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Energy-band structure of Cd_3As_2 at low temperatures and the dependence of the direct gap on temperature and pressure*

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Electron-effective-mass values obtained from low-temperature Shubnikov–de Haas, magneto-Seebeck, and Hall measurements on Cd_3As_2 have been gathered from the literature. Using Kane's model for an HgTe-type inverted energy-band structure, the dispersion relation for the conduction band has been obtained along with a Γ_8-Γ_6 energy gap of 0.11 eV. The heavy-hole valence band is split from the conduction band at Γ by a residual gap of ~ 0.01 eV. There is a second conduction band whose minimum at Γ is approximately 0.6 eV above the Γ_8 valence band and perhaps a third one ~ 0.4 eV above the latter. Theoretical estimates of the variation of the energy gap at Γ as a function of temperature and pressure are obtained. Those are found to be consistent with our band model as well as with our analysis of existing temperature data ($\partial E_0/\partial T \sim 5 \times 10^{-4}$ eV/K) and pressure data ($\partial E_0/\partial P \sim -2 \times 10^{-5}$ eV/bar).

I. INTRODUCTION

In a previous publication[1] we proposed a model for the band structure of cadmium arsenide (Cd_3As_2) at room temperature which is consistent with all the available data and which reflects the unusual character of this compound (mobility of $\sim 10^4$ cm^2/V sec with 2×10^{18} electrons/cm^3). It was shown that the band structure is or approaches that of a semimetal such as HgTe with an indirect overlap of the conduction and heavy-hole valence bands. However, in this case, the low symmetry of the crystal does not lead to a degeneracy of these bands at Γ. It was in fact found that a small residual gap $E_r \sim 0.04$ eV splits the two Γ_8 bands.

The purpose of this paper is twofold. First, low-temperature data from magneto-Seebeck, Hall, de Haas–van Alphen, Shubnikov–de Haas, and magneto-optical experiments are gathered[2–8] in order to obtain the corresponding band structure. The procedure is similar to that described in Ref. 1. Second, in order to check our model, a theoretical band-structure calculation is performed. The temperature coefficient of the Γ_8-Γ_6 energy gap E_0 is evaluated and found to be in agreement with the one deduced from our room-temperature and low-temperature models. The pressure coefficient of this direct gap is deduced from the theoretical calculation mentioned above and compared with existing pressure data. In particular, it is shown that Clavaguera's recent piezoresistance data could be the first direct observation of the band-structure reversal in Cd_3As_2.[9]

II. DETERMINATION OF THE BAND STRUCTURE AT LOW TEMPERATURES

A. Effective-mass results

As in Ref. 1, our starting point is the fact that the conduction and light-hole valence bands of Cd_3As_2 are inverted as in HgTe. This was shown in a convincing manner by Wagner *et al.*[10] from interband magnetoabsorption measurements at 20 K on $Cd_{3-x}Zn_xAs_2$ and $Cd_3As_xP_{2-x}$ alloys. By using Kane's three-band model adapted to the inverted band structure, one can show[1] that the electron effective mass $m^*(E_F)$ at the Fermi energy E_F varies with the electron concentration n as follows:

$$\left(\frac{m^*(E_F)/m_0}{1 - m^*(E_F)/m_0}\right)^2 = \lambda^2\left(\frac{E_0}{E_P}\right)^2 + \frac{4\hbar^2\lambda^2(3\pi^2 n)^{2/3}}{2m_0\alpha E_P}, \tag{1}$$

where $E_P = P^2(2m_0/\hbar^2)$, P being the momentum matrix element. It is obvious that a straight-line plot can be obtained from Eq. (1) if α and λ are constants. These parameters are in fact slowly varying functions of n which in the range $0.9 \times 10^{18} < n < 3.5 \times 10^{18}$ cm^{-3} both vary by less than 6% so that α and λ can be treated as constants. Figure 1 shows that a reasonable straight line can be obtained with the 21 data points in this range. A least-squares fitting is used to obtain the illustrated line which is extrapolated in Fig. 2 to higher values of n. In the latter figure, the experimental points fall near the extrapolated line up to $n \sim 9 \times 10^{18}$ cm^{-3} after which they suddenly break away.

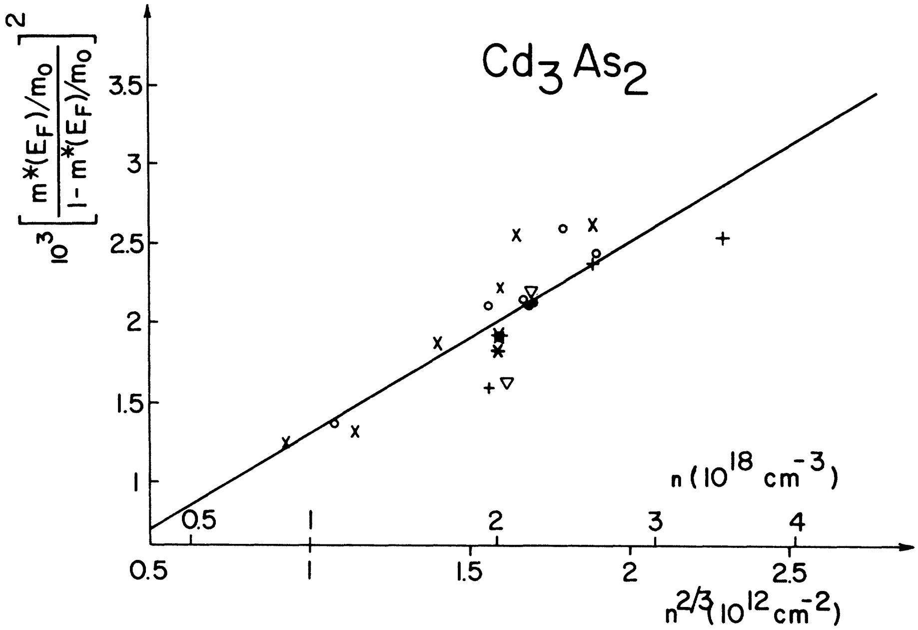

FIG. 1. Variation of the low-temperature effective mass with electron concentration for $n < 4\times10^{18}\,\mathrm{cm}^{-3}$ taken from Refs. 2 (×), 3 (●), 4 (*), 5 (+), 6 (■), 7 (▽), and 8 (○). In order to use the data of Refs. 7 and 8, we have calculated the density-of-states effective mass $(m_\parallel^* m_\perp^{*2})^{1/3}$ from the effective-mass anisotropy ratio of each sample.

As in Ref. 1, this departure from the line can be attributed to the filling of a second conduction band whose minimum is ΔE_{12} above that of the first conduction band and/or to an inaccuracy of the Kane model at higher energies.

From the slope and intercept of the straight line, we obtain

$$E_P/\alpha E_0^2 = 8.3\times10^2\ \mathrm{eV}^{-1}, \tag{2}$$

and from Eq. (4) of Ref. 1, an expression for E_F as a function of electron concentration n (in cm^{-3})

$$E'_F = \tfrac{1}{2}E_0\left[(1+12\times10^{-12}n^{2/3})^{1/2}-1\right], \tag{3}$$

where

$$E'_F = E_F - \hbar^2 k_F^2/2m_0 . \tag{4}$$

Here, k_F is the wave number at the Fermi energy and is related to n in a spherical degenerate band

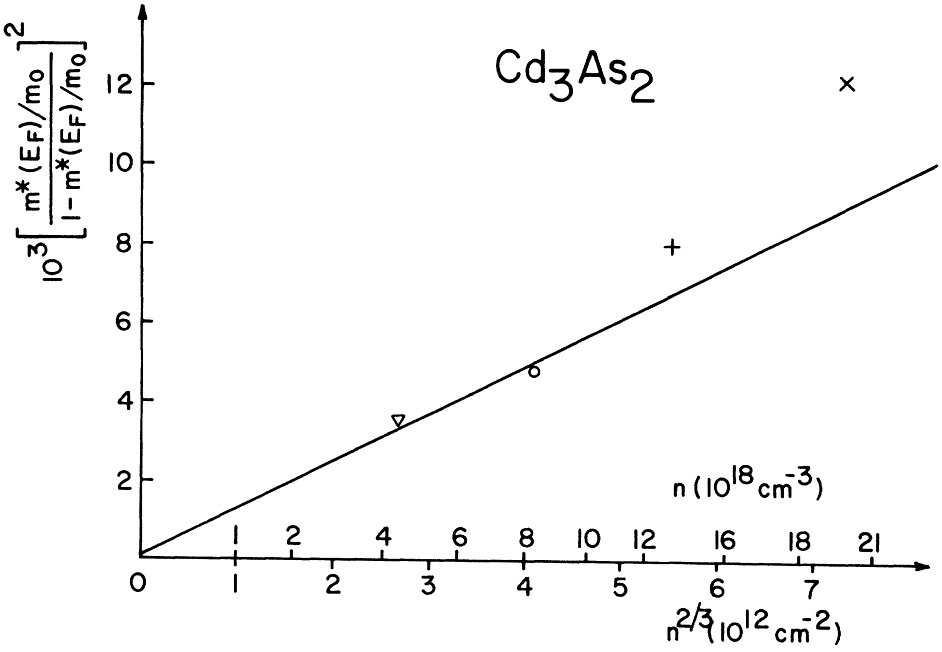

FIG. 2. Variation of the low-temperature effective mass with electron concentration for $n > 4\times10^{18}\,\mathrm{cm}^{-3}$ taken from Refs. 2 (×), 5 (+), 7 (▽), and 8 (○). The straight line is that obtained in Fig. 1.

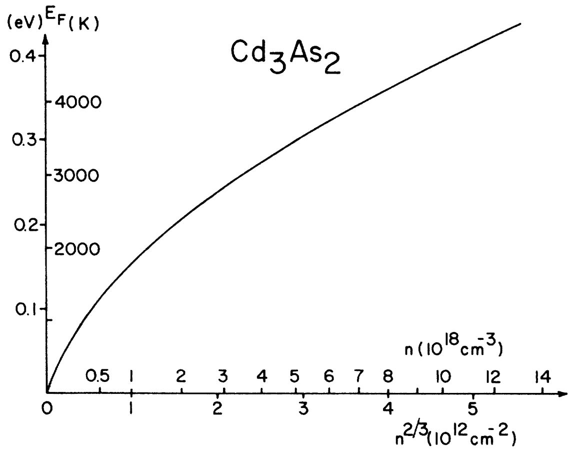

FIG. 3. Variation of the Fermi energy as a function of electron concentration, according to Eqs. (3)–(5).

by

$$k_F = (3\pi^2 n)^{1/3}\,. \qquad (5)$$

The straight line also yields

$$E_0 = 0.12(\lambda/\alpha)\ \text{eV}\,.$$

From the definitions of α and λ, and using $\Delta = 0.27$ eV,[11] the ratio $\lambda/\alpha = 0.94$ and varies by ~0.2% over the considered range of n. Thus, $E_0 = 0.11$ eV. Equations (3)–(5) can now be used to illustrate the variation of the Fermi energy with n (Fig. 3). Furthermore, Eq. (2) yields $E_P = 13$ eV. Finally, the electron effective mass at the bottom of the conduction band is equal to $m^*(0)/m_0 = 0.010$.

B. Optical results

Only two papers so far have reported low-temperature optical absorption results for Cd_3As_2. The first was that of Turner *et al.*[12] who reported an absorption edge of 0.17 eV at 77 K for a sample of carrier concentration ~2×10^{18} cm^{-3}. More recently, Radoff and Bishop[13] studied the temperature dependence of the absorption edge of the $Cd_3As_xP_{2-x}$ alloy system including one sample of Cd_3As_2 with $n \sim 2\times10^{18}$ cm^{-3} whose absorption edge was 0.18 eV between 8 and ~120 K and then decreased linearly to 0.14 eV at 300 K. The above are direct transitions from the heavy-hole valence band to the first available states in the conduction band[1] and are thus the result of the Burstein-Moss shift due to the large carrier density ever present in Cd_3As_2. Consequently, interband magnetoabsorption data should also exhibit a low-energy cutoff at the Fermi energy whose value is approximately that of the absorption edge mentioned above. Haidemenakis *et al.*[4] performed such measurements at liquid-helium temperature and indeed observed a cutoff at 0.14 eV for a sample also having $n \sim 2\times10^{18}$ cm^{-3}. Unlike the absorption edge mentioned above, this cutoff is due to transitions between Landau levels at Γ and should be larger than ~0.18 eV because of the residual gap E_r. The discrepancy may arise from the manner in which the authors of Refs. 12 and 13 evaluate the position of the absorption edge from their data. On the other hand, the data from the magnetoabsorption measurements may be unreliable so that it would be useful to repeat this experiment.

C. Band structure of Cd_3As_2

The results of Secs. II A and II B allow us to describe the characteristics of the energy band structure of cadmium arsenide at low temperatures as follows:

(i) Equations (3)–(5) give the Fermi energy as a function of n (Fig. 3) as well as the dispersion relation $E(k)$ for the conduction band (Fig. 4). Regarding the values of $m^*(0)/m_0$ and of E_P, we note that our results are consistent with Rosenman's Shubnikov–de Haas results between 1.5 and 40 K ($E_P = 15 \pm 2$ eV)[8] and with Wagner's interband magnetoabsorption measurements ($E_P = 14 \pm 2$ eV).[10]

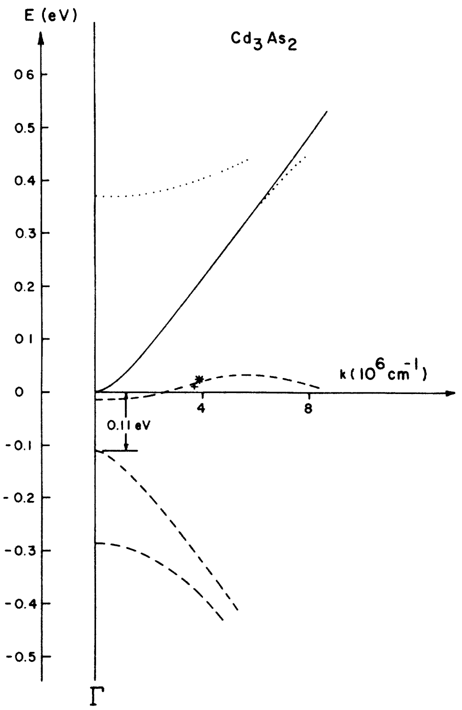

FIG. 4. Proposed electronic energy-band structure for Cd_3As_2 at low temperatures. The dotted lines indicate the possible alternatives to explain the break in the electron effective-mass data.

Furthermore, our room-temperature value[1] of E_P is only 7% greater than the present result which implies a weak temperature dependence of E_P. An almost identical situation has been found in HgSe, which also belongs to the class of HgTe-type zero-gap semiconductors.[14]

(ii) The Γ_8^c-Γ_6^v energy separation is 0.11 eV. This value agrees with the interband magnetoabsorption results on $Cd_{3-x}Zn_xAs_2$ and $Cd_3As_xP_{2-x}$ alloys performed by Wagner *et al.*[10] at low temperature. A linear extrapolation of their E_0 values to Cd_3As_2 yields an inverted band structure with a gap of ~0.1 eV. The knowledge of the E_0 value determines the maximum of the light-hole valence band which in Fig. 4 has been drawn as the mirror image of the conduction band.

(iii) The approximate shape and position of the Γ_8^v band in the (1,1,0) direction can be drawn, as was done in Ref. 1, from the optical data already mentioned. Since the fundamental absorption edge is due to a direct transition from this band to the lowest conduction band, this can be done by using the absorption edge of samples whose electron concentration is also known. Unfortunately, only two such data are available at low temperatures and both have the same electron concentration, namely, 2×10^{18} cm^{-3}. From Fig. 3 this corresponds to a Fermi energy of 0.24 eV from which one must subtract $2k_BT$ due to the smearing of the Fermi surface. In the case of Ref. 12, which gave 0.17 eV at 77 K, a value of ~0.19 eV is obtained which corresponds to a wave number $k\sim3.7\times10^6$ cm^{-1}. As mentioned in Ref. 1, this value of k is only accurate within 10% because of the reported anisotropy of the Fermi surface.[7,8] But this in no way affects the qualitative nature of our arguments. From this k value on the conduction band curve, one drops a perpendicular of length 0.17 eV which gives a point (+) on the heavy-hole valence band illustrated in Fig. 4. The same procedure was performed with the other datum point[13] (*) which was taken at 8 K. However, these two points are insufficient to deduce the shape of the Γ_8^v band so that we had to use that obtained at room temperature[1] and translate the curve vertically to accommodate the present data. If the shape of the valence band does indeed have the same shape at all temperatures we may note that the residual gap E_r decreases and the overlap with the conduction band increases as the temperature is lowered.

(iv) The value of the spin-orbit splitting[11] $\Delta=0.27$ eV at 77K has been used to draw the split-off valence band.

(v) As was discussed in Ref. 1, the discontinuity in the behavior of the electron effective mass (Fig. 2) occurring at $n\sim9\times10^{18}$ cm^{-3} can be attributed either to the X_3 conduction band at $\Delta E_{12}\sim0.37$ eV above the bottom of the Γ_8^c band or to a deviation from the Kane-model prediction (see Fig. 4). The small variation of this discontinuity when coming from room temperature to low temperature does not enable us to exclude either alternative. But if indeed the X_3 band is at this energy, this would indicate a trend to lower values of ΔE_{12} for lower temperatures. While a crossover of the two conduction bands could not be brought about by a temperature variation, it is conceivable that in $Cd_{3-x}Zn_xAs_2$ and $Cd_3As_xP_{2-x}$ alloys such a crossing could occur. This point of view is consistent with the theoretical predictions of Lin-Chung.[15] Furthermore, the application of pressure could also bring about such a crossover. With regard to the X_1 band, which was found in Ref. 1 to be ~0.6 eV above the Γ_8^v band from room-temperature optical measurements, we really cannot make any prediction as to its position at low temperatures since there are no available experimental data in this range of temperatures.

III. CALCULATION OF BAND PARAMETERS

The compatibility of the various findings at room and at low temperatures can be checked with the help of a theoretical band-structure estimate. Since the predictions on the energy band structure within the Kane model are most sensitive to the information at Γ, a calculation was performed at this special symmetry point. The nonrelativistic pseudopotential method was used on the higher-symmetry effective fluorite structure as in Lin-Chung's paper.[15] Two considerations prevailed in these calculations. First, the atomic form factor for Cd is quite uncertain judging from the proliferation of local form factors[16] and experimental data, some of which[17,18] are gathered in Fig. 5. As a consequence, the sensitivity or rather insensitivity of any theoretical finding on the exact shape of the Cd form factor had to be checked. Second, the effect of ionic motion on the band structure had to be estimated since the findings of Ref. 1 and Sec. II are at different temperatures. The Yu-Brooks procedure[19] involves the use of a Debye-Waller factor $e^{-W_i(G)}$ which modulates the structure factor $S_i(\vec{G})$. The matrix element of the pseudopotential $V_{ps}(\vec{r})$ between plane waves in the local approximation is then

$$\langle\vec{k}+\vec{G}\,|\,V_{ps}(\vec{r})\,|\,\vec{k}\rangle=\sum_i V_i(\vec{G})S_i(\vec{G})e^{-W_i(G)}\,,$$

where $\vec{G}$ is a reciprocal-lattice vector, $V_i(\vec{G})$ is the form factor for the i ion, and

$$W_i(G)=\tfrac{1}{2}G^2\langle u_i^2\rangle\,,$$

$\langle u_i^2\rangle$ being the thermal average of the squared-ion displacement. The phonon information on Cd_3As_2, however, is rather scarce, being limited to a knowledge of the average acoustic phonon velocities. One has $v_l \approx 3.5\times10^5$ cm/sec, attributed to Lebourgeois in a footnote in Clavaguera's paper[9] and verified by our own measurements, and $v_t \approx \frac{1}{2} v_l$.[20,21] One can thus only hope for a very crude estimate of the effect of the phonons on the energy band structure. Considering this, we use Ziman's estimate of the Debye-Waller factor for a monoatomic lattice[22]

$$W_t(G)=\begin{cases}\frac{3}{2}\hbar^2G^2T/Mk_B\Theta_D^2\,, & T\gtrsim\Theta_D\,,\\ \frac{3}{8}\hbar^2G^2/Mk_B\Theta_D\,, & T\ll\Theta_D\,,\end{cases}$$

where we interpret M as being the average ionic mass and Θ_D as a Debye temperature

$$\Theta_D=(\hbar\bar{v}/k_B)(6\pi^2N/V)^{1/3}\,,$$

where

$$\bar{v}=[\tfrac{1}{3}(1/v_l^3+1/v_t^3)]^{-1/3}\,,$$

and V/N is chosen to be the average volume per ion. We thus obtain $\Theta_D=200$ K.

The band calculations are performed on the reduced reciprocal-lattice vector set (0,0,0), (1,1,1), and (2,0,0) while using Löwdin's perturbation technique[23] on the other higher-energy reciprocal-lattice vectors. We believe this to be sufficient for our purposes. We use the As form factor of Lin-Chung[15] and the Cd local form factors of Fig. 5 to get the following information:

$$\left(\frac{\partial E_0}{\partial a}\right)_T=1.0\text{–}1.4\ \text{eV/a.u.}\,, \qquad (6a)$$

$$\left(\frac{\partial E_0}{\partial T}\right)_a=(2.7\text{–}3.5)\times10^{-4}\ \text{eV/K}\,, \qquad (6b)$$

$$E_P=12.6\text{–}13.6\ \text{eV}\,, \qquad (6c)$$

where a is twice the effective fluorite structure lattice constant ($a=23.96$ a.u. for Cd_3As_2) and $E_0=E(\Gamma_{15})-E(\Gamma_1)$ is the nonrelativistic equivalent of the direct $E(\Gamma_8)-E(\Gamma_6)$ energy gap. The value of $(\partial E_0/\partial T)_a$ is found to be sensitive to the exact value of Θ_D, decreasing by 40% on going from $\Theta_D=200$ K to $\Theta_D=250$ K, and is thus essentially indicative. The range of values associated with the parameters of Eqs. (6) comes from the use of the various Cd form factors in the calculations. The direct energy gap varies between 0 and −0.8 eV. E_0 is negative, thus implying an InSb-type electronic band structure. But, as pointed out by Lin-Chung, this is to be expected of a nonrelativistic calculation on a simple crystal structure. Nevertheless, the small sensitivity of the above results to rather dramatic changes in the energy gap guarantees their indicative value even for an inverted band structure. A first conclusion can be drawn at this point, namely, that the calculated parameter E_P is in agreement with the fitted value we have deduced from experimental evidence.

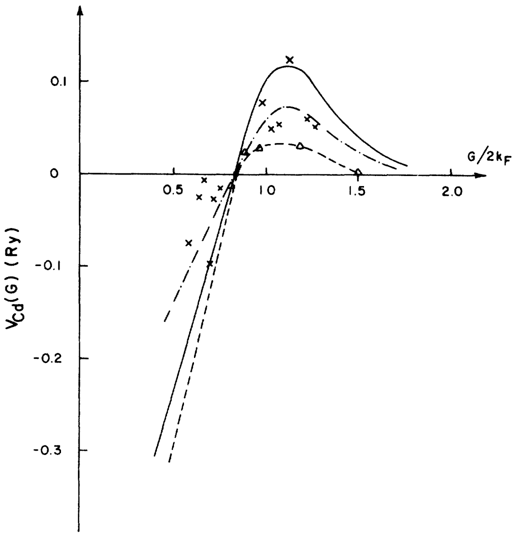

FIG. 5. Some experimental data for the Cd atomic form factor are reproduced from Refs. 17 (×) and 18 (Δ). The three pseudopotentials used are also plotted.

A. Thermal dependence of the energy gap

We wish to check the total change in the direct gap between room temperature and low temperature. In order to do so, we must estimate the change in lattice constant between the two temperature extremes. This is done by fitting a simple thermal linear-expansion model[22] to the available room-temperature coefficient[24] of

$$\frac{1}{a}\left(\frac{\partial a}{\partial T}\right)_P=1.1\times10^{-5}\ \text{K}^{-1}\,.$$

In this model, one relates the change in lattice constant to the average phonon energy $\langle E\rangle$ in a Debye approximation

$$\frac{a-a_0}{a_0}\propto\langle E\rangle\propto T^4\int_0^{\Theta_D/T}dx\,\frac{x^3}{e^x-1}\,, \qquad (7)$$

where a_0 is the lattice parameter at absolute zero. This yields a total lattice parameter change of

$$\Delta a/a_0\sim2.6\times10^{-3}$$

for which the change in direct gap is found to be

$$E_0(300\ \mathrm{K}) - E_0(0\ \mathrm{K}) = 0.13\text{–}0.17\ \mathrm{eV}.$$

This is again somewhat insensitive to the exact Cd form factor. It is, however, sensitive to Θ_D and decreases by 20% on going from $\Theta_D = 200$ K to $\Theta_D = 250$ K. In view of the strong dependence of the predicted temperature variations with Θ_D one can only conclude that our fitted value for the change in E_0 between room and low temperatures is of the right order of magnitude and sign. The thermal dependence of the energy gap at room temperature and constant pressure P can also be estimated

$$\left(\frac{\partial E_0}{\partial T}\right)_P = \left(\frac{\partial E_0}{\partial a}\right)_T \left(\frac{\partial a}{\partial T}\right)_P + \left(\frac{\partial E_0}{\partial T}\right)_a \sim 6\times 10^{-4}\ \mathrm{eV/K}. \tag{8}$$

The first term on the right-hand side represents the contribution from the lattice expansion and the second, the contribution from the phonons. The only possible check on this is from the work of Radoff and Bishop[13] who measured the temperature dependence of the 0.14-eV optical transmission edge E_{opt} in $\mathrm{Cd_3As_xP_{2-x}}$ alloys. Their findings lead to

$$\left(\frac{\partial E_{\mathrm{opt}}}{\partial T}\right)_P \sim -1.7\times 10^{-4}\ \mathrm{eV/K}.$$

There are three contributions to this derivative. The first is from changes in the Fermi level caused by changes in the gap; this was the only contribution considered by Radoff and Bishop. Second, there is the effect of thermal smearing at the Fermi energy ($\sim 2k_BT$) which was considered by Aubin.[25] Lastly, there is the heretofore neglected residual gap E_r which changes as a function of temperature and which affects the direct transitions between the heavy-hole valence band and the conduction band (see Fig. 4). If one labels the valence-band energy at k_F as E_v, one has

$$\left(\frac{\partial E_{\mathrm{opt}}}{\partial T}\right)_P \approx \left[\frac{\partial}{\partial T}(E_F - 2k_BT - E_v)\right]_P.$$

The term $(\partial E_v/\partial T)_P$ can be estimated to be

$$\left(\frac{\partial E_v}{\partial T}\right)_P \sim \frac{E_v(300\ \mathrm{K}) - E_v(0\ \mathrm{K})}{200} = -5\times 10^{-4}\ \mathrm{eV/K}. \tag{9}$$

The value of $\Delta T \sim 200$ K in the denominator of Eq. (9) is obtained by assuming that $E_v(T) - E_v(0)$ is proportional to $a - a_0$ [Eq. (7)]. One thus has

$$\left(\frac{\partial E_F}{\partial T}\right)_P = -1.5\times 10^{-4}\ \mathrm{eV/K},$$

which can be related to the thermal change in the energy gap through Eq. (4) of Ref. 1. We find

$$\left(\frac{\partial E_0}{\partial T}\right)_P = 5\times 10^{-4}\ \mathrm{eV/K}$$

at room temperature. Thus, considering the very approximate determination of $(\partial E_0/\partial T)_a$ in Eq. (8) this last value for $(\partial E_0/\partial T)_P$ at room temperature is compatible with the theoretical estimate. As a corollary, this is also an indirect verification of the presence of the residual gap and of its temperature dependence.

B. Pressure dependence of the energy gap

There is one last piece of information which can be extracted from the simple band-structure calculation. This is the pressure dependence of the energy gap at room temperature

$$\left(\frac{\partial E_0}{\partial P}\right)_T = \left(\frac{\partial E_0}{\partial a}\right)_T \left(\frac{\partial a}{\partial P}\right)_T.$$

One needs, however, an estimate of the compressibility

$$K = -\frac{3}{a}\left(\frac{\partial a}{\partial P}\right)_T.$$

This can be obtained from Ref. 21 which gives

$$K^{-1} = \rho(v_l^2 - \tfrac{4}{3}v_t^2),$$

where ρ is the mass density of $\mathrm{Cd_3As_2}$, namely, 6.21g/cm^3, and $(v_l^2 - \frac{4}{3}v_t^2)$ equals 9×10^{10} cm^2/sec.^{2} Consequently, one finds

$$\left(\frac{\partial E_0}{\partial P}\right)_T \sim -1.7\times 10^{-5}\ \mathrm{eV/bar}.$$

There is unfortunately no direct observation of this parameter. The only pressure measurements are those of Cisowski and Żdanowicz[26] and of Clavaguera.[9] These are piezoresistance measurements. The question is then how to relate the energy gap to their data. It was claimed by Cisowski and Żdanowicz that the positive piezoresistance in $\mathrm{Cd_3As_2}$ was directly related to changes in the effective mass of the carriers induced by changes in the gap. One should be careful, however, in drawing quick conclusions from piezoresistance data as there are other variables in the expression for the resistivity of degenerate semiconductors which are even more important than the mass. Referring to the general consensus that the dominant scattering mechanism for $\mathrm{Cd_3As_2}$ at room temperature is through optical phonons[5,27] and to the Zawadzki *et al.*[28] formula for this contribution in the elastic-scattering limit, one gets

$$\rho_{\mathrm{op}} = \frac{2[m^*(E_F)]^2 k_BT}{n\hbar^3 k_F}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)F_{\mathrm{op}},$$

where ϵ_∞ and ϵ_0 are the infinite- and zero-frequency dielectric constants, respectively, and F_{op} is a factor which takes into account the symmetry of the conduction-band electron wave functions. The expression given by Zawadzki *et al.*[28] is

$$F_{op}=A+2[b^2(\tfrac{1}{2}b-c\sqrt{2})^2-(b^2+c^2)]B + \tfrac{4}{3}[(b^2+c^2)^2-b^2(\tfrac{1}{2}b-c\sqrt{2})^2]C\,,$$

where

$$A=1-(2/\xi)\ln(\xi+1)+1/(\xi+1)\,,$$

$$B=1-4/\xi+(6/\xi^2)\ln(\xi+1)-2/\xi(\xi+1)\,,$$

$$C=1-\frac{3}{\xi}+\frac{9}{\xi^2}-\frac{12}{\xi^3}\ln(\xi+1)+\frac{3}{\xi^2(\xi+1)}\,,$$

$$\xi=(2k_F\lambda_s)^2\,,\quad \lambda_s=\left[\frac{\hbar^2\epsilon_0}{4m^*(E_F)e^2}\left(\frac{\pi}{3n}\right)^{1/3}\right]^{1/2}$$

is the screening length for a degenerate electron gas. For an HgTe-type inverted band structure, one has[28]

$$b^2=(1/3D)\Delta^2(E_0+E_F')\,,$$

$$c^2=(2/3D)(\Delta+\tfrac{3}{2}E_F')^2(E_0+E_F')\,,$$

$$D=(\Delta+\tfrac{3}{2}E_F')(\Delta+E_F')E_F'+(\Delta+E_F')^2(E_0+E_F') + \tfrac{1}{2}(E_0+E_F')E_F'^2\,,$$

while, for an InSb-type band structure, one has[29]

$$b^2=(1/3D)\Delta^2E_F'\,,$$

$$c^2=(2/3D)(\Delta+\tfrac{3}{2}|E_0|+\tfrac{3}{2}E_F')^2E_F'\,,$$

$$D=(\Delta+\tfrac{3}{2}|E_0|+\tfrac{3}{2}E_F')(\Delta+|E_0|+E_F')(|E_0|+E_F') + (\Delta+|E_0|+E_F')^2E_F'+\tfrac{1}{2}(|E_0|+E_F')^2E_F'\,.$$

Substituting the various known parameters of Cd_3As_2, for $n=2\times10^{18}$ cm^{-3}, $\epsilon_0=36$, and $\epsilon_\infty=12$,[30] we find

$$\rho_{op}=0.376[m^*(E_F)/m_0]^2F_{op}\quad(\Omega\,\mathrm{cm})\,.$$

In Table I we have reproduced the parameters $m^*(E_F)/m_0$, E_F, F_{op}, and ρ_{op} at a few values of the direct energy gap E_0 within the Kane model. As a consequence, the calculated resistivity would be approximately 1.6×10^{-4} Ω cm which is within reach of the experimental values on the best single crystals of cadmium arsenide.[9,26] As Table I shows, the dependence of the resistivity of Cd_3As_2 over the range of gaps considered is mostly through the wave-function symmetry factors F_{op} and to a lesser extent on the effective mass $m^*(E_F)/m_0$. This is so only for a degenerate semiconductor since F_{op} hardly varies with E_0 for either type of band-edge symmetry in a nondegenerate one. Care must then be taken, when analyzing piezoresistance data, to consider all the variables entering the Zawadzki formula.

TABLE I. Electron effective mass $m^*(E_F)/m_0$, Fermi energy E_F, Zawadzki F_{op} factor, and room-temperature resistivity ρ_{op} calculated at a few values of the direct energy gap E_0 within the Kane model for $n=2\times10^{18}$ cm^{-3}. A negative energy gap indicates an InSb-type electronic band structure.

E_0 (eV)	E_F (eV)	$\frac{m^*(E_F)}{m_0}$	F_{op}	ρ_{op} (μΩ cm)
0.30	0.150	0.0470	0.235	195
0.25	0.164	0.0451	0.231	176
0.20	0.180	0.0434	0.231	163
0.15	0.198	0.0421	0.236	157
0.10	0.219	0.0412	0.247	157
0.05	0.241	0.0406	0.265	164
0	0.267	0.0404	0.289	178
−0.05	0.244	0.0406	0.319	198
−0.10	0.224	0.0412	0.353	225
−0.15	0.206	0.0420	0.389	258
−0.20	0.190	0.0431	0.426	298
−0.25	0.176	0.0445	0.461	344
−0.30	0.163	0.0461	0.495	395

The more-detailed hydrostatic piezoresistance measurements $\rho(P)/\rho(0)$ of Clavaguera[9] indicate that the phenomenon in Cd_3As_2 is nonlinear. In fact, $\rho(P)/\rho(0)$ is paraboliclike with a shallow minimum around 2–3 kbar going to a value of 1.2 at 20 kbar. This general shape is not unlike that of the calculated $\rho(E_0)$ in Table I in going from 0.2 to −0.05 eV. It is thus tempting to associate a gap variation of 0.25 eV with a 20-kbar pressure change. This would imply that

$$\left(\frac{\partial E_0}{\partial P}\right)_T\sim-1.3\times10^{-5}\ \mathrm{eV/bar}\,.$$

This value is very close to the band calculation prediction of -1.7×10^{-5} eV/bar. It should be pointed out that the presence of a minimum in resistivity as the energy gap decreases with pressure is consistent with an observed maximum in mobility as the gap is decreased by alloying Cd with Zn in the $Cd_{3-x}Zn_xAs_2$ system.[31] One then expects to find, from the above values of $(\partial E_0/\partial P)_T$, a band crossing at pressures in the neighborhood of 15 kbar. Again looking at the piezoresistance data of Clavaguera, one notes a small irregularity, a dip, around 10–12 kbar. This suggests associating the irregularity with changes in the numerous variables involved in the expressions for the resistivity as the energy gap goes through zero. This fine structure would be the result of refinements on the simple model calculation. The proposed value of the pressure dependence of the energy gap is then

$$\left(\frac{\partial E_0}{\partial P}\right)_T\sim-1.8\times10^{-5}\ \mathrm{eV/bar}\,,$$

which is consistent with both the general shape of the piezoresistance curve and the irregularity at 12 kbar.

The anisotropy observed by Clavaguera is also consistent with our band model. The peculiar shape of the heavy-hole valence band is surely the result of a conduction-band–valence-band coupling. The maximum in this band is in the (1,1,0) direction judging from Lin-Chung's calculations.[15] This in turn implies a maximum coupling in the (1,1,0) direction and thus anisotropy in the electronic wave functions at the Fermi level. Indeed, Clavaguera does observe a maximum uniaxial pressure piezoresistance in this very direction.

IV. CONCLUSION

The present paper reinforces the view put forth in our previous work that the electronic energy band structure of Cd_3As_2 is of the HgTe type. There is thus a band reversal in $Cd_{3-x}Zn_xAs_2$ and $Cd_3As_xP_{2-x}$ alloys. Unfortunately, the degeneracy of these alloys at the crossover point precludes any spectacular anomaly in transport and optical properties. As suggested in Sec. I the first direct observation of this crossover may have been in Clavaguera's piezoresistance measurements. It may also be possible to observe this crossover in an appropriate alloy sample by magnetic susceptibility and mobility measurements as a function of temperature.

We suggest optical and Shubnikov–de Haas measurements under uniaxial pressure in order to obtain information on the deformation of the heavy-hole valence band dispersion and of the Fermi surface. This may shed light on the interpretation of Clavaguera's uniaxial piezoresistance data.

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