximately three days that the apparatus was left at temperature with the argon gas flowing, cadmium arsenide was vapour-transported along the tube to be deposited in well-defined temperature regions. Because the argon was passed over heated cadmium before reaching the Cd_3As_2 charge, there was no tendency for dissociation of Cd_3As_2 to $CdAs_2$. The main regions of deposition and growth were as follows:

A; 120 to 260°C. Cadmium deposit. B; 260 to 335°C. Small crystalline droplets adhering to the tube (not analysed). C; 335 to 385°C. (i) Rhomboidal platelets (fig. 2a) growing suspended from the roof of the tube and approxim-

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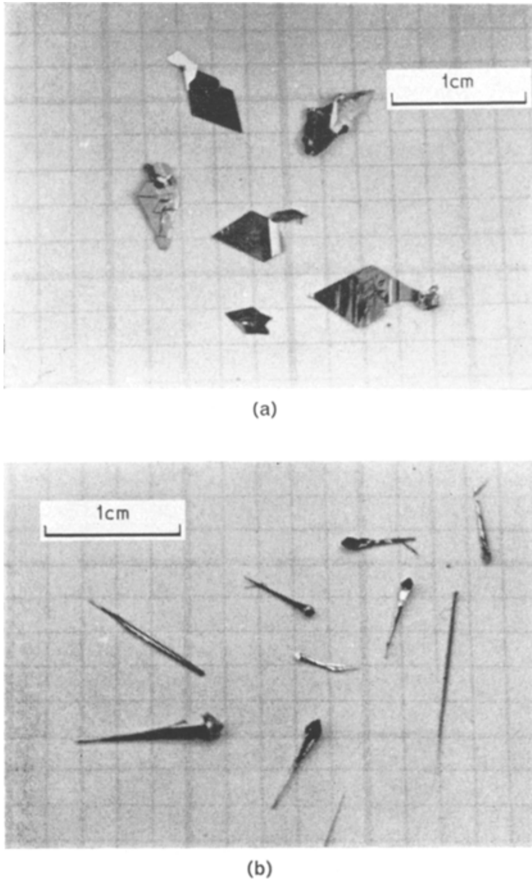

(a)

(b)

Figure 2 (a) and (b) Photographs of crystals.

ately perpendicular to the gas flow. (ii) Needle-shaped or acicular crystals similar to crystals grown in reference [8]. D; 385 to 460°C. (i) Small crystals on the roof of the tube. (ii) Dagger-like crystals growing from the bottom of the tube (fig. 2b).

All the crystals grown in regions C and D were of Cd_3As_2, and Debye-Scherrer photographs obtained from powdered specimens from these regions showed similar diffraction lines to those present for the starting material.

The rhomboidal platelets in section C were each of very uniform thickness although the surfaces were not always smooth (because of lighting conditions the appearance of these surface features is enhanced in fig. 2a). Cd_3As_2 has a tetragonal structure with $a = 12.67$Å and $c = 25.4$Å [9]. If a pseudocubic cell of $a = 12.7$Å approximately is assumed then all the faces on these crystals are of type $\{111\}$, including the main faces. Within the tetragonal cell they are $\{112\}$.

3. Galvanomagnetic Measurements

The Cd_3As_2 platelets were very thin (varying in thickness from approximately 4×10^{-3} cm to 4×10^{-2} cm). For electrical measurements, platelets having the most uniform thickness were selected. The method used was that of Paux [10] for measuring the resistivity and Hall effect of discs of arbitrary shape. Four copper wires (44 gauge) were soldered to corners of the crystals to provide the probes required. A mean thickness was measured for each sample using a travelling microscope. As required by the method, the current was passed through pairs of leads in turn and the potential established between the other two probes measured. The current was supplied from a constant current supply and measurements were made for both directions of electric current and magnetic field. Electrical measurements were made on a number of crystals and the results are summarised in table I for those samples which withstood the thermal stresses involved when measurements were made over a range of temperatures.

As the Hall effect was found to be magnetic-field dependent, particularly at room temperature and above, the low field coefficients obtained for magnetic induction of $0.02T$ are shown for samples T and Z in fig. 3. These are compared with results taken from references [11] and [12] for bulk samples. The curves show that at the lower temperatures, where the Hall coefficients are almost independent of both magnetic induc-

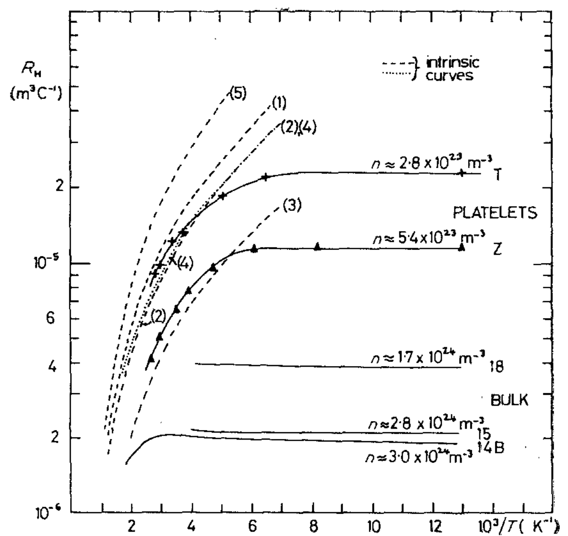

Figure 3 Hall effect in the crystals compared with that for bulk samples. (For numbering of curves, see text.)

TABLE I Galvanomagnetic coefficients (R_H at 0.02T and $\Delta\rho/\rho_0$ at 0.6T).

Sample	300 K			80 K				
	ρ_0 (10^{-6} Ω m)	R_H (10^{-6} m^3 C^{-1})	$\Delta\rho/\rho_0$	ρ_0 (10^{-6} Ω m)	R_H (10^{-6} m^3 C^{-1})	$\Delta\rho/\rho_0$	$1/(eR_H) \simeq n$ (10^{23} m^{-3})	$R_H/\rho_0 = \mu_H$ (m^2 V^{-1} sec^{-1})
T	0.62	12.2	0.53	0.23	23	3.9	2.8	9.8
Z	0.40	6.4	0.37	0.19	11.6	2.6	5.4	6.1
U	0.24	2.8	0.42	0.06	3.0	3.2	21	5.0

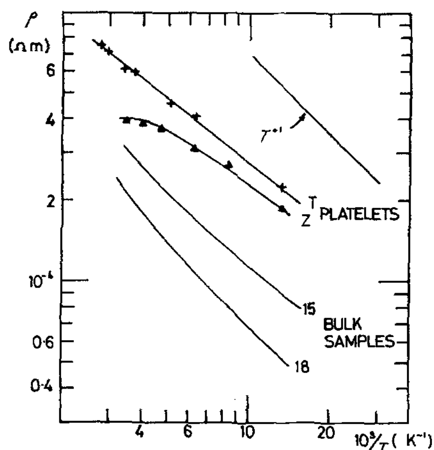

Figure 4 Resistivity of the platelets compared with the resistivity for typical bulk specimens.

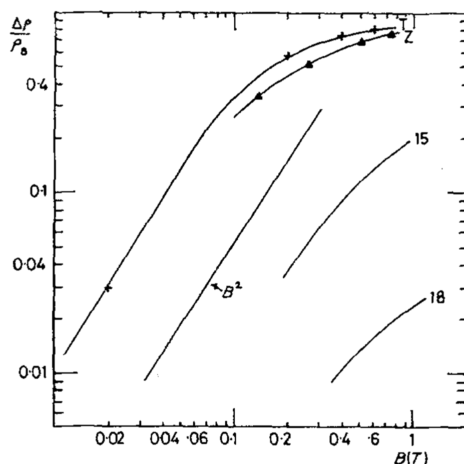

Figure 5 Magnetoresistance at liquid N_2 temperature.

tion and temperature, the carrier concentration ranges from approximately 2×10^{24} electrons m^{-3} down to 3×10^{23} electrons m^{-3}. The latter value in particular indicates an unusually low carrier concentration for Cd_3As_2.

The resistivity shows a temperature dependence of T^{+1} at low temperatures (fig. 4) corresponding to a T^{-1} dependence for carrier mobility in a degenerate sample. Within the temperature range for which measurements were made, the resistivity has not been found to fall with increase of temperature, although in the case of sample Z it has begun to level off due to the increased carrier concentration. Fig. 5 shows the magnetoresistance of the samples at liquid nitrogen temperatures as a function of magnetic induction. The platelets all show very similar values of magnetoresistance and these values are considerably higher than for the bulk samples.

4. Discussion

Although various values of band-gap have been attributed to cadmium arsenide, recent work suggests a zero band-gap model. Wagner *et al* [13] suggested an α-Sn-like zero band-gap model and this model or one with a very small gap is supported by the theoretical paper of Lin-Chung [14]. More recently, Rogers *et al* [15] have suggested that the heavy hole valence band is displaced from the centre of the zone.

For all samples, whether platelets or bulk samples, electron concentrations are such that degenerate statistics must be used. Assuming that the decrease in Hall coefficient with increase of temperature for each of the samples arises from thermal excitation between a valence and conduction band, it is then possible to consider what parameters would be necessary for the different proposed band structure models. A simple parabolic band structure with single conduction and valence bands separated by a small direct energy gap would require a band-gap at least as small as 0.025 eV, a small effective mass for the electrons and a much larger effective mass for the holes. If instead the conduction band is assumed to have the form of the Kane model [16] then a small energy gap at $k = 0$

gives rise to a slender conduction band. Consequently, a large electron concentration would be associated with a high value of Fermi energy such that the Fermi level lies high within the conduction band. Considerable overlap between the conduction and valence bands would be necessary to begin to fit the Hall data of fig. 3. For a similar reason, the α-Sn-like model involving a Kane-type conduction band is not suitable.

However, considering the model of Rogers *et al.* (fig. 11 in their paper), a rather larger direct energy gap E_g at $k = 0$ means that the Kane-type conduction band is less slender than would be the case for a very small direct energy gap. The electron concentration in the conduction band will be

$$n = \frac{1}{2\pi^2}\left(\frac{3}{2}\right)^{3/2}\left(\frac{k_B T}{Q}\right)^2 \int_0^\infty \frac{x^{\frac{1}{2}}(x+E_g)^{\frac{1}{2}}(2x+E_g)}{1+\exp(x-\zeta)}\,dx$$

where Q is a constant here assumed to be 8.5×10^{-10} eV-m as for other materials, T is absolute temperature, k_B is Boltzmann's constant and ζ is the reduced Fermi level. The hole concentration will be

$$p = N \cdot 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2} \cdot \exp\left(-\zeta - \frac{\Delta E}{k_B T}\right)$$

where a parabolic band is assumed, m_h^* is the hole effective mass, h is Planck's constant and N is the number of band extrema within the reduced zone. If it is assumed after [15] that the extrema are along the ⟨1 0 0⟩ directions (considering Cd_3As_2 as pseudocubic) and within the reduced zone then $N = 6$, if at the zone edge $N = 3$.

The energy difference ΔE is small and can be taken as zero, a small deviation from this value having less effect than variation of other parameters. These parameters are set as follows:

(1) $E_g = 0.38$ eV, $m_h^* = 0.12\ m_0$ based on references [13] and [17] $N = 3$.
(2) As above but $N = 6$.
(3) $E_g = 0.50$ eV, $m_h^* = 0.5\ m_0$, $N = 3$ based on reference [15].
(4) $E_g = 0.50$ eV, $m_h^* = 0.12\ m_0$, $N = 3$.
(5) $E_g = 0.20$ eV, $m_h^* = 0.12\ m_0$, $N = 3$.

Then by equating electron and hole concentrations, the variation of the intrinsic concentration can be obtained as a function of temperature. As the hole mobility can be expected to be appreciably less than the electron mobility, the intrinsic Hall coefficient can be obtained directly from the intrinsic concentration. The variation of intrinsic Hall coefficient with temperature for these sets of parameters is superimposed on fig. 3. It can be seen that a choice for E_g of 0.38 eV, or somewhat less, and a heavy hole effective mass of 0.12 m_0 would fit the experimental data. Then the electron effective mass at the bottom of the band will be $m^*(0) = 0.02\ m_0$. For intrinsic conditions the reduced Fermi level would be approximately 2 (for $N = 3$) and almost independent of temperature. In the constant carrier concentration region below room temperature, the Fermi level is approximately 0.03 eV for a carrier concentration of 3×10^{23} m^{-3} and 0.15 eV for a carrier concentration of 2.5×10^{24} m^{-3}, the approximate carrier concentration for which many of the measurements described in the literature have been carried out. Earlier measured values of band-gap of 0.14 and 0.6 eV can then be accounted for respectively by a transition from the heavy hole valence band to the conduction band with Burstein shift, and by either a direct optical transition between the light balence band and the conduction band, or by a transition involving a second conduction band.

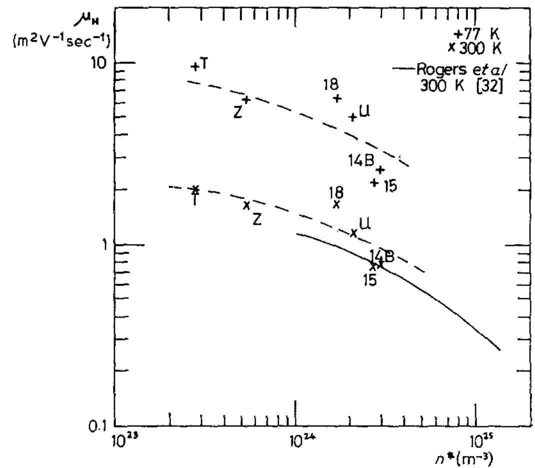

Figure 6 Hall mobility as a function of carrier concentration n^* (n^* at 77 K).

Fig. 6 shows the Hall mobility (at room temperature and 77 K) as a function of carrier concentration as measured at liquid nitrogen temperature. The curve given by Rogers *et al* for room temperature is included for comparison.

Despite the scatter of experimental points, there is a steady increase of Hall mobility with decrease of carrier concentration.

Annealing of cadmium arsenide samples under an excess pressure of arsenic has not been found by Spitzer *et al* [18] to reduce the electrical and thermal conductivity. Ugai and Zyubina [19] reported a reduced carrier concentration for samples which included ones annealed in arsenic. However, attempts to reproduce these results by annealing bulk samples in arsenic vapour produced samples showing similar temperature dependence of the electrical resistivity, but the material was apparently multi-phase. Doi *et al* [20] produced an increase in electron concentration by annealing in arsenic. Therefore it can be considered that in the present growth method the presence of cadmium vapour in the argon gas flow was significant in producing crystals of a reduced carrier concentration.

If growth in an excess cadmium pressure reduces the electron carrier concentration, this suggests anti-structure disorder. This is a type of disorder which in particular is likely to occur in intermetallic compounds of the type M_nX_m where M and X have approximately the same size and the difference in electronegativity is not too large. The electronegativity difference between Cd and As has the comparatively small value of 0.5 [21]. Cd_3As_2 is thought to be almost covalent. For instance, Suchet [22, p. 119] quotes a crystalline ionicity, λ, = 0.32, corresponding to an almost covalent compound. Thus it is consistent that arsenic could substitute for cadmium to produce antistructure disorder.

5. Application

Material possessing this reduced carrier concentration might be particularly useful for the construction of fast thermal radiation detectors using the Nernst effect. Such a detector employing a Cd_3As_2-NiAs eutectic has already been discussed by Goldsmid and Sydney [23]. The presence of the NiAs merely gave increased mechanical strength and did not improve the thermal properties. In the case of the Cd_3As_2 platelets, they are of a size which is suitable for use in a detector and an increased figure of merit can be expected. Reducing the carrier concentration also increases the magnetoresistance and this is desirable for the use of Cd_3As_2 in magnetoresistive devices.

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