

## Physical Properties of Several II-V Semiconductors

W. J. TURNER, A. S. FISCHLER, AND W. E. REESE

Research Laboratory, International Business Machines Corporation, Poughkeepsie, New York

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The physical properties of single crystals of the noncubic II-V semiconducting compounds  $Zn_3As_2$ ,  $ZnAs_2$ ,  $ZnSb$ ,  $Cd_3As_2$ ,  $CdAs_2$ , and  $CdSb$  have been investigated. Energy gaps in these materials vary from approximately 0.13 to 1.0 eV. Mobilities at 297°K range from 10 cm<sup>2</sup>/volt sec to 15 000 cm<sup>2</sup>/volt sec and increase at low temperature. Resistivity and mobility anisotropy have been investigated in detail for  $CdAs_2$ . Except for the  $A_3^{II}B_2^V$  compounds, high optical transmission has been observed from the intrinsic edge to approximately 30 microns.

### INTRODUCTION

THE purpose of this paper is to describe in general the physical properties of the II-V semiconductors:  $Zn_3As_2$ ,  $ZnAs_2$ ,  $ZnSb$ ,  $Cd_3As_2$ ,  $CdAs_2$ , and  $CdSb$ . The preparation, purification and crystal growth have been carried out by Silvey, Lyons, and Silvestri and are described elsewhere.<sup>1,2</sup> All measurements were on single-crystal material and more emphasis was placed on  $CdAs_2$ <sup>3,4</sup> and  $CdSb$ <sup>3,5</sup> than the other compounds because the technology of crystal growth was more advanced and the physical properties of these were found to be interesting.

### EXPERIMENTAL

Hall effect and resistivity measurements were made using conventional dc methods. The thermal conductivity and Seebeck coefficients were measured at room temperature using the method described by Harman *et al.*<sup>6</sup> This consists of allowing the Peltier heat generated at the current contacts to maintain a temperature gradient along the sample. From measurements of this gradient and the associated thermal voltages produced across the sample, one can calculate the Seebeck coefficients and the thermal conductivity. Transmission and reflection measurements were made at 300° and 77°K on optically polished monocrystalline samples in the spectral range of 0.8–38 microns. Absorption coefficients and reflectivities were calculated from these data using the well-known formulas for the transmission and reflection coefficients for a plane parallel plate. The x-ray data referred to are by various workers<sup>7–11</sup>

while the cyclotron resonance studies were made at 24 000 and 35 000 Mc/sec at helium temperatures by Stevenson.<sup>12,13</sup>

### GENERAL

Table I outlines some of the general properties of the materials. It should be noted that none of the materials are cubic. Therefore, it was necessary to make measurements as a function of crystal orientation. The electrical and optical properties of  $ZnAs_2$  and  $CdAs_2$  showed marked anisotropy. For  $CdAs_2$  it was possible to interpret the results of a detailed study of the anisotropy. Irreversible changes in the Hall coefficient and resistivity are observed above 400°K in all cases as a result of thermal dissociation of the compounds. Consequently, most electrical measurements were made in the temperature range of 77–400°K. This meant that the intrinsic electrical properties usually could not be measured. The gaps were, therefore, determined from optical absorption data. There does not appear to be any simple relationship between the energy gap and the melting point as has been observed for other materials, e.g., III-V compounds. In fact it is difficult to discern any trends in the energy gaps. For example  $Zn_3As_2$  and  $ZnAs_2$  have comparable gaps while  $Cd_3As_2$  has a small gap compared to  $CdAs_2$ . Moreover,  $ZnSb$  and  $CdSb$  have gaps which are of the same order of magnitude and approximately 3 times that of  $Cd_3As_2$ .

The approximate Hall mobilities at room temperature are shown. The six compounds have a wide range of mobilities. The hole mobilities in the zinc compounds are very low. In the cadmium compounds hole mobility has been measured only for  $CdSb$  where it is considerably greater than in the zinc compounds. Judging from cyclotron resonance effective mass data the holes in  $CdAs_2$  might be expected to be more mobile than the electrons; hence, more mobile than the holes in  $ZnAs_2$ . An increase in mobility and decrease in gap are observed in other compounds as the metallic atom is replaced with one of higher atomic number but in the same group, e.g.,  $AlSb$ ,  $GaSb$ ,  $InSb$ . Thus, the higher mobilities in the cadmium compounds are consistent with this trend. The electron mobility in  $Cd_3As_2$  is very

<sup>1</sup> G. A. Silvey, V. J. Lyons, and V. J. Silvestri (to be published).

<sup>2</sup> G. A. Silvey and V. J. Lyons, *J. Electrochem. Soc.* **106**, 61C (1959).

<sup>3</sup> W. J. Turner, A. S. Fischler, and W. E. Reese, *J. Electrochem. Soc.* **106**, 206C (1959).

<sup>4</sup> A. S. Fischler (to be published).

<sup>5</sup> W. J. Turner, A. S. Fischler, and W. E. Reese *Proceedings of the Prague Semiconductor Conference* (to be published).

<sup>6</sup> T. C. Harman, J. H. Cahn, and M. J. Logan, *J. Appl. Phys.* **30**, 1351 (1959).

<sup>7</sup> M. V. Stackelberg and R. Paulus, *Z. physik. Chem.* **B28**, 427 (1935).

<sup>8</sup> K. E. Almin, *Acta. Chem. Scand.* **2**, 400 (1948).

<sup>9</sup> H. Cole, F. W. Chambers, and H. Dunn, *Acta Cryst.* **9**, 685 (1956).

<sup>10</sup> M. E. Senko, H. M. Dunn, J. Weidenborner, and H. Cole, *Acta Cryst.* **12**, 76 (1959).

<sup>11</sup> N. R. Stemple and M. E. Senko, *Acta Cryst.* (to be published).

<sup>12</sup> M. J. Stevenson, *Phys. Rev. Letters* **3**, 464 (1959).

<sup>13</sup> M. J. Stevenson, *Proceedings of the Prague Semiconductor Conference* (to be published).

TABLE I. General physical properties of several II-V semiconductors.<sup>a</sup>

Compound	Type	Crystal system <sup>b</sup>	Melting point (°C)	$\Delta E_{op}$ (ev) at 297°K	Lowest carrier concentration (cm <sup>-3</sup> ) <sup>c</sup>	Mobility at 297°K (cm <sup>2</sup> /volt sec)	Thermal conductivity (watts/cm °K)	Thermo-electric power ( $\mu$ v/°K)	Effective mass
Zn <sub>3</sub> As <sub>2</sub>	<i>p</i>	tetragonal	1015 <sup>e</sup>	0.93	10 <sup>18</sup>	10			
ZnAs <sub>2</sub>	<i>p</i>	monoclinic	768 <sup>d</sup>	$E\parallel c, 0.90$ $E\perp c, 0.93$	10 <sup>16</sup>	50			
ZnSb	<i>p</i>	orthorhombic	546 <sup>e</sup>	0.53	4×10 <sup>18</sup>	10	1.1×10 <sup>-2</sup>	110	$m_l/m_0=0.175\pm 0.010^g$ $m_t/m_0=0.146\pm 0.010$ Sign of carrier unidentified
Cd <sub>3</sub> As <sub>2</sub>	<i>n</i>	tetragonal	721 <sup>e</sup>	0.13	3×10 <sup>18</sup>	15 000	1.1×10 <sup>-1</sup>	140	$m^*/m_0=0.10\pm 0.05$ electrons
CdAs <sub>2</sub>	<i>n</i>	tetragonal	621 <sup>e</sup>	$E\parallel c, 1.00$ $E\perp c, 1.04$	5×10 <sup>14</sup>	<i>a</i> axis, 100 <i>c</i> axis, 400			$m_l/m_0=0.150\pm 0.030^f$ $m_t/m_0=0.580\pm 0.040$ electrons $m_l/m_0=0.094\pm 0.030$ $m_t/m_0=0.346\pm 0.025$ holes
CdSb	<i>p</i>	orthorhombic	456 <sup>e</sup>	0.46	10 <sup>16</sup>	300	1×10 <sup>-20</sup>	300 <sup>f</sup>	$m_l/m_0=0.140\pm 0.010^f$ $m_t/m_0=0.159\pm 0.010$ Sign of carrier unidentified

<sup>a</sup> See note added in proof.

<sup>b</sup> See text for references.

<sup>c</sup> M. Hanson, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, New York, 1958), 2nd ed.

<sup>d</sup> V. J. Lyons, *J. Phys. Chem.* **63**, 1142 (1959).

<sup>e</sup> Undoped material.

<sup>f</sup> For carrier concentration of 10<sup>18</sup> cm<sup>-3</sup>.

<sup>g</sup> M. J. Stevenson, *Proceedings of the Prague Semiconductor Conference* (to be published).

high considering the carrier concentration. For CdAs<sub>2</sub> the electron mobility in the *c* direction is four times that in the *a* direction.

Despite low room-temperature mobilities and relatively large carrier concentrations, cyclotron resonance has been observed in CdAs<sub>2</sub>,<sup>12,13</sup> CdSb and ZnSb.<sup>13</sup> A comprehensive discussion of the cyclotron resonance

data will be presented by Stevenson in a forthcoming paper.<sup>14</sup> An average value of electron effective mass in Cd<sub>3</sub>As<sub>2</sub> was obtained from optical and thermoelectric data. The approximate room temperature values of carrier concentration, Hall mobilities, thermal conductivities, and Seebeck coefficients are also listed for convenience.

## DETAILED RESULTS AND DISCUSSION

### Zn<sub>3</sub>As<sub>2</sub>

Below 659±3°C zinc arsenide (Zn<sub>3</sub>As<sub>2</sub>)<sup>15</sup> is tetragonal with a *c/a* ratio of 2.007.<sup>9</sup> This form is called the  $\alpha$  phase while the phase which exists above 659±3°C is called the  $\beta$  phase and has an unknown crystal structure. The electrical properties of two *p*-type samples of Zn<sub>3</sub>As<sub>2</sub> are shown in Fig. 1. Measurements carried out above 400°K resulted in irreversible changes in the Hall coefficient and resistivity due to thermal decomposition. The dashed curves are a semilogarithmic plot of Hall coefficient vs 10<sup>3</sup>/*T*. The lower curve is for an undoped sample while the upper curve is for a selenium-doped sample. The semilogarithmic plot of resistivity vs 10<sup>3</sup>/*T* is shown (solid lines) for the same samples. The lower resistivity is for the undoped sample. As demonstrated in these curves for Se it was found that group VI elements act as compensators in *p*-type Zn<sub>3</sub>As<sub>2</sub>. Therefore, as was described by Silvey and co-workers<sup>1</sup> great pains were taken to remove

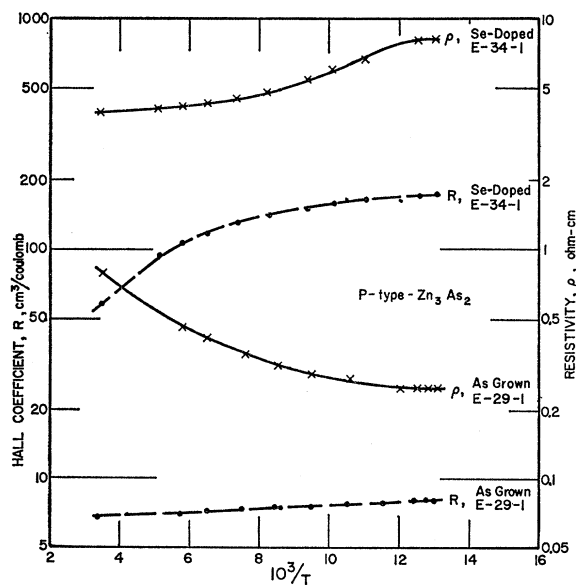


FIG. 1. Hall coefficient and resistivity of an undoped sample (E-29-1) and a selenium-doped sample (E-34-1) of *p* type Zn<sub>3</sub>As<sub>2</sub>.

<sup>14</sup> M. J. Stevenson (to be published).

<sup>15</sup> G. A. Silvey, *J. Appl. Phys.* **29**, 226 (1958).

sulfur and selenium which are always present in arsenic and are not detectable spectroscopically. The Hall coefficient for the undoped E-29-1 sample is almost flat over the temperature range and indicates a net hole concentration of approximately  $10^{18} \text{ cm}^{-3}$ . A logarithmic plot of mobility vs absolute temperature is shown for the same samples in Fig. 2. At higher temperatures the mobility follows a  $T^{-1.1}$  law. As one might expect for the Se-doped sample the onset of impurity scattering occurs at higher temperatures than for the undoped sample. The values of mobility for the doped sample above  $100^\circ\text{K}$  are somewhat higher than the undoped sample. This is not to be expected and may result from differences in orientation of the two samples. The optical absorption coefficient  $K$  vs photon energy in ev is shown in Fig. 3. The optical edge from this curve is taken to be 0.93 ev.

**ZnAs<sub>2</sub>**

Although the semiconducting behavior of ZnAs<sub>2</sub> has been reported earlier by Heike<sup>16</sup> and Fritzsche,<sup>17</sup> relatively little physical information has been published. Von Stackelberg and Paulus<sup>7</sup> reported ZnAs<sub>2</sub> to be orthorhombic. However, Senko<sup>10</sup> and co-workers have found it to be monoclinic.

Measurements of Hall coefficient and resistivity for *p*-type ZnAs<sub>2</sub><sup>18</sup> samples were made in the temperature range  $77^\circ$  to  $600^\circ\text{K}$ . Above  $400^\circ\text{K}$  the thermal dissociation of ZnAs<sub>2</sub> into Zn<sub>3</sub>As<sub>2</sub> and As<sub>4</sub> prevented reproducible electrical measurements. Nevertheless, an intrinsic gap of approximately 1.2 ev was obtained from the resistivity data.

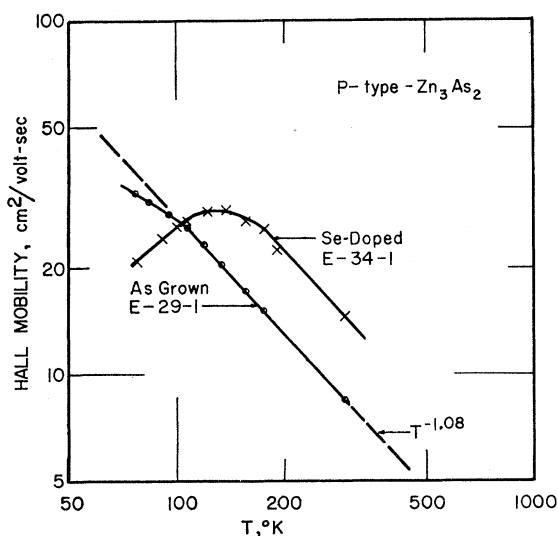


FIG. 2. Temperature dependence of the Hall mobility in Zn<sub>3</sub>As<sub>2</sub> for the samples of Fig. 1.

<sup>16</sup> W. Heike, Z. anorg. Chem. **118**, 264 (1921).

<sup>17</sup> C. Fritzsche, Ann. Physik **17**, 94 (1955).

<sup>18</sup> W. J. Turner, A. S. Fischler, V. J. Lyons, and W. E. Reese, Bull. Am. Phys. Soc. **3**, 379 (1958).

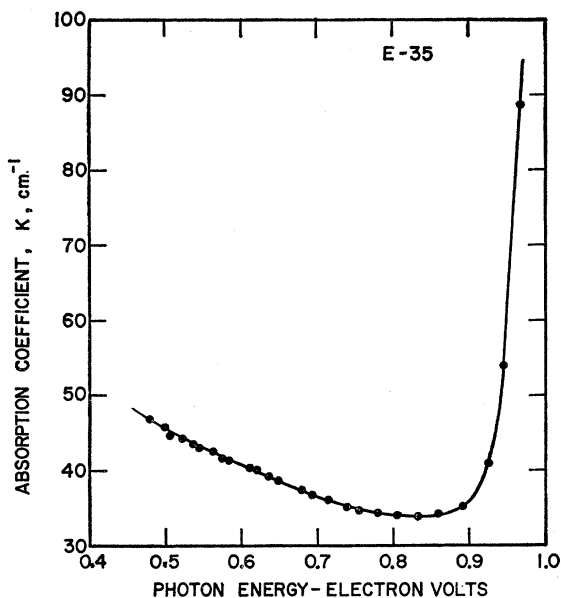


FIG. 3. Optical absorption coefficient as a function of photon energy for a typical sample of Zn<sub>3</sub>As<sub>2</sub>.

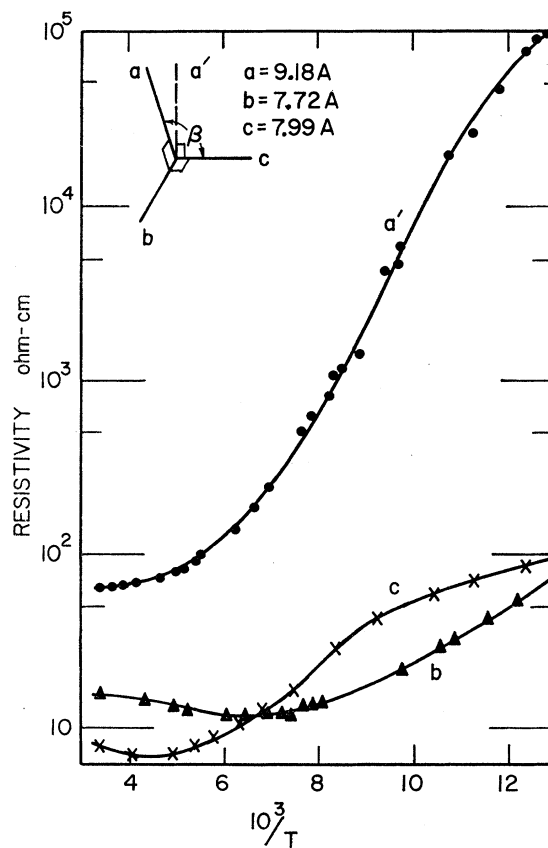


FIG. 4. Resistivity of three oriented samples of ZnAs<sub>2</sub> cut from the same single crystal.

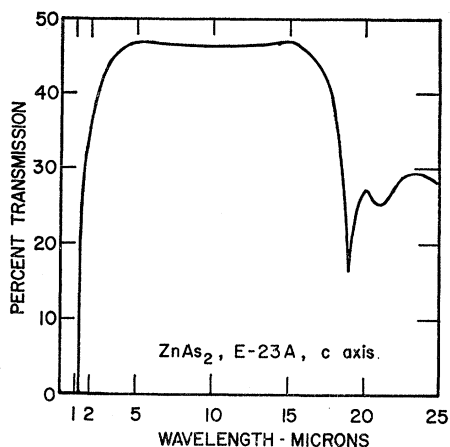


FIG. 5. Optical transmission of  $\text{ZnAs}_2$  (uncorrected for reflection losses) as a function of wavelength for unpolarized light propagated in the  $c$  direction.

Three oriented samples of  $\text{ZnAs}_2$  E-23A were cut with their lengths parallel to the directions  $a'$ ,  $b$ , and  $c$ , as shown in the upper left-hand corner of Fig. 4. The  $b$  and  $c$  refer to crystal axes, while  $a'$  is normal to  $b$  and  $c$  and is inclined at approximately  $12^\circ$  to the monoclinic  $a$  axis.

At room temperature the resistivity in the  $a'$  direction is a factor of ten larger than the resistivity in the  $c$  direction. At nitrogen temperature this factor increases to 1000. For the same temperature range, Hall measurements were made for various orientations of magnetic

field and sample current. These measurements indicated comparable Hall anisotropy. At room temperature the average value of the Hall coefficient would indicate a net carrier concentration of  $10^{16} \text{ cm}^{-3}$ . The large anisotropy in the resistivities and the Hall coefficients which increases with decreasing temperature may result from (1) the presence of multiple valence bands as suggested by Fox<sup>19</sup> or (2) the presence of unknown inhomogeneities introduced during crystal growth. Since pressure contacts were unsatisfactory the usual method of resistivity profiling could not be used. This, coupled with the low symmetry, made it impossible to distinguish the effect of inhomogeneities from true electrical anisotropy.

Optical transmission studies have been made on oriented single crystals. Figure 5 shows the transmission as a function of wavelength for light traveling in the  $c$  direction through an optically polished single crystal plate 0.94 mm thick. The curve is uncorrected for reflection losses. The optical gap as determined by extrapolating the slope of the curve of absorption coefficient vs photon energy to zero absorption is 0.92 eV. Transmission curves for the light traveling in the  $a'$  and  $b$  directions are similar in shape, but differ in magnitude as might be expected for an anisotropic crystal. All samples exhibit high transmission from the intrinsic edge to the 19-micron absorption band. Then the transmission gradually decreases and finally falls to zero at about 32 microns. An average value of 3.38 for the index of refraction was determined from multiple

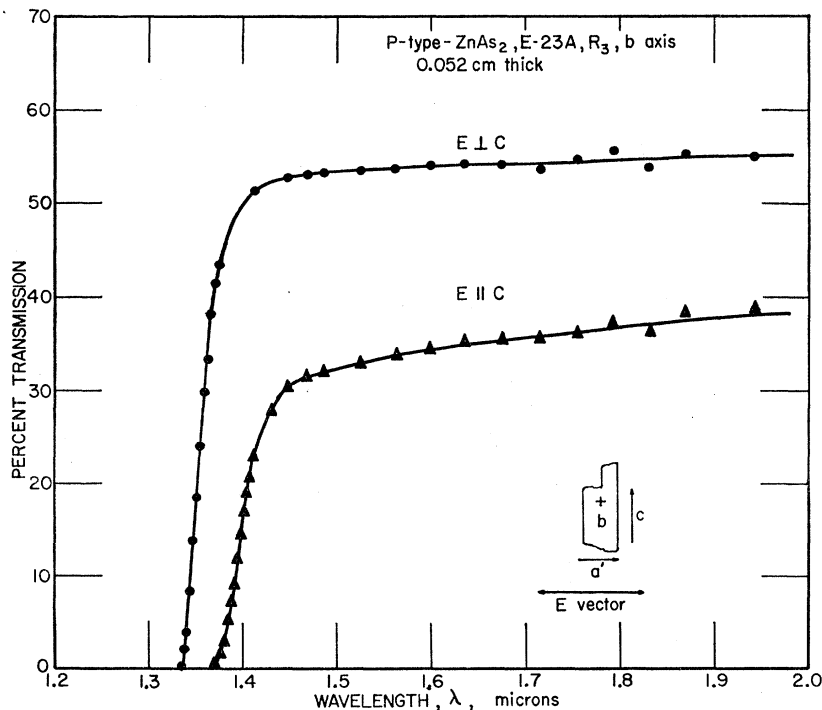


FIG. 6. Transmission of polarized light through a polished plate of  $\text{ZnAs}_2$  for two orientations of the  $E$  vector.

<sup>19</sup> D. Fox, Bull. Am. Phys. Soc. 3, 379 (1958).

reflection peaks in the transmission curve of a thin unoriented sample with nonpolarized light. Perhaps the most interesting feature of ZnAs<sub>2</sub> other than the resistivity anisotropy can be seen in the results of polarized light transmission studies near the edge. Figure 6 shows the transmission vs wavelength for a "b axis" sample. The higher transmission occurs when the E vector is perpendicular to the c axis. For E parallel to the c axis the transmission is reduced by 30%. Part of this drop is due to a change of the index of refraction. However, only about 7% absolute out of 20% absolute change could be attributed to reflection loss differences. It also is significant that the apparent gap for E perpendicular to the c axis is approximately 0.03 eV larger than for E parallel to the c axis. Although both the electrical and optical measurements indicated that ZnAs<sub>2</sub> is highly anisotropic, it is apparent that the low symmetry as well as crystal inhomogeneities make

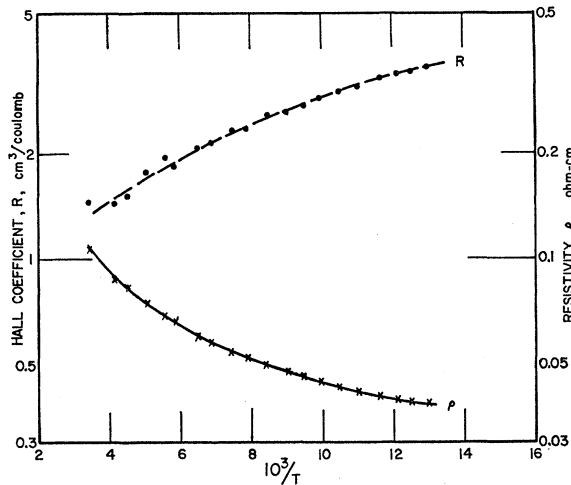


FIG. 7. Hall coefficient and resistivity of sample P-9 of p-type ZnSb.

investigation of the nature of this anisotropy very difficult if not impossible.

**ZnSb**

This material is orthorhombic.<sup>8</sup> As grown it was p type with a net carrier concentration of approximately  $4 \times 10^{18} \text{ cm}^{-3}$  obtained from Hall data (Fig. 7). The Hall mobility (Fig. 8) at 300°K as computed from  $R/\rho$  is only  $10 \text{ cm}^2/\text{volt sec}$ . Even with this high carrier concentration it was possible to get an appreciable amount of light through several optical samples. The optical absorption coefficient vs photon energy obtained for a typical sample is seen in Fig. 9. Although the intrinsic edge is quite rounded it is still possible to estimate the gap at approximately 0.53 eV. Further work is in progress to determine this more precisely. The long-wavelength cutoff is near 27 microns or 0.045 eV. Cyclotron resonance absorption measurements by Stevenson indicate the surfaces of constant energy for

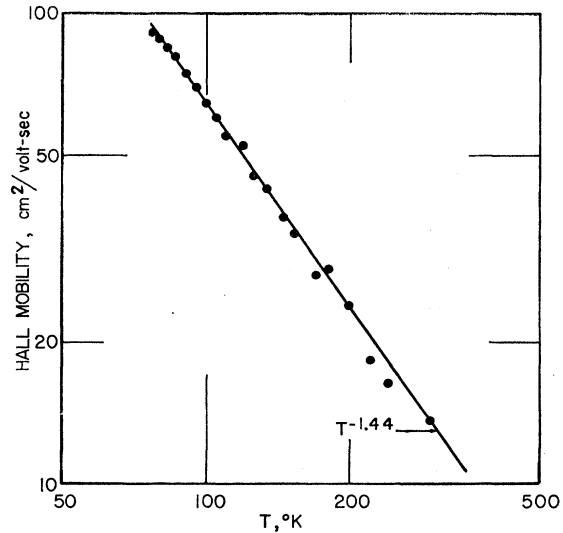


FIG. 8. Temperature dependence of the Hall mobility for the sample of ZnSb shown in Fig. 6.

one of the carriers are slightly prolate spheroids with a symmetry axis along the a direction.<sup>13</sup> Room temperature thermal measurements on ZnSb yield a Seebeck coefficient of  $110 \mu\text{V}/^\circ\text{K}$  and a thermal conductivity of  $1.1 \times 10^{-2} \text{ watt/cm } ^\circ\text{K}$  for the  $4 \times 10^{18}\text{-cm}^{-3}$  hole concentration.

**Cd<sub>3</sub>As<sub>2</sub>**

Cd<sub>3</sub>As<sub>2</sub> is tetragonal<sup>7,20</sup> with a solid-solid phase transition at 578°C.<sup>21</sup> While this transition leads to

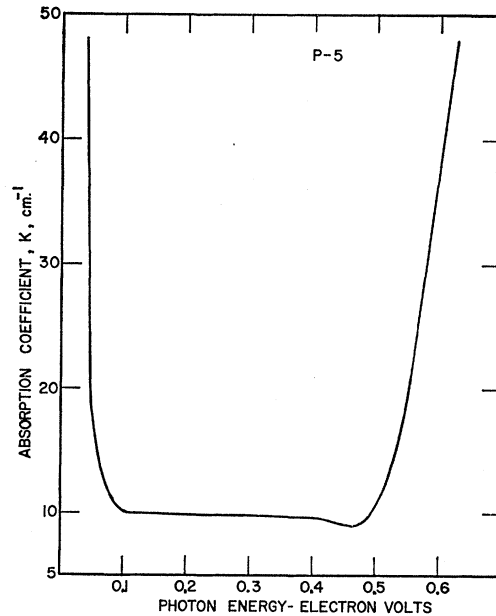


FIG. 9. Optical absorption coefficient of ZnSb, as a function of photon energy.

<sup>20</sup> N. R. Stemple (private communication).  
<sup>21</sup> M. Hanson, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed., p. 156.

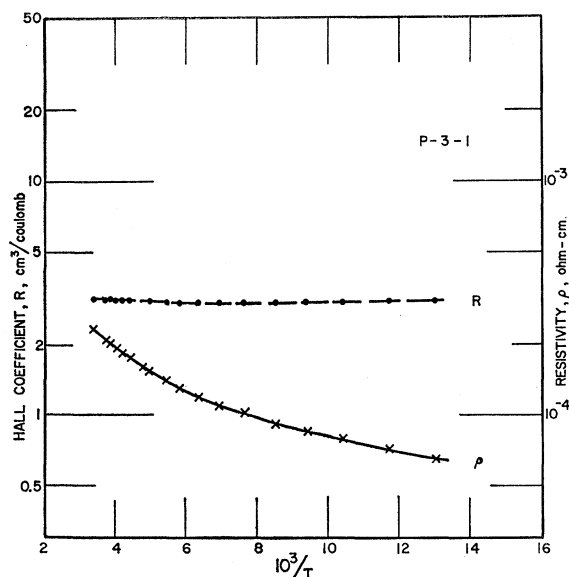


FIG. 10. Hall coefficient and resistivity of a sample of *n*-type  $\text{Cd}_3\text{As}_2$  cut from a pulled crystal.

extremely poor physical appearance of the crystals,  $\text{Cd}_3\text{As}_2$  has the highest electron mobility of all the II-V compounds studied. Rosenberg and Harman<sup>22</sup> have reported room temperature mobilities as high as 10 000  $\text{cm}^2/\text{volt sec}$  while the authors, have measured a Hall mobility of 15 000  $\text{cm}^2/\text{volt sec}$  at room temperature

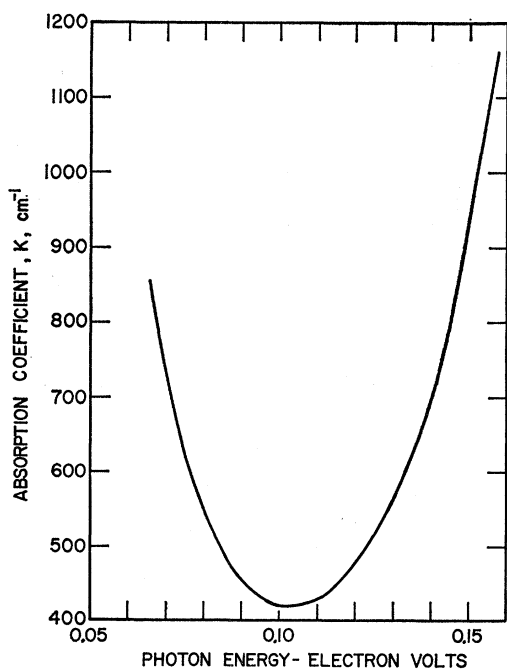


FIG. 11. Optical absorption coefficient as a function of photon energy for a sample of *n*-type  $\text{Cd}_3\text{As}_2$ .

<sup>22</sup> A. J. Rosenberg and T. C. Harman, *J. Appl. Phys.* **30**, 1621 (1959).

on pulled crystals with a mobility temperature variation of  $T^{-0.88}$ . The technique of growing the crystals affected mobility greatly. Mobilities at room temperature varied from about 4000  $\text{cm}^2/\text{volt sec}$  for crystals grown by a directional freeze method to 15 000  $\text{cm}^2/\text{volt sec}$  for pulled crystals. Figure 10 shows a typical plot of  $R$  and  $\rho$  vs  $10^3/T$ . While the data is shown only to 77°K the measurements have been extended to helium temperature. Even at the lowest temperatures the Hall coefficient continued to be flat and the resistivity never reached a minimum. Moss<sup>23</sup> has reported an electrical gap for  $\text{Cd}_3\text{As}_2$  of 0.14 eV while a value of 0.13 eV seems appropriate from a plot of absorption coefficient vs photon energy (Fig. 11). An estimate of the electron effective mass of  $0.1m_0 \pm 0.05m_0$  was obtained from (1) the value of the absorption coefficient in the free-carrier region, (2) the wavelength of the minimum in reflectivity due to the electronic contribution to the electric susceptibility at long wavelengths, and (3) the value of the thermoelectric power.

For samples of net electron concentration of approximately  $3 \times 10^{18} \text{ cm}^{-3}$ , a room temperature Seebeck coefficient of 143  $\mu\text{V}/^\circ\text{K}$  and a thermal conductivity of 0.11 watt/cm  $^\circ\text{K}$  was observed.

### $\text{CdAs}_2$

As grown  $\text{CdAs}_2$  is *n*-type. The purest material studied had a net electron concentration in excess of  $5 \times 10^{14} \text{ cm}^{-3}$ . Since  $\text{CdAs}_2$  is tetragonal,<sup>11</sup> both Hall and resistivity are tensor quantities. It can be shown that the number of independent components of the Hall tensor is two, corresponding to the cases when  $H$  is

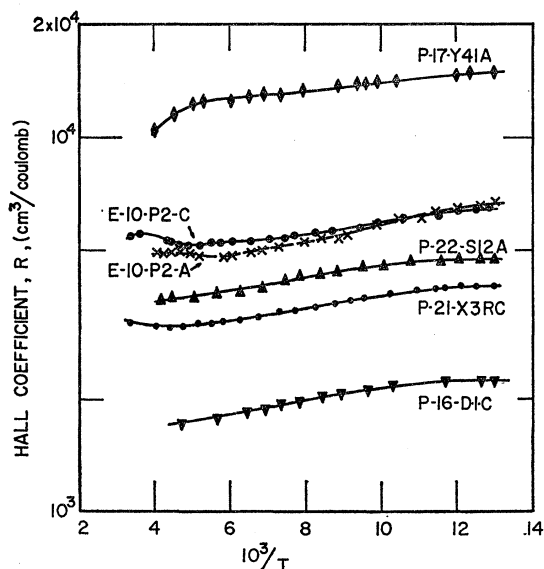


FIG. 12. Hall coefficient for several oriented samples of *n*-type  $\text{CdAs}_2$  in the extrinsic temperature range.

<sup>23</sup> T. S. Moss, *Proc. Phys. Soc. (London)* **B63**, 167 (1950).

parallel and  $H$  is perpendicular to the fourfold symmetry axis ( $c$  axis).<sup>24</sup> The Hall coefficient has been studied as a function of sample orientation and direction of magnetic field. Within experimental error the independent components of the Hall tensor are equal.<sup>4</sup> The Hall coefficient  $R$  vs  $10^3/T$  is shown in Fig. 12 for several samples. The variation in  $R$  is small over the temperature range of 77–295°K and can be attributed to a change in the scattering mechanism.

Resistivity vs  $10^3/T$  is shown in Fig. 13 for the samples of Fig. 12. Both resistivity and Hall data indicate a region of predominantly lattice scattering from 77–295°K. The Hall mobility varies approximately as  $T^{-3/2}$  although in no sample did  $\log \mu$  show a linear dependence on  $\log T$  over an extended temperature range.

There are two independent components of the resistivity tensor corresponding to the principal  $a$  and  $c$  directions. Samples E-10P2-A and E-10P2-C were cut from adjacent slices of the same crystal with their length parallel to  $a$  and  $c$  crystal axes, respectively. Since their carrier concentrations were the same, the ratio of Hall mobilities could be directly determined from the resistivity data.

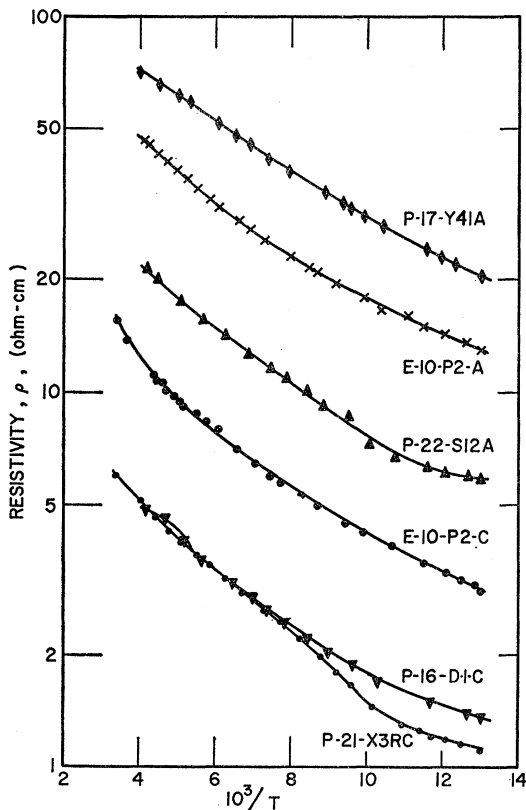


Fig. 13. Resistivity for the samples of Fig. 12.

<sup>24</sup> J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, New York, 1957).

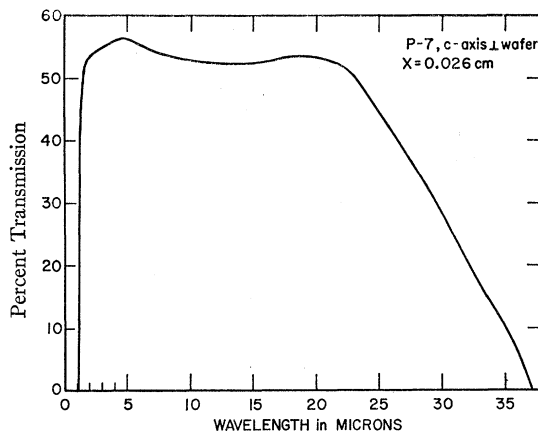


Fig. 14. Optical transmission of a polished plate of CdAs<sub>2</sub> cut perpendicular to the  $c$  axis. The curve is uncorrected for the reflection loss which was approximately 39%.

Resistivity anisotropy with isotropic Hall coefficient indicates that the surfaces of constant energy may be represented by ellipsoids of revolution oriented along the  $c$  axis of the tetragonal system, i.e., the axis of fourfold symmetry.<sup>25</sup> An isotropic relaxation time is indicated by the same temperature variation of the mobilities. Using a single ellipsoidal model and an isotropic relaxation time the ratio of electron effective mass in the  $a$  direction to that in the  $c$  direction is equal to the resistivity ratio. The value so obtained is 4.0. This is in good agreement with the value of 3.87 obtained by Stevenson<sup>12,13</sup> from cyclotron resonance.

The absence of a longitudinal magnetoresistance supports the assumption of  $c$ -oriented constant energy surfaces. The mobility computed from the transverse magnetoresistance assuming ellipsoidal energy surfaces and lattice scattering is in substantial agreement with the Hall mobility.

CdAs<sub>2</sub> shows maximum optical transmission for non-polarized light when the light is propagated along the  $c$  axis of the crystal. A typical curve of transmission vs wavelength is shown in Fig. 14 for a polished plate 0.026 cm thick cut perpendicular to the  $c$  axis. The curve is uncorrected for reflection losses. The high flat transmission over the wide spectral range makes this a potential infrared window material. Polarized light studies have been carried out near the intrinsic edge. Figure 15 shows the results for light propagated perpendicular to a sample containing the  $c$  axis in the plane of the sample. From these curves the apparent optical gaps are 1.04 eV for the  $E$  vector perpendicular to  $c$  and 1.00 eV for  $E$  parallel to  $c$ . In the straight-line region of the edge, one notes that the absorption coefficient for  $E$  parallel to the  $c$  axis is almost double the value for  $E$  perpendicular. As suggested by Dumke,<sup>26</sup> this could mean that the matrix element between the

<sup>25</sup> V. A. Johnson, *Phys. Rev.* **75**, 1631 (1949).

<sup>26</sup> W. P. Dumke (private communication).

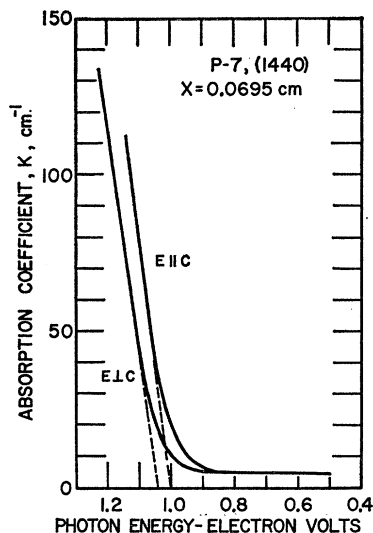


FIG. 15. Optical absorption coefficient of  $\text{CdAs}_2$  near the intrinsic edge for two directions of polarization relative to the  $c$  axis.

valence and conduction bands of the component of the momentum operator parallel to the  $c$  axis is greater than the matrix element of the component perpendicular to the  $c$  axis. This is consistent with the observed effective-mass data.

### CdSb

While several investigators<sup>3,5,27-37</sup> have reported on electrical and thermal properties of CdSb, until recently optical data were not available.<sup>3,5</sup> The optical absorption coefficient as a function of photon energy (Fig. 16) has been measured at 78°K and 300°K. The optical energy gap is found to be 0.465 eV at 300° and 0.585 eV at 78°K. If it is assumed that the energy gap  $E_g$  depends on temperature as  $E_g(T) = E_g(0) + \alpha T$ , then a value of  $-5.4 \times 10^{-4}$  eV/°K is found for  $\alpha$ .

Resistivity measurements (Fig. 17) on single-crystal samples of  $p$ -type CdSb give a value of about 0.5 eV for the energy gap extrapolated to absolute zero. To obtain the energy gap from the Hall curve (Fig. 17) at elevated temperatures one must know the temperature variation of  $\mu_e/\mu_h < 1$ , where  $\mu_e$  and  $\mu_h$  are electron and hole mobilities, respectively.

The extrinsic behavior of  $p$ -type materials shows a marked dependence upon impurity scattering. At any given temperature an increase in the Hall constant

<sup>27</sup> E. Justi and G. Lautz, Z. Naturforsch. **7a**, 191 (1952).

<sup>28</sup> E. Justi and G. Lautz, Z. Naturforsch. **7a**, 602 (1952).

<sup>29</sup> E. Justi and G. Lautz, Abhandl. braunschweig. wiss. Ges. **4**, 107 (1952).

<sup>30</sup> I. M. Pilat, Phys. Metals and Metallography **4**, 31 (1957).

<sup>31</sup> G. Kretschmar, R. F. Potter, and P. R. Bradshaw, Bull. Am. Phys. Soc. **4**, 134 (1958).

<sup>32</sup> J. Yahia and R. Overstreet, Bull. Am. Phys. Soc. **4**, 134 (1958).

<sup>33</sup> A. Euchen and G. Geldhoff, Bull. Physik Ges. **169** (1912).

<sup>34</sup> V. A. Iurkov and N. W. Alekseeva, Soviet Phys.-Tech. Phys. **1**, 898 (1957).

<sup>35</sup> H. Hida, Kanazawa Daigaku Kogakubu Kiyo **2**, 6 (1957).

<sup>36</sup> A. J. Strauss, J. Electrochem. Soc. **106**, 206C (1959).

<sup>37</sup> G. Lautz, Z. Naturforsch. **8a**, 361 (1953).

from sample to sample, corresponds to a lower resistivity (Fig. 17) and to a stronger mobility-temperature dependence (Fig. 18).

Lautz<sup>37</sup> reported no reversal of the sign of the Hall coefficient to temperatures approaching the melting point (734°K). However, Silvestri<sup>38</sup> has measured a cadmium vapor pressure above CdSb of  $10^{-3}$  mm Hg at 560°K, and the authors have found CdSb to become more  $p$ -type due to loss of cadmium. Therefore care must be exercised in attributing the lack of a Hall reversal to  $\mu_h > \mu_e$ .

Indium-doped material prepared in this laboratory which showed  $n$ -type conductivity at room temperature exhibited reversals in the sign of the Hall coefficient both at lower temperatures (200°K) and higher temperatures (400°K). Upon thermal cycling to (525°K) the  $n$ -type region disappeared.

Thermal measurements were made using the apparatus previously mentioned. For silver-doped CdSb with a hole concentration of  $3 \times 10^{18}$   $\text{cm}^{-3}$  the Seebeck coefficient was 323  $\mu\text{V}/^\circ\text{K}$  and the thermal conductivity was  $10^{-2}$  watt/cm  $^\circ\text{K}$ .

### SUMMARY

The II-V semiconductors studied are noncubic with complex unit cells. Nevertheless, cyclotron resonance measurements in  $\text{CdAs}_2$ , CdSb, and ZnSb indicate relatively simple constant-energy surfaces. This provides a basis for analysis of the results of other physical data. The thermal dissociation of the compounds at relatively low temperatures ( $T > 400^\circ\text{K}$ ) makes high-temperature electrical and thermal studies difficult. This complicates the interpretation of the absence of Hall reversals in  $p$ -type  $\text{Zn}_3\text{As}_2$ ,  $\text{ZnAs}_2$ , and CdSb. Although the temperature variation of the mobilities

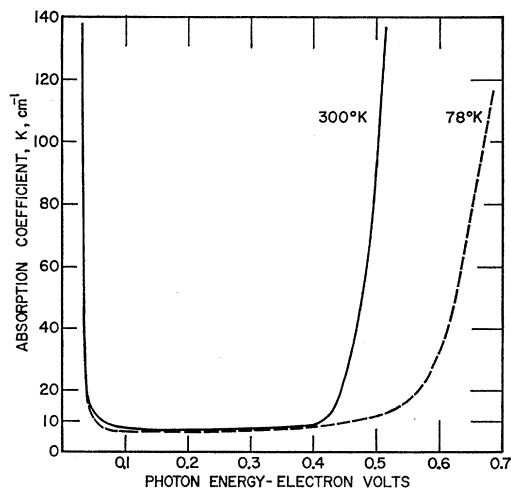


FIG. 16. Optical absorption coefficient versus photon energy for a typical sample of  $p$ -type CdSb at 300°K and 78°K.

<sup>38</sup> V. J. Silvestri, J. Phys. Chem. **64**, 826 (1960).



may be such that at elevated temperatures the electron mobility is less than the hole mobility, e.g., CdSb, this cannot be established by electrical measurements without regard to thermal dissociation.

The compounds show a wide spectrum of mobilities (see Table I) with the electron mobility of Cd<sub>3</sub>As<sub>2</sub> comparable to that of the highest reported for semiconductors at  $3 \times 10^{18} \text{ cm}^{-3}$ .

Both ZnAs<sub>2</sub> and CdAs<sub>2</sub> show marked anisotropy in their optical and electrical properties. For CdAs<sub>2</sub> the anisotropy of the Hall mobility can be directly related to the oblate ellipsoids of constant energy for a single conduction-band minimum at  $k=0$ . Additional transport experiments as well as direct observation by cyclotron resonance of effective mass anisotropy support this simple energy-band model.

ZnAs<sub>2</sub>, ZnSb, CdAs<sub>2</sub>, and CdSb all show a wide region of high optical transmission while Cd<sub>3</sub>As<sub>2</sub> shows free-carrier absorption and dispersion in reflectivity due to free-carrier resonance. Finally, both CdSb and ZnSb have low thermal conductivities. These properties serve to point the way toward future detailed studies.

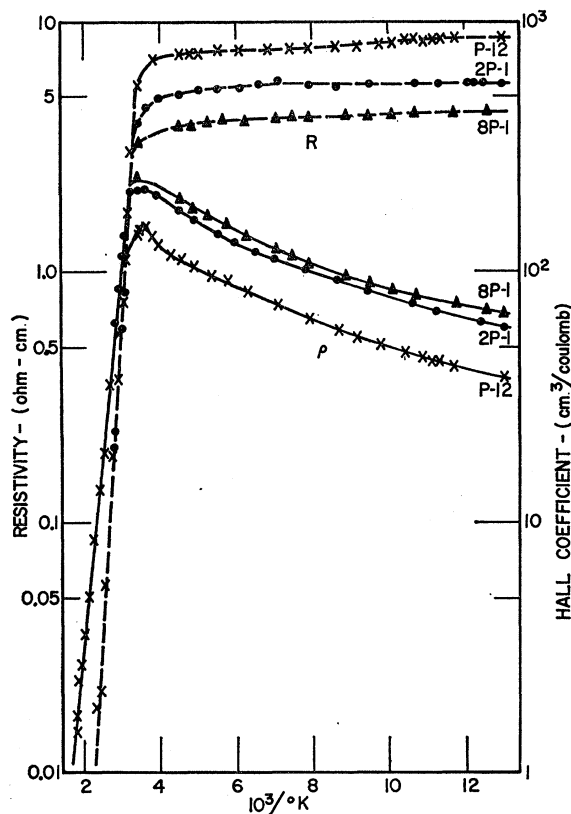


FIG. 17. Resistivity and Hall coefficient for several samples of p-type CdSb.

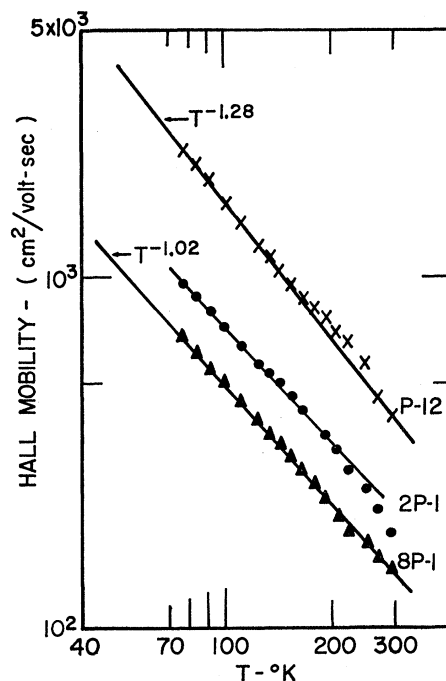


FIG. 18. Temperature dependence of the Hall mobility for the p-type CdSb samples of Fig. 17.

Note added in proof. The following additional information on ZnSb, Cd<sub>3</sub>As<sub>2</sub>, and CdSb was obtained after the paper was submitted for publication.

ZnSb. The authors have measured a value of hole mobility of  $10 \text{ cm}^2/\text{volt sec}$  at room temperature. Mobility values as high as  $300 \text{ cm}^2/\text{volt sec}$  have been reported.<sup>39</sup>

Cd<sub>3</sub>As<sub>2</sub>. Zdanowicz<sup>40</sup> reports an electrical energy gap of 0.14 eV and effective mass value of  $0.05m_0$  from thermoelectric power measurements.

CdSb. Stourac, Tauc, and Závětova<sup>41</sup> and Andronik and Kot<sup>42</sup> report anisotropy of the Hall coefficient and resistivity with a resulting hole mobility anisotropy.

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<sup>39</sup> R. A. Smith, *Semiconductors* (Cambridge University Press, Cambridge, England, 1959), p. 463.

<sup>40</sup> W. Zdanowicz, *Proceedings of the Prague Semiconductor Conference* (to be published).

<sup>41</sup> L. Štourač, J. Tauc, and M. Závětová, *Proceedings of the Prague Semiconductor Conference* (to be published).

<sup>42</sup> I. K. Andronik and M. V. Kot: *Fiz. Tverdogo Tela* 2 1128 (1960).