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Band structure of cadmium arsenide at room temperature*

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Electron effective-mass values obtained from room-temperature magneto-Seebeck and Hall measurements on Cd_3As_2 have been gathered from the literature. Using Kane's model for an α-Sn-type inverted electronic energy band structure, the dispersion relation for the conduction band has been obtained along with a Γ_8-Γ_6 energy gap of 0.19 eV. Combining these results with the available room-temperature optical data, the relative positions of other bands have been obtained. The heavy-hole valence band, whose maximum is displaced from Γ by $\sim 10\%$ of the distance to the Brillouin-zone edge, has a possible small overlap with the conduction band. These two Γ_8 bands are split at Γ by a residual gap of ~ 0.04 eV. There is a second conduction band whose minimum at Γ is ~ 0.6 eV above the Γ_8 valence band and perhaps a third one ~ 0.4 eV above the latter.

I. INTRODUCTION

Cadmium arsenide (Cd_3As_2) has long been considered an unusual semiconductor because of its high electronic mobility and the large number of carriers always present. At room temperature, mobilities of 10 000 cm^2/V sec have been reported[1-13] with 2×10^{18} electrons/cm^3. An impressive amount of data on this compound has accumulated in the literature over the years, but a convincing model for the band structure which would satisfy all these data and all workers involved has not been forthcoming. The situation has been complicated by the ever present degeneracy of this material which excludes the conduction-band edge from any transport or optical phenomena. A number of authors[6,8,9,14-17] have reported magneto-Seebeck and Hall measurements and have calculated a value for the electron effective mass. However, the value obtained is that at the Fermi level and therefore a function of the carrier concentration of the sample, although in some cases the bottom of the band value was obtained. Similarly, the lowest optical-absorption edge[3,18,19] is shifted by the Burstein-Moss effect.

In spite of these difficulties, two band models have been proposed from experimental results[9,19] and one from theoretical calculations.[20] These three models will be discussed below. In all of them, the effect of alloying with zinc has been considered (i.e., $Cd_{3-x}Zn_xAs_2$ alloys) since solid solutions throughout the composition range are possible and Zn_3As_2 does not present the problems of degenerate samples.[21-25] The same can be said of Cd_3P_2 and $Cd_3As_{2-x}P_x$ alloys which have also been useful in the study of Cd_3As_2.[19,26-28] The use of alloys to facilitate the understanding of semiconducting compounds is not new, having been used extensively in III-V compounds by following the variation of band gaps, etc., with alloy composition. A striking example is the fundamental gap variation in $GaAs_{1-x}P_x$ alloys which displays two straight-line segments as the alloy composition is varied.[29] This illustrates the replacement of the (0, 0, 0) edge by the (1, 0, 0) edge as the lowest conduction band as one goes from GaAs to GaP.

The most important question concerning cadmium arsenide is whether or not the energy band gap is "negative" as in gray tin or HgTe or positive as in InSb. These two possibilities are, respectively, the bases of what will be referred to as the Wagner and Rogers models. From their magneto-optical measurements at 20 K, Wagner *et al.*[19] obtained the energy gaps of $Cd_{3-x}Zn_xAs_2$ and $Cd_3As_{2-x}P_x$ alloys which vary linearly with x. An extrapolation to $x=0$, i.e., to Cd_3As_2, suggests a negative gap of 0.1 eV, i.e., an inversion of the conduction and light-hole valence bands in these alloys similar to that in $Cd_xHg_{1-x}Te$ alloys. From their transport and optical measurements, Rogers *et al.*[9] suggest either a zero indirect gap or a small indirect overlap in Cd_3As_2 between the conduction and heavy-hole valence bands. With the addition of zinc, any existing overlap goes to zero and a positive gap appears. A theoretical band-structure determination of Cd_3As_2 (as well as that of Zn_3As_2, Cd_3P_2, and Zn_3P_2 which are crystallographically similar) was performed by Lin-Chung,[20] who postulated a simplified crystal structure to reduce the pseudopotential calculations to reasonable proportions. The real crystal structure has 160 atoms per unit cell.[30] This large number is due to the 16 different configurations of the Cd vacancies in as many cubic cells. By supposing that these vacancies were occupied, Lin-Chung obtained a fluorite structure which was used in the calculations and then subtracted the average effect of the fictitious Cd atoms. Furthermore, all spin-orbit effects were neglected. Estimates of the effect of these simplifications were considered in an attempt to compare the results with existing optical transition data. In particular, the hypothetical crystal structure would have a direct energy gap at Γ of ~0.5 eV, whereas in the real crystal this gap would be ~0.2 eV or less. Three conduction bands are predicted in this model with the lowest minimum at Γ and the others at *X*, which is equivalent to Γ in the real crystal structure. It is interesting to note that for Zn_3As_2 this order is reversed, meaning that in $Cd_{3-x}Zn_xAs_2$ alloys a crossover of the Γ and *X* conduction bands should occur.

In this paper, data from magneto-Seebeck and Hall,[6,8,9,14-17] and from optical experiments[3,9,14,18,19,31-33] have been gathered. Reference will also be made to magnetoresistance,[17] thermo-reflectance,[34,35] Shubnikov–de Haas,[7] de Haas–van Alphen,[36] and magneto-optical results.[14,19] The reason for doing this was to propose and to describe precisely a band structure consistent with all these data. A necessary first step was to choose a type of band structure from the three models described above. The most convincing is the Wagner model, which arose from a straight-line extrapolation of the energy gaps of $Cd_{3-x}Zn_xAs_2$ and $Cd_3As_{2-x}P_x$ alloys to a negative value for Cd_3As_2.[19] Rogers *et al.*[9] resorted to several assumptions in their analysis to obtain a simplified dispersion relation for the conduction band and in particular assumed that the energy gap E_0 is much less than the spin-orbit splitting Δ, an approximation which is not valid in Cd_3As_2 as will be seen below. Lin-Chung[20] had to use a hypothetical fluorite crystal structure and neglect spin-orbit effects. Although her calculated band structure resembles closely that of III-V semiconducting compounds, she does accept the possibility of a HgTe structure as proposed by Wagner *et al.*[19] Furthermore, room-temperature transport measurements in $Cd_{3-x}Zn_xAs_2$ alloys[25] show an anomaly at $x \sim 0.6$, which is also consistent with a crossover of conduction and valence bands.

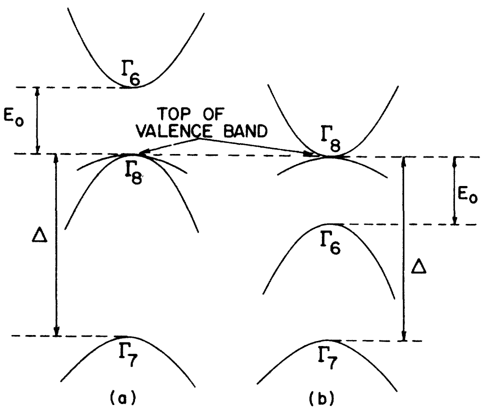

FIG. 1. Schematic diagram of (a) the normal electronic energy band structure such as that found in InSb and (b) the inverted or α-Sn band structure.

Kane's model[37] has been successfully used for many semiconducting compounds including Cd_3As_2.[6,16,17] The present paper will also make use of Kane's model, but unlike previous publications, will take into account the negative energy gap of Cd_3As_2. Moreover, the often encountered assumption that Δ is much greater or much less than E_0 will be avoided since it is not reasonable for Cd_3As_2.

II. THEORETICAL CONSIDERATIONS

In contrast to the usual InSb-type semiconductors whose energy band structure is shown in Fig. 1(a), the compounds HgTe, HgSe, β-HgS, and some $Cd_xHg_{1-x}Te$ alloys are known to have the α-Sn band ordering[38,39] which is illustrated in Fig. 1(b). It can be seen that the Γ_6 level is below the Γ_8 level and is part of the light-hole valence band. The Γ_8 level, which is the light-hole valence band in InSb, here is part of the conduction band, whereas the heavy-carrier subband of Γ_8 remains the same. Thus, the conduction and heavy-hole bands are degenerate at $k=0$ and the thermal gap is zero. On the other hand, the interacting levels Γ_6 and Γ_8 are still separated by a finite energy E_0.

The three-band approximation of Kane's model[37,39] should provide a reasonable average of the various band properties of Cd_3As_2 over constant-energy surfaces. Indeed, Shubnikov–de Haas[7] and de Haas–van Alphen[36] measurements have shown that the Fermi surface of Cd_3As_2 consists of one ellipsoid centered at Γ whose anisotropy factor is 1.18 for electron concentrations up to at least 8×10^{18} cm^{-3}. The dispersion relation at the Fermi surface in this spherically symmetric band model can be written in the form

$$E_F(\hbar^2k_F^2/2m_0) = E'_F(E'_F+E_0)\alpha\,, \qquad (1)$$

where

$$\alpha = 1+\tfrac{1}{3}\Delta/(E'_F+\tfrac{2}{3}\Delta)\,. \qquad (2)$$

Here, k_F is the wave number at the Fermi level, $\hbar$ is the Planck constant divided by 2π, m_0 is the free-electron mass, $E_P=(2m_0/\hbar^2)P^2$ with P proportional to the Γ_8-Γ_6 momentum matrix element, and $E'_F=E_F-\hbar^2k_F^2/2m_0$ is the Fermi energy measured from the bottom of the conduction band minus the corresponding free-electron kinetic energy. In order to obtain a closed-form expression for E_F' and also for the effective mass at the Fermi level $m^*(E_F)$ as a function of the electron concentration n, it will be necessary to make use of simplifying assumptions regarding α and a forthcoming parameter λ which is defined as

$$\lambda = \alpha - \frac{\frac{1}{3}E_F'\Delta}{(E_F' + \frac{2}{3}\Delta)^2}\left(1 - \frac{E_F'}{E_0 + 2E_F'}\right). \tag{3}$$

For $E_F' = 0$, Eqs. (2) and (3) yield values of $\lambda = \alpha = \frac{3}{2}$, whereas for $E_F' = \infty$, one obtains $\lambda = \alpha = 1$. For other values of E_F' it is easy to see that α is always slightly greater than λ and also that λ and α are well behaved, slowly varying functions of E_F' (and therefore of n). It would therefore be a reasonable approximation to treat λ and α as constants in the range of $n = 0.7$ to 3.5×10^{18} cm^{-3} which includes most of the available data on Cd_3As_2. The validity of this approximation will become apparent in Sec. III. The solution of the quadratic equation so obtained for E_F' is

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

the negative-root solution being rejected since Cd_3As_2 is always highly degenerate. The electron effective mass $m^*(E_F)$ is then given by

$$\left(\frac{m^*(E_F)/m_0}{1 - m^*(E_F)/m_0}\right)^2 = \lambda^2\left(\frac{E_0}{E_P}\right)^2 + \frac{4\hbar^2\lambda^2(3\pi^2 n)^{2/3}}{2m_0\alpha E_P}, \tag{5}$$

which represents the equation of a straight line if the left-hand side is plotted as a function of $n^{2/3}$.

III. TRANSPORT AND OPTICAL ANALYSES

The available room-temperature data of $m^*(E_F)$ obtained from magneto-Seebeck and Hall measurements[6,8,9,14-17] for various electron concentrations are plotted in Fig. 2. A straight line least-squares fit using Eq. (5) was performed for the 16 samples lying in the range $n = (0.7 - 3.5) \times 10^{18}$ cm^{-3}. The resulting line illustrated in Fig. 2 has been extrapolated to higher values of n. It is interesting to note that the experimental points fall on the extrapolated line for concentrations up to $n \sim 13 \times 10^{18}$ cm^{-3}, after which they suddenly break away. This departure from the line, as will be discussed further on, is attributed to the presence of another conduction band and/or to an inaccuracy of the Kane model at higher energies.

From the slope and intercept of the above fit, we obtain

$$E_P/\alpha E_0^2 = 3.0 \times 10^2 \text{ eV}^{-1}, \tag{6}$$

which allows us to express Eq. (4) as follows:

$$E_F' = (\tfrac{1}{2}E_0)[(1 + 4.4 \times 10^{-12} n^{2/3})^{1/2} - 1] \quad (n \text{ in cm}^{-3}). \tag{7}$$

The straight line also yields

$$E_0 = 0.21(\lambda/\alpha) \text{ eV}. \tag{8}$$

From the discussion of Sec. II concerning λ and α,

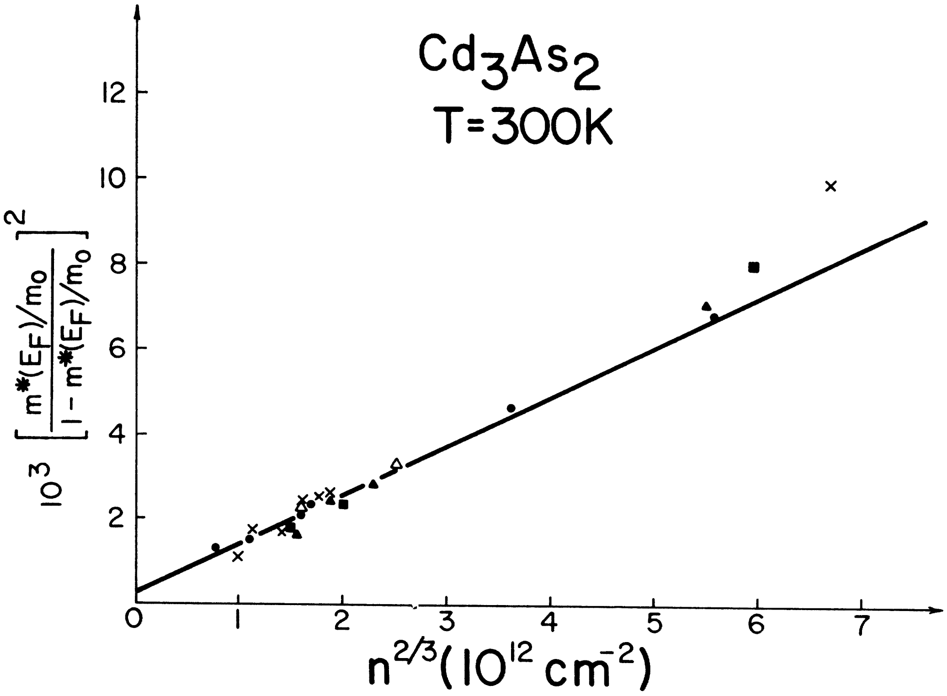

FIG. 2. Variation of the effective mass with electron concentration taken from Refs. 6 (×), 9 (▲), 14 (△), 15 and 16 (●), and 8 and 17 (■). The straight line was obtained from a least-squares fit of the 16 points lying in the range $n = (0.7 - 3.5) \times 10^{18}$ cm^{-3}.

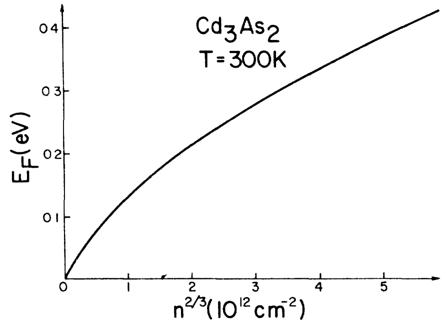

FIG. 3. Variation of the Fermi energy as a function of electron concentration according to Eq. (7).

it is apparent that E_0 will be equal to or slightly less than 0.21 eV. A more quantitative result can be easily obtained from Eq. (8) which, from the definitions of λ and α, is essentially a cubic equation in E_0. It contains the ratio E_F'/E_0 which is obtained directly from Eq. (7) and Δ which is set at 0.30 eV.[40] This equation was solved numerically for various values of n in the range of interest. The result is virtually independent of n and is given by $E_0 = 0.19$ eV. Since E_0 is now known, Eq. (7) can be used to illustrate the variation of the Fermi energy with n (Fig. 3). In addition, Eq. (6) readily yields $E_P = 14$ eV. Finally, the electron effective mass at the bottom of the conduction band is equal to $m^*(0)/m_0 = 0.016$.

It is now possible to justify the validity of the approximation which assumed that λ and α are essentially independent of n over the range of interest. Using $E_0 = 0.19$ eV, Eqs. (2) and (3) show that λ lies between 1.15 and 1.24, whereas α lies between 1.24 and 1.33. More important for the calculation of E_0 is the ratio λ/α which varies by only 0.5%.

The optical results found in the literature will also be important in the determination of the energy-band structure. The lowest absorption edge has been reported to be 0.13,[3] 0.14,[18,19] and 0.16 eV,[9] for $n \sim 2\times10^{18}$ cm^{-3}. At $n = 3.5\times10^{18}$ cm^{-3} and $n = 13\times10^{18}$ cm^{-3}, the edge is observed to be 0.20 and 0.36 eV, respectively.[9] These values are due to the ever present Burstein-Moss shift in Cd_3As_2 caused by the large free-carrier density. The next higher transition has been reported to be 0.6 eV.[18,31,33] The strength of this transition indicates that it is direct. Finally, a transition was also observed at 0.8 eV.[9]

IV. BAND STRUCTURE OF CADMIUM ARSENIDE

From the above results, it is now possible to describe the characteristics of the energy-band structure of Cd_3As_2 at room temperature.

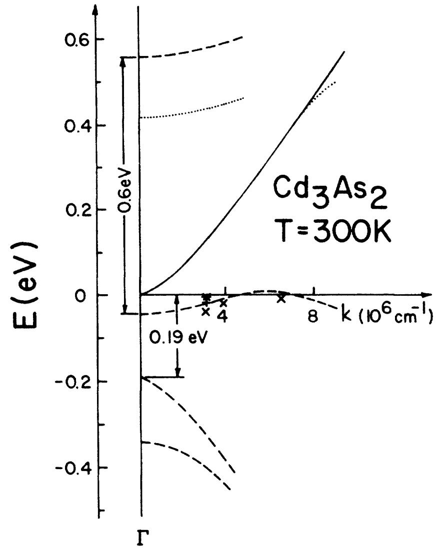

FIG. 4. Proposed electronic energy band structure for Cd_3As_2 at room temperature. The full curve comes from a fit of the Kane model to the transport data. The dashed curves were deduced from this latter one using optical data and are less accurate. The dotted lines indicate the possible alternatives to explain the break in the electron-effective-mass data.

(i) From Eq. (7), we know the Fermi energy as a function of n and therefore it is possible to draw the dispersion relation $E(k)$ for the conduction band (Fig. 4). The shape of this band being related to $m^*(0)/m_0$ and to E_P, it is interesting to note at this point that the calculated value for E_P agrees with the Shubnikov–de Haas results of Rosenman ($E_P = 15 \pm 2$ eV)[7] and with the low-temperature interband magneto-absorption results of Wagner *et al.* ($E_P = 14 \pm 2$ eV).[19] This, in turn, implies a weak temperature dependence of E_P as for example in HgSe.[41]

(ii) The Γ_8^c-Γ_6^v energy gap is 0.19 eV. This determines the maximum of the light-hole valence band, which may be drawn as approximately the mirror image of the conduction band (Fig. 4). This value of E_0 agrees with the straight-line extrapolation towards Cd_3As_2 of the optical edge of $Cd_{3-x}Zn_xAs_2$ alloys found at room temperature by Wagner *et al.*[19] Moreover, combining this value of E_0 with that of Zn_3As_2 (0.99 eV) (Ref. 34) and assuming a linear variation of the energy gap in these alloys, the crossover of the conduction and valence bands would occur at $x \sim 0.5$, which is consistent with the observed anomaly of the electron effective mass[25] at $x \sim 0.6$.

(iii) The fundamental absorption edge at ~0.14 eV must be attributed to a transition from the heavy-hole valence band to the lowest conduction band. It has been suggested that this transition is indirect because it is much weaker than the 0.6-eV transition.[9,18] However, the fact that it is still observable[28] at 8 K would exclude this possibility. We prefer the suggestion of Wagner *et al.*[19] to the effect that this transition is direct but unallowed at Γ.

We will attempt to deduce the approximate shape and position of the heavy-hole Γ_8^v band by using the observed fundamental edge for samples whose electron concentration was known. For example, at $n = 3.5 \times 10^{18}$ cm^{-3}, the absorption edge is at 0.20 eV. From Fig. 3, this carrier concentration corresponds to a Fermi energy of ~0.23 eV from which one must subtract $2k_BT = 0.052$ eV due to the smearing of the Fermi surface.[42] The difference 0.18 eV corresponds to a wave vector $k \sim 3.9 \times 10^6$ cm^{-1}. The observed anisotropy of the Fermi surface[7,36] would slightly modify this value of k depending on the direction in the Brillouin zone. There is thus a small (~10%) uncertainty on k. But this does not affect the qualitative nature of our arguments. From this k value on the conduction-band curve, one drops a perpendicular of length 0.20 eV which gives a point on the heavy-hole band. This procedure was performed for the five points shown in Fig. 4. A closer look, however, shows that three of these points come from the same author[9] and seem to fall on a parabola. Since a parabolic shape for the heavy-hole valence band would not be unrealistic, we attempted to fit a parabola through these three points. The curvature obtained corresponded to an effective mass of $\sim 0.12 m_0$, which is the result obtained by Haidemenakis *et al.*[14] from magnetoabsorption data. To take into account the presence of the other two points, the resulting parabola was translated slightly towards higher energies (Fig. 4). The maximum of this band is not at Γ but displaced by ~10% of the distance to the Brillouin zone edge. This is also in accord with Lin-Chung's prediction[20] of an absolute maximum of the heavy-hole valence band in the (1, 1, 0) direction. The shape of the band is finally smoothed out towards Γ and reveals a residual gap E_r between the Γ_8 bands. This gap is to be expected from group theoretical arguments. Even though the C_{4v}^{12} space group of Cd_3As_2 does allow for twofold orbital degeneracy at Γ,[20] the double group does not.[13] Thus, barring accidental degeneracy, the Γ_8 bands must be split at Γ. Our predicted approximate value for E_r is 0.04 eV (see Fig. 4). Considering that those components of the residual potential[20] responsible for this splitting have their largest matrix elements of the order of 0.1 eV, our value for E_r is not unreasonable.

(iv) The position of the split-off valence band was drawn with its maximum at 0.30 eV below the heavy-hole band at the Γ point.[40]

(v) The interpretation of the second and much stronger absorption edge at 0.6–0.8 eV can now be undertaken. From the conduction- and valence-band dispersions in Fig. 4, one might be tempted to assign it to a transition between the mirror Γ_6^v-Γ_8^c bands or between the split-off Γ_7^v and conduction Γ_8^c bands. This interpretation can be discarded, however, by the following analysis of the optical-transition probability. This probability is proportional to the joint density of states and to the square of the momentum matrix element between initial and final states.[43] On the one hand, the joint density of states is proportional to $(m_r^*)^{3/2}$, the reduced effective mass being defined as

$$m_r^* = (1/m_i^* + 1/m_f^*)^{-1}, \tag{9}$$

where m_i^* and m_f^* are the initial-state effective hole mass and final-state effective electron mass, respectively. Typical values, for the transitions we are contemplating at k_F, are

$$m_r^*(\Gamma_8^v\text{-}\Gamma_8^c) \sim 0.04 m_0,$$

$$m_r^*(\Gamma_6^v\text{-}\Gamma_8^c) \sim 0.02 m_0,$$

$$m_r^*(\Gamma_7^v\text{-}\Gamma_8^c) \sim 0.03 m_0.$$

On the second hand, the momentum matrix element strength can be compared for the various valence-band initial states, since the wave functions in the Kane model are known[44] [taking care to correct for the typographical error in the parameter c^2 in Eq. (2.6) which should read $c^2 = (2/3D)(\Delta + \frac{3}{2}E')^2(E_0 + E')$]. For instance, in the case of the Γ_8^v-Γ_8^c direct transition, which corresponds to the fundamental absorption edge, one would have

$$|(\Gamma_8^c|\vec{p}|\Gamma_8^v)|^2 \propto a^2P^2 ,$$

where a is the coefficient of the s-symmetry part of the Γ_8^c wave functions. It can thus be seen that this Γ_8^v-Γ_8^c transition is forbidden at Γ since $a = 0$ in this case. But at k_F, for an electron occupancy of 2×10^{18} cm^{-3}, one has $a^2 = 0.34$. This transition is thus allowed with a strength proportional to $0.3P^2$. Repeating this same analysis for the other states, one has at k_F

$$|(\Gamma_8^c|\vec{p}|\Gamma_6^v)|^2 \propto 0.2P^2,$$

$$|(\Gamma_8^c|\vec{p}|\Gamma_7^v)|^2 \propto 0.3P^2.$$

It is thus obvious from the joint density of states and the momentum matrix element strength that all transitions between valence and conduction bands have similar transition probabilities and thus similar contributions to the optical-absorption coefficient. It is therefore probable that only the lowest energy (Γ_8^v-Γ_8^c) could be resolved.

The change in absorption coefficient is found to be of the order of 10 for this transition.[9,18] Additional factors of 2 would probably go unnoted. An explicit calculation of the absorption coefficient[43] using the band parameters found in Sec. III, yields 10^4 cm^{-1} for the fundamental absorption edge and 10^3 cm^{-1} for the other possible higher-energy transitions. This calculated value at the absorption edge is 10 times larger than the observed value of 10^3 cm^{-1}.[9,18] This can be explained by the unusual dispersion of the heavy-hole band which restricts the transitions to those parts of the Brillouin zone around the (1, 1, 0) directions, i.e., those of the Γ_8^v maximum. The 0.6–0.8 eV optical edge, for which the absorption coefficient increases by a factor of 100,[9,18] can only be from a valence state to a higher-energy conduction band at Γ. Reduced effective mass arguments would favor a transition from Γ_8^v to the s-type X_1 band[20] since the valence-band effective hole mass is quite large and negative. The reduced effective mass is estimated to be $m_r^*(\Gamma_8^v\text{-}X_1) \sim 0.2m_0$. The transition probability ratio between this and the $\Gamma_8^v\text{-}\Gamma_8^c$ transition, assuming the $\Gamma_8^v\text{-}X_1$ momentum matrix element to be of the same order as P, would then be

$$\frac{[m_r^*(\Gamma_8^v\text{-}X_1)]^{3/2}\,|(X_1|\vec{p}|\Gamma_8^v)|^2}{[m_r^*(\Gamma_8^v\text{-}\Gamma_8^c)]^{3/2}\,|(\Gamma_8^c|\vec{p}|\Gamma_8^v)|^2} \sim 40 .$$

We thus predict a $\Gamma_8^v\text{-}X_1$ direct transition at Γ which is about 40 times stronger than the $\Gamma_8^v\text{-}\Gamma_8^c$ one. This is quite close to the factor of 100 found experimentally, and justifies our conclusion that there is a second conduction band (X_1) at 0.6–0.8 eV above the heavy-hole valence band. Consequently, another transition from the split-off band to this X_1 band should occur at 0.9–1.1 eV with a slightly smaller intensity. But as this affects the optical-absorption coefficient only by a factor less than 2 in a high absorption region, it would go unnoted in transmission or reflection measurements. Recently reported thermoreflectance measurements[35] indicate, however, a transition at around 0.9 eV which may well be this one.

One last comment is warranted. The measurements of Żdanowicz[18] on thin films of Cd_3As_2 clearly indicate a reproducibility problem in the location of the optical edges. The one at 0.2 eV is shifted to higher energies from the bulk by about 0.1 eV while the one at 0.6 eV varies from 0.6 to 0.8 eV depending on sample. We believe that this sample quality problem associated with films explains the 0.8 eV value quoted by Rogers *et al.*[9] That is why we have more confidence in the value of 0.6 eV found by Zivitz and Stevenson[33] on bulk samples. They also attributed this transition to the $\Gamma_{15}\text{-}X_1$ bands.

(vi) We can now come to the matter of the discontinuity in the behavior of the electron effective mass (Fig. 2) occurring at $n \sim 13 \times 10^{18}$ cm^{-3}. From Fig. 3, this corresponds to a Fermi energy of ~0.41 eV above the bottom of the first conduction band. One could then interpret, as Groves[38] attempted for α-Sn, this break as the manifestation of another conduction band at this energy (see Fig. 4). Magnetotransport measurements had also given a value of 0.4 eV (Ref. 17) when interpreting the data within a two-conduction band model. In view of the results of (v) and of Lin-Chung's predictions[20] about the higher-energy conduction bands, this would be the X_3 band. This implies an $X_1 - X_3$ band ordering different from the one calculated by Lin-Chung. The X_3 states would go unnoticed optically since transitions coming from Γ_8^c, Γ_8^v, and Γ_7^v bands are forbidden at Γ. There might be one between the Γ_6^v and X_3 bands but the transition probability is approximately equal to that of the $\Gamma_8^v\text{-}\Gamma_8^c$ one. Thus, this transition would also be unobservable. Alternatively, the deviation from the Kane-model predictions could simply be a sign that this model starts to lose its validity at energies $\gtrsim 0.4$ eV. Such a deviation is not unexpected judging from Lin-Chung's dispersion relation for the conduction band.[20] The dotted part of the conduction band illustrated in Fig. 4 shows the curvature required to explain the break in the electron-effective-mass data. The situation is thus unclear at this time as to whether or not there is a conduction band at ~0.4 eV above the Γ_8^c minimum.

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