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Energy-band structure and electron mobility of cadmium phosphide at low temperatures

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Electron-effective-mass values obtained from low-temperature Shubnikov–de Haas, magneto-Seebeck, and Hall measurements on Cd_3P_2 have been gathered from the literature. Using Kane's model for an InSb-like energy-band structure, the dispersion relation for the conduction band has been obtained along with a Γ_6-Γ_8 energy gap E_0 of 0.575 eV, an interband-momentum-matrix element P of 6.9×10^{-8} eV cm, and an electron effective mass at the conduction-band edge m_0^*/m_0 of 0.048. Combining these results with the available low-temperature optical data, the relative positions of other bands have been deduced. In particular, the spin-orbit splitting of the valence band at the Γ point Δ is 0.23 eV. There is a second, higher-lying conduction band whose minimum at Γ is approximately 0.08 eV above the bottom of the first one. Using the energy-band structure scheme so obtained, a calculation of the electron mobility of Cd_3P_2 was performed as a function of carrier concentration at 77 K. The limiting scatterings were taken to be polar-optical-phonon scattering, acoustical-phonon scattering, and scattering by charged impurities. A comparison of the results with experimental mobility data leads to a value for the static dielectric constant ϵ_0 of 26 and for the high-frequency dielectric constant ϵ_∞ of 17.

I. INTRODUCTION

Cadmium phosphide (Cd_3P_2), along with Cd_3As_2, Zn_3P_2, and Zn_3As_2, belongs to a class of materials with the general formula A_3B_2, where A is a group-II and B a group-V element, that have the tetragonal crystal structure.[1] In recent years, considerable attention has been given to the study of these materials as a result of their attractive properties. For example, Cd_3As_2 is a semimetal with a remarkably high electron mobility (about 55 000 cm^2/V sec at 77 K for an electron density of 2×10^{18} cm^{-3}),[2] a small electron effective mass, and a HgTe-like inverted electronic-energy-band structure,[3-5] whereas Zn_3As_2 is a p-type semiconductor with a very low hole mobility (about 10^2 cm^2/V sec at 77 K for $\sim 5 \times 10^{17}$ holes/cm^3),[6] a comparatively large hole effective mass, and a conventional InSb-like energy-band structure. An extensive survey of the most essential results concerning this class of II–V binary compounds including their preparation, crystal structure, transport and optical properties, and applications can be found in the review articles by Nasledov and Shevchenko[7] and by Żdanowicz and Żdanowicz.[8]

Cd_3P_2, which is the material to be discussed in the present paper, is an n-type degenerate semiconductor with electron concentrations lying in the range 10^{17}–5×10^{18} cm^{-3} for undoped samples, and with electronic mobilities varying from about 2000 to 3000 cm^2/V sec at room temperature and from about 8000 to 15 000 cm^2/V sec at 77 K.[9-14] However, it has been possible to prepare copper-doped Cd_3P_2 crystals[9] with electron concentrations as low as about 10^{15} cm^{-3} at room temperature,[13] but it should be mentioned that p-type samples have hitherto never been obtained. Specifically, an important effort has been devoted in the last decade to the investigation of the properties of Cd_3P_2, mainly for two reasons. First, this compound has proved to be a likely candidate for a semiconductor laser in connection with its highly remarkable optical properties. Recent work in this field includes the observation of optically pumped coherent laser emission,[14] low-temperature photoconductivity,[15-17] photoluminescence,[15,18,19] optical transmission,[3,9,13,15,16] reflectivity,[16,20,21] and low-temperature interband magnetoabsorption.[3] Second, Cd_3P_2 is an endpoint component of the high-mobility variable-band-gap $Cd_3As_{2-x}P_x$ pseudobinary alloy system, which has received much attention recently.[3,13,19,21-23] In particular, this system exhibits a semiconductor-semimetal transition at an intermediate alloy composition[3-5,13,24] similar to that in the alloy system $Cd_{3-x}Zn_xAs_2$.[3-5,25] Also interesting in the $Cd_3As_{2-x}P_x$ alloys is the thermoelectric figure of merit, which reaches rather large values at room temperature; indeed, the $x = 1.4$ material has proved to be comparable with the best thermoelectric materials known so far.[22,23]

A theoretical energy-band structure calculation for Cd_3P_2 was performed by Lin-Chung,[26] who used a hypothetical fluorite crystal model and the pseudopotential method to overcome the computational difficulties originating from the exceptionally complicated real-crystal structure of this substance; the unit cell for Cd_3P_2 contains eight formula units, i.e., 40 atoms or 128 valence electrons. The calculation, which neglected spin-orbit couplings and other relativistic effects, showed that (i) Cd_3P_2 has an energy-band structure similar to that of many III-V compounds with a direct energy gap at the center of the Brillouin zone of 0.96 eV and a bottom-of-the-conduction-band effective mass at Γ of $0.126m_0$, where m_0 is the free-electron mass, and (ii) in contrast to the case of Cd_3As_2 in which the valence-band maximum appears slightly (~10%) off center of the Brillouin zone,[4,5,27] the valence-band maximum of Cd_3P_2 is located exactly at Γ. In an attempt to compare her results with the existing interband-optical-transition and transport data, Lin-Chung estimated the essential changes in the energy-band structure as one goes from the hypothetical to the real-crystal structure and as one takes the spin-orbit interaction and relativistic corrections into account. As a result, the predicted direct energy gap at Γ for Cd_3P_2 in its real structure would be approximately 1.6 times smaller than the calculated one, that is, about 0.6 eV. It is finally worth noting that a second higher-lying conduction band was also predicted in this model with its minimum at X (which is equivalent to Γ in the real-crystal structure).

The first direct determination of the electron effective mass in Cd_3P_2 was reported by Heller *et al.*[28,29] for two single crystals, containing, respectively, 2.2×10^{17} and 1.23×10^{18} electrons per cm^3, from an analysis of the temperature dependence of the amplitude of Shubnikov–de Haas oscillations between 1.3 and 42 K in magnetic fields up to 85 kG. The values obtained for m^*/m_0 were 0.05 ± 0.005 and 0.061 ± 0.001, respectively. In addition, the effective-mass value obtained for the high-carrier-concentration sample with the magnetic field perpendicular to the tetragonal c axis of the crystal was found, to within experimental error, to be equal to that obtained with the parallel orientation of the magnetic field, thus indicating that, at least for electron concentrations up to 1.23×10^{18} cm^{-3}, the conduction band of Cd_3P_2 consists of a single, nearly spherically symmetric surface. These authors also fitted their Shubnikov–de Haas data to a nonparabolic Kane-type conduction-band model and deduced a value of 17 ± 2 eV for E_P, the energy associated with the momentum matrix element P characterizing the strength of the conduction-band–valence-band coupling in Kane's formulation.[30]

In an effort to obtain a better understanding of the band structure, Radautsan *et al.*[31,32] obtained the concentration dependence of the electron-effective mass at the Fermi level in Cd_3P_2 at 90 K from the saturation value of the thermoelectric power and the Hall coefficient in high magnetic fields, assuming strong degeneracy conditions. They found that the value of m^*/m_0 increases from 0.055 to 0.075 when the electron concentration varies from 4.4×10^{17} to 4.76×10^{18} cm^{-3}. Such results provided further support to the previous study of Heller *et al.*[28,29] concerning the concentration dependence of m^*, clearly showing that Cd_3P_2 has indeed a nonparabolic conduction band. It is interesting to note that the possibility of deviations from a quadratic energy-wave-vector dispersion law for Cd_3P_2 was first put forth by Żdanowicz and Wojakowski[10] from their early analysis of the dependence of the electron-effective mass upon temperature between 240 and 380 K. Analyzing their low-temperature effective mass versus electron concentration data in terms of Kane's isotropic three-band model adapted to an InSb-like structure,[33] and assuming the valence-band spin-orbit splitting to be $\Delta=0.15$ eV, Radautsan and co-workers predicted a $\Gamma_6-\Gamma_8$ energy separation $E_0=0.47$ eV, along with the electron-effective mass at the conduction-band edge $m_0^*/m_0=0.048$, and $E_P=10.8$ eV (or, equivalently, $P=6.4\times10^{-8}$ eV cm). This value for E_P is substantially lower than that deduced by Heller *et al.*[28,29] Although too small by about 20% if compared with the available optical data,[3,9,13-21] the value of E_0 so obtained is nevertheless not completely inconsistent with the energy gap determined from the temperature dependence, in the intrinsic range, of the Hall coefficient ($E_0=0.52$ eV)[10] and of the electrical resistivity [$E_0=0.6\pm0.06$ eV (Ref. 9) and 0.51 eV (Ref. 10)], and also with the theoretical value of 0.5 eV predicted empirically by Suchet.[34] The results of Radautsan *et al.* regarding the applicability of Kane's model for the Cd_3P_2 conduction band were recently confirmed by the work of Blom and Burg,[12] who reported measurements of the transverse Nernst, Righi-Leduc, and Maggi-Righi-Leduc effects on five unoriented Cd_3P_2 single crystals, with electron concentrations in the range 5.5×10^{16}–1.71×10^{18} cm^{-3}, at 110 and 300 K in magnetic fields up to 18 kG. Indeed, these authors could quantitatively describe their results using a Kane-type conduction band with $E_0=0.50$ eV and $m_0^*=0.040m_0$. Finally, it is worth mentioning that other workers also analyzed successfully their own data on Cd_3P_2 within the framework of a nonparabolic Kane-type conduction band, namely, (i) Wagner *et al.*,[3] who determined the energy gap of a series of alloys of the $Cd_{3-x}Zn_xAs_2$ and $Cd_3As_{2-x}P_x$ systems, including Cd_3P_2 from interband magnetoabsorption measurements at low temperatures, and (ii) Radoff and Bishop[13] who obtained the energy gap, along with its variation with temperature,[35] of $Cd_3As_{2-x}P_x$ alloys for $0\le x\le2$ from the temperature dependence of the optical-transmission edge between 8 K and room temperature.

Very recently, two papers[11,36] appeared in the literature on the study of the magnetoresistance of Cd_3P_2 as a function of magnetic field at 77 and 300 K. The first of these is by Radautsan *et al.*,[11] who showed that the magnetic-field dependence of the magnetoresistivity cannot be described correctly in terms of a simple one-band model, but may be explained by assuming a two-band conductivity. These authors thus concluded to the presence of a second higher-lying conduction band in Cd_3P_2, in agreement with the theoretical calculations of Lin-Chung.[26] In the second paper, Żdanowicz and Bodnar[36] arrived at a totally different conclusion from measurements of the magnetoresistivity on samples with electron concentrations of about 5×10^{17} cm^{-3}. In fact, assuming a spherically symmetric, parabolic conduction band, their deduced mobilities are found in reasonable agreement with the various mobility data for Cd_3P_2.[9-14]

Thus, a coherent and convincing model for the electronic-energy-band structure of Cd_3P_2 which would satisfy all workers involved has not been forthcoming in spite of the impressive amount of data on this material which has accumulated in the literature over the years. The purpose of this paper is twofold. First, low-temperature data from magneto-Seebeck, Hall, Shubnikov–de Haas, thermomagnetic,[9-12,22,23,28,29,31,32,36] and optical[3,9,13-21] experiments are gathered. The reason for doing this is to propose and to describe as precisely as possible a reliable energy-band structure model for Cd_3P_2 consistent with all these data. The procedure adopted is essentially similar to that described in Refs. 4 and 5. Second, an electron-mobility calculation is carried out as a function of carrier concentration at 4.2 K and at liquid-nitrogen temperature. The contribution of ionized impurities, acoustic phonons, and optical phonons to the electronic scattering is properly evaluated taking the actual Cd_3P_2 energy-band structure into account. A value for the low- and high-frequency dielectric constants is derived from the fitting of these results to the experimental ones appearing in the literature.

II. DETERMINATION OF THE ENERGY-BAND STRUCTURE AT LOW TEMPERATURES

A. Theoretical considerations

By using Kane's isotropic three-band model adapted to the InSb-like energy-band structure,[30] the electron-effective mass m^* at the Fermi level, under complete statistical degeneracy conditions, can be expressed as a function of the electron concentration n as follows[4,5]:

$$\left(\frac{m^*/m_0}{1-m^*/m_0}\right)^2=\lambda^2\left(\frac{E_0}{E_{\underline{P}}}\right)^2+\frac{2\hbar^2\lambda^2(3\pi^2n)^{2/3}}{m_0\alpha E_{\underline{P}}}\,, \qquad (1)$$

where E_0 is the $\Gamma_6-\Gamma_8$ energy gap, $E_{\underline{P}}=(2m_0/\hbar^2)P^2$, $\hbar$ is the Planck constant divided by $2\pi, m_0$ is the free-electron mass,

$$\alpha=1+\tfrac{1}{3}\Delta/(E'_F+E_0+\tfrac{2}{3}\Delta)\,, \qquad (2)$$

$$\lambda=\alpha-\frac{\frac{1}{3}\Delta E'_F}{(E'_F+E_0+\frac{2}{3}\Delta)^2}\left(1-\frac{E'_F}{E_0+2E'_F}\right), \qquad (3)$$

Δ is the spin-orbit splitting of the valence band at the Γ point, and

$$E'_F=\left(\frac{E_0}{2}\right)\left[\left(1+\frac{2\hbar^2E_{\underline{P}}(3\pi^2n)^{2/3}}{m_0\alpha E_0^2}\right)^{1/2}-1\right] \qquad (4)$$

is the Fermi energy E_F measured from the bottom of the conduction band minus the corresponding free-electron kinetic energy $(\hbar^2/2m_0)(3\pi^2n)^{2/3}$. Equations (1) and (4) hold only if the parameters α and λ, defined in Eqs. (2) and (3), are constants. α and λ are in fact well-behaved slowly varying functions of E'_F, and therefore of n. As it will become apparent below, it is indeed a reasonable approximation to treat these two parameters as constants in the range of $n=(0.44-1.23)\times10^{18}$ cm^{-3} which includes most of the available effective mass data on Cd_3P_2. Obviously, Eq. (1) represents the equation of a straight line if the left-hand side is plotted as a function of $n^{2/3}$.

B. Optical results

In recent years, a number of papers have appeared which discuss the low-temperature optical properties of as-grown, as well as copper-doped Cd_3P_2. We review here briefly the various experimental results which have been obtained so far and which will be of help in the energy-band-structure determination of this material. In 1970, Bishop, Moore, and Swiggard[14] reported the observation of optically pumped coherent laser emission with wavelength near 2.12 μm (0.585 eV) in as-grown Cd_3P_2 crystals with $n\sim10^{17}$ cm^{-3} at 4.2 K. Bishop and co-workers also reported low-temperature photoluminescence measurements on unintentionally doped crystals of Cd_3P_2 and on highly compensated copper-doped samples.[15,18,19] Two distinguishable emission peaks were obtained in the undoped samples, namely, a narrow, strong luminescence peak at about 0.58 eV, and a subsidiary peak positioned some 20 meV below the major peak. The relative intensities of the two photoluminescence peaks were found to vary from sample to sample, indicating that they involved transitions to energy levels associated with two different species of residual impurities or defects whose concentration varied from crystal to crystal. In particular, with the addition of copper, the efficient luminescence observed in the as-grown crystals was replaced by a broad, weak emission at lower energy, and the strong narrow peak at 0.58 eV completely disappeared.[15,16] The authors ascribed the two photoluminescence peaks near 0.58 eV in the as-grown Cd_3P_2 to transitions from one band edge to narrow n-type impurity or defect bands at or quite near the opposite (conduction) band edge. The position of the strong luminescence peak was further studied by Bishop and Radoff[19] as a function of temperature between 8 and 160 K in several alloys of the $Cd_3As_{2-x}P_x$ system, including one sample of Cd_3P_2. These authors showed that the luminescence line in Cd_3P_2 shifted to lower energies as the sample temperature was increased. In the same paper, Bishop and Radoff also reported measurements of the temperature dependence of the optical-absorption edge for the same alloys and for the same temperature range. The optical-absorption edge in Cd_3P_2 was found to occur at energies about 20 meV above the corresponding major photoluminescence peak at all temperatures in the investigated range.[15,19] In a more recent work,[13] Radoff and Bishop extended their optical transmission studies in the $Cd_3As_{2-x}P_x$ alloy system to room temperature, and obtained an absorption-edge temperature coefficient for Cd_3P_2 of about -2×10^{-4} to -3×10^{-4} eV/K. On the other hand, it is worth mentioning that these authors analyzed their optical data in terms of the Kane energy-band model, and predicted a value for the low-temperature Cd_3P_2 energy gap of about 0.59 eV. In 1971, Wagner *et al.*[3] published a series of interband magnetoabsorption measurements at 20 K in several $Cd_{3-x}Zn_xAs_2$ and $Cd_3As_{2-x}P_x$ alloys in magnetic field strengths up to 110kG. The analysis of their data, assuming a nonparabolic Kane-type conduction band, also produced a $\Gamma_6-\Gamma_8$ energy gap of 0.59 eV for Cd_3P_2 at low temperatures. In a very recent paper, Plenkiewicz, Dowgiatto, and Królicki[17] reported measurements of the photoconductivity in Cd_3P_2 in the range from 1 to 2.5 μm at 77 and 300 K. The photoconductivity spectrum they obtained revealed the presence of four peaks at energies of 0.56, 0.57, 0.65, and 0.88 eV, respectively, at liquid-nitrogen temperature. The major peak at 0.57 eV was interpreted according to the Lin-Chung hypothetical fluorite model as being due to the fundamental transition Γ_{15}-Γ_1, but the nature of the other three remaining peaks was not explained. This value of 0.57 eV obtained by Plenkiewicz *et al.* for the major photoconductivity peak corresponds closely to that of 0.58 eV previously reported by Bishop *et al.*,[15] who also performed photoconductivity measurements in as-grown Cd_3P_2 samples in the vicinity of the fundamental band gap at 4.2 K. There are, however, two essential differences between the spectral distribution of the photoconductive response obtained by these latter authors and that reported by Plenkiewicz *et al.* First, Bishop *et al.* observed, in addition, a second weaker peak at 0.59 eV, which was associated with the onset of intrinsic or band-edge to band-edge transitions. This peak is absent in the photoconductivity spectrum reported by Plenkiewicz *et al.* Second, the photoconductivity measurements of Bishop *et al.* performed over a range of photon energies up to about 0.68 eV, did not exhibit evidence of the presence of the peak at 0.65 eV, as reported by Plenkiewicz *et al.* This last point deserves some attention and will be discussed further below. On the other hand, Bishop *et al.*[15] also obtained the photoconductivity spectrum of copper-doped Cd_3P_2 at 77 K. They showed that with the introduction of copper acceptors, the 0.58-eV peak below the band edge in the photoconductivity spectrum of as-grown Cd_3P_2 disappeared, then giving rise to a strong band-edge photoconductivity spectrum which correlated systematically with the onset of interband optical absorption. Finally, it is worth mentioning the work by Radoff and Bishop,[16] who observed a subsidiary, rather broad peak near 0.48 eV in the photoconductive response of copper-doped Cd_3P_2 at 80 K. No such peak could be detected in the as-grown material. The observation of this subsidiary peak in the photoconductivity of copper-doped material was attributed to the presence of deep copper levels (0.1 eV above the valence band edge) which gave rise to optical transitions to the conduction band.

C. Effective-mass results

The available low-temperature data of m^* in Cd_3P_2, obtained from magneto-Seebeck and Hall measurements at 90 K[11,31,32] and from Shubnikov-de Haas experiments between 1.3 and 42 K[28,29] for various electron concentrations, are plotted in Fig. 1. The agreement between the two sets of results, determined by totally unrelated methods, is remarkably good. Also shown in Fig. 1 are the three data points deduced by Blom and Burg[12] from thermomagnetic transport measurements at 110 K. However, these three latter points appear to be consistently too low in regard to the previous ones, and will be ignored in the present study. A straight-line least-squares fit using Eq. (1) is performed for the six samples lying in the electron concentration range $(0.44-1.23)\times10^{18}$ cm^{-3}. The effective-mass data point for the low-carrier concentration sample of Heller *et al.*[28,29] has not been included in the least-squares fit, owing to the large experimental uncertainty (10%) with which it was determined. Also ignored in the fitting are the two effective-mass data points for the $n=3.11\times10^{18}$ cm^{-3} and $n=4.76\times10^{18}$ cm^{-3} samples of Radautsan *et al.*[11,32]; the reason for doing this is related to our interpretation of the optical results of Plenkiewicz *et al.*[17] which will be discussed below. Let us only mention here that such a procedure differs essentially from that followed by Radautsan *et al.*,[11] who included in their analysis all of their effective-mass data points over the investigated electron concentration range from 0.44×10^{18} to 4.76×10^{18} cm^{-3}. We obtain

$$\left(\frac{m^*/m_0}{1-m^*/m_0}\right)^2 = 2.58\times10^{-3}+1.28\times10^{-15}\,n^{2/3}\,, \tag{5}$$

where n is expressed in cm^{-3}. It is interesting to remark that the experimental points fall near the illustrated line in Fig. 1 up to an electron concentration of about $(1.5-2)\times10^{18}$ cm^{-3}. Beyond these values, an apparent deviation from the low-concentration linear behavior occurs, which is not inconsistent with the existence of a second, higher-lying conduction band as inferred from the optical results of Plenkiewicz *et al.*[17] This will be discussed in greater detail in Sec. II D.

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

$$E_P/\alpha E_0^2 = 34.0\ \text{eV}^{-1}\,, \tag{6}$$

which allows us to express Eq. (4) in the following numerical form

$$E'_F = \tfrac{1}{2}E_0[(1+0.497\times10^{-12}\,n^{2/3})^{1/2}-1]\,, \tag{7}$$

with n in cm^{-3}.

The straight line also yields

$$E_0 = 0.578(\lambda/\alpha)\ \text{eV}. \tag{8}$$

From the definitions of α and λ [Eqs. (2) and (3)], and using $\Delta=0.23$ eV,[37] the ratio $\lambda/\alpha=0.994$ and varies only by 0.3% over the considered electron-concentration range. According to Eq. (8), it thus follows that $E_0=0.575$ eV. Since E_0 is now known, Eq. (7) can be used to illustrate the variation of the Fermi energy with n (Fig. 2). Furthermore, Eq. (6) readily yields $E_P=12.4$ eV (or, equivalently, $P=6.86\times10^{-8}$ eV cm). Finally, the electron-effective mass at the bottom of the conduction band is found to be $m_0^*/m_0=0.0478$. At this stage, it is now possible to judge the seriousness of the approximation which assumed that α and λ are essentially independent of n over the range of interest. Using $E_0=0.575$ eV, Eqs. (2) and (3) show that for n between 0.44×10^{18} and 1.23×10^{18} cm^{-3}, α varies between 1.100 and 1.096, whereas λ varies between 1.095 and 1.088. Obviously, this justifies, *a posteriori*, the validity of the present analysis.

D. Band structure of Cd_3P_2

From the above results, it is now possible to describe the characteristics of the energy-band structure of cadmium phosphide at low temperatures as follows:

(i) Equation (7) gives the Fermi energy as a function of n (Fig. 2) as well as the dispersion relation

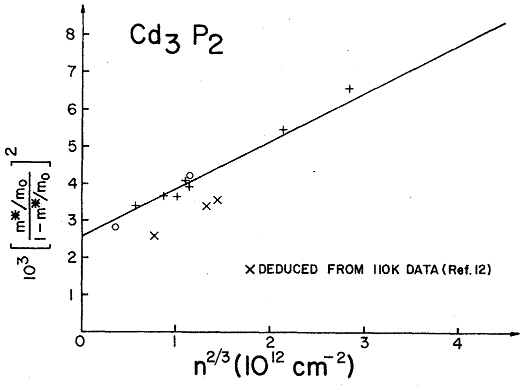

FIG. 1. Variation of the low-temperature electronic effective mass at the Fermi level with electron concentration. Data are taken from Refs. 28 and 29 (○), and 31 and 32 (+). The straight line was determined from a least-squares fit of the six points lying in the range $n=(0.44-1.23)\times10^{18}$ cm^{-3}. Also shown are the three 110-K data points (×) deduced by Blom and Burg (Ref. 12).

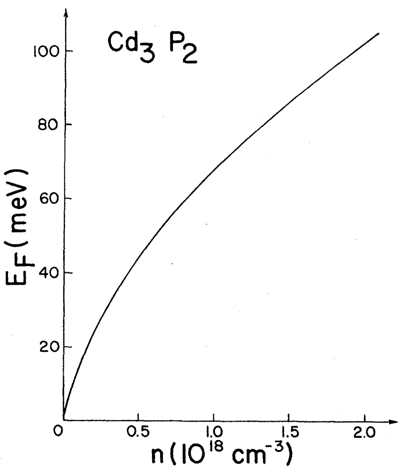

FIG. 2. Variation of the Fermi energy E_F as a function of electron concentration n, according to Eq. (7) with $E_0=0.575$ eV.

$E(k)$ for the conduction band (Fig. 3). Regarding the value of the electron-effective mass at the conduction-band edge, it is interesting to note that our result agrees quite well with that obtained by Radoff and Bishop[13] from the analysis of optical transmission-edge data at 8 K ($m_0^*/m_0 = 0.047$). On the other hand, the value found for the momentum matrix element between the Γ_6 and Γ_8 wave functions is substantially lower than that previously derived by Heller *et al.*[29] from Shubnikov–de Haas experiments between 1.3 and 42 K ($E_P = 17 \pm 2$ eV). However, our value of E_P is in satisfactory agreement with the corresponding low-temperature values reported by Blom and Burg[12] ($E_P = 12.9$ eV) and by Radautsan *et al.*[32] ($E_P = 10.8$ eV). It is also quite consistent with the value of 13 eV obtained at low temperatures by the present authors[5] in cadmium arsenide, and with the value of 11.6 eV derived by Blom *et al.*[24] for the alloy $Cd_3As_{1.4}P_{0.6}$ at 110 K.

(ii) The $\Gamma_6 - \Gamma_8$ energy gap is 0.575 eV. This value is in excellent agreement with the various existing low-temperature optical results,[3,13-19] and also with the value predicted theoretically by Lin-Chung.[26] Furthermore, it is consistent with most of the transport data reported in the literature.[9,10,12,32] It is worth mentioning here that the fact of ignoring the two high-carrier concentration samples of Radautsan *et al.*[11,31,32] in the analysis of the data giving conduction-band mass versus concentration allows us, contrary to these latter authors, to obtain a satisfactory agreement with *both* optical and transport results. Obviously, this gives strong evidence in support of the present analysis. The knowledge of the E_0 value determines the maximum of the light-hole valence band, which has been drawn in Fig. 3 as the mirror image of the conduction band.

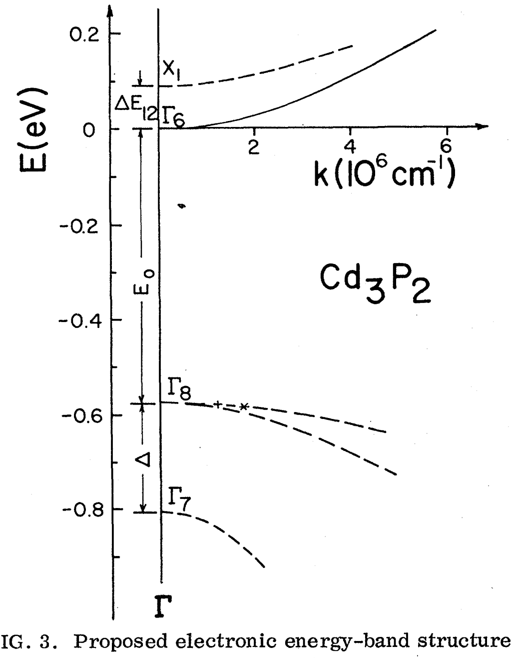

FIG. 3. Proposed electronic energy-band structure for Cd_3P_2 at low temperatures. The full curve comes from a fit of the Kane model to the transport data. The dashed curves were deduced from this latter one using optical data and are less accurate.

(iii) In the light of our previous work on Cd_3As_2,[4,5] and according to the various optical measurements in the Cd_3As_2–Cd_3P_2 semiconductor alloy system at both room and low temperatures,[3,13,21] the fundamental optical-absorption edge at about 0.6 eV must be attributed to a direct, Burstein–Moss shifted transition from the heavy-hole valence band to the lowest conduction band. The approximate shape of the heavy-hole band can thus be drawn by using the observed absorption edge for samples whose electron concentration is also known. However, only one such datum is presently available at low temperatures, with an electron concentration of about 2×10^{17} cm^{-3}.[13,19] From Fig. 2, this corresponds to a Fermi energy of about 25 meV from which one must subtract $2k_BT$ due to the smearing of the Fermi surface.[35] At 80 K, the difference is about 11 meV and corresponds to a wave number $k \sim 1.2 \times 10^6$ cm^{-1}. From this k value on the conduction-band curve, one drops a perpendicular of length 0.59 eV, which is the observed absorption edge at 80 K.[13,19] This gives a point (+) on the heavy-hole valence band illustrated in Fig. 3. The same procedure was performed with another datum point (∗) taken by the same authors on the same sample, but at a different temperature, namely, 8 K.[13,19] Since a parabolic shape for the heavy-hole band would not be unrealistic,[3,4] we can attempt to fit through these two points a parabola with its maximum at Γ.[26] Choosing this maximum at the top of the light-hole band as a third point[38] leads to a curvature corresponding to an effective mass of approximately $0.13m_0$. This is remarkably close to the valence-band masses reported in Cd_3As_2,[3,4,39] and in $Cd_{1.7}Zn_{1.3}As_2$.[3,40]

(iv) The apparent departure from the low-concentration linear behavior in the variation of the electron-effective mass (Fig. 1) occurring at $n \sim (1.5-2) \times 10^{18}$ cm^{-3} could be attributed, *a priori*, either to the manifestation of another, higher-lying conduction band or to a deviation from the Kane model prediction. From Fig. 2, this corresponds to a Fermi energy of about 0.08–0.10 eV above the bottom of the first conduction band. Judging from Lin-Chung's dispersion relation for the conduction band,[26] and especially, considering the recent low-temperature photoconductivity measurements of Plenkiewicz *et al.*,[17] we may exclude the second alternative. In fact, Plenkiewicz *et al.* indeed observed a transition at 0.65 eV at liquid-nitrogen temperature. According to the room-temperature reflectance results in the $Cd_3As_{2-x}P_x$ alloy system reported by Zivitz and Stevenson,[21] and in the light of our previous study on Cd_3As_2,[4,5] this transition must be assigned to the Γ_8-X_1 bands. This in turn implies that there is a second conduction band (X_1) at $\Delta E_{12} \sim 75$ meV above the bottom of the lowest conduction band. Such a ΔE_{12} value closely corresponds to the above mentioned 0.08–0.10-eV energy range in which the apparent change in the behavior of the electron-effective mass occurs. The presence of a second conduction band *close* to the first one Γ_6 was already pointed out by Plenkiewicz *et al.*[17] Also, Radautsan *et al.*[11] recently concluded from studies of the magnetic field dependence of the magnetoresistance at 77 and 300 K that the conduction band of Cd_3P_2 consists of two bands. A last point may deserve some attention here. This comes from the fact that Bishop *et al.*,[15] who also performed photoconductivity measurements in as-grown and copper-doped cadmium phosphide at low temperatures did not observe the transition at 0.65 eV, as did Plenkiewicz *et al.*, though their measurements extended to photon energies of about 0.68 eV. This point remains unclear at this time. As far as the exact position of the X_1 band with respect to the lowest conduction band is concerned, it would be useful if a new measurement of the 77-K photoconductivity of Cd_3P_2 could be made.

(v) According to our previous work on cadmium arsenide,[4,5] the higher-energy photoconductivity peak at 0.88 eV reported by Plenkiewicz *et al.*[17] should be attributed to a direct transition at Γ from the split-off Γ_7 valence band to the *s*-type X_1 band. Since $\Delta = E(\Gamma_8) - E(\Gamma_7)$, it is thus easy to deduce from the data of Plenkiewicz *et al.* a value for the spin-orbit valence-band splitting at Γ of Cd_3P_2. In fact, we obtain $\Delta = 0.88 - 0.65 = 0.23$ eV.[37] This value of Δ is slightly smaller than that found in Cd_3As_2 at low temperatures (0.27 eV).[5] The position of the split-off valence band has been drawn with its maximum at 0.23 eV below the Γ_8 valence band at the Γ point (Fig. 3).

III. ANALYSIS OF ELECTRON MOBILITY AT 77 K

In this section, we present the calculation of the electron mobility of Cd_3P_2 as a function of carrier concentration at 77 K. The limiting electron scattering mechanisms are taken to be polar-optical-phonon scattering, charged-centers scattering, and acoustical-phonon scattering. For small-gap semiconductors, and in particular for the case of Γ_6 conduction-band edge symmetry, i.e., for InSb-like materials, the necessary expressions to calculate the contributions of these various mobility limiting scattering mechanisms were derived by Zawadzki and co-workers,[41–44] and have been reproduced by Caron *et al.*[5] and by Jay-Gerin *et al.*[45,46] taking care to correct for the typographical errors. The electron mobilities allowed by the three scattering mechanisms considered are given by

$$\mu_{cc} = \frac{\epsilon_0^2 \hbar^3 k_F^3}{2\pi e^3 (m^*)^2 N F_{cc}} , \tag{9}$$

$$\mu_{ac} = \frac{\pi e \hbar^3 d v_\parallel^2}{k_B T E_d^2 (m^*)^2 k_F F_{ac}} , \tag{10}$$

and

$$\mu_{op} = \frac{\hbar^3 k_F}{2 e k_B T (1/\epsilon_\infty - 1/\epsilon_0)(m^*)^2 F_{op}} . \tag{11}$$

In these equations, e is the magnitude of the electronic charge, $\hbar$ is Planck's constant divided by 2π, k_B is Boltzmann's constant, T is the absolute temperature, N is the total concentration of ionized impurities, d is the material density, $v_\parallel$ is the longitudinal velocity of sound in the material, E_d is the acoustical deformation-potential constant, and ϵ_0 and ϵ_∞ are the low- and high-frequency dielectric constants, respectively. The F factors for each scattering mode are rather involved functions defined in the above-mentioned references. It is worth mentioning, however, that the mixing of *s*- and *p*-like components in the total conduction-band wave function also allows a nonvanishing coupling of electrons to the transverse acoustical phonons, as is transparent in the following expression for F_{ac}:

$$F_{ac} = F_{ac}^{\parallel} + (v_\parallel^2 / v_\perp^2) F_{ac}^{\perp} , \tag{12}$$

where the symbols $\parallel$ and $\perp$ refer to the longitudinal and transverse modes, respectively. Finally, k_F is the wave number at the Fermi energy, and is related to the electron concentration n in a spherical degenerate band[28,29] by

$$k_F = (3\pi^2 n)^{1/3} . \tag{13}$$

In order to calculate the electronic mobilities from Eqs. (9)–(11), we must specify the numerical values for four material parameters. The latter are E_d which is taken, somewhat arbitrarily, as 10 eV, d which is 5.60 g/cm^3 for Cd_3P_2,[47] and $v_\parallel$ which is 4.2×10^5 cm/sec as deduced from the quantity $v_\parallel^2 - \frac{4}{3} v_\perp^2 = 12 \times 10^{10}$ cm^2/sec^2, measured experimentally by Opilska and Opilski,[48] on assuming that $v_\perp = \frac{1}{2} v_\parallel$. The dependence of the electron-effective mass at the Fermi level m^* upon n is given by Eq. (5), and the Γ_6-Γ_8 energy gap E_0, Δ, and E_P are 0.575, 0.23, and 12.4 eV, respectively. Two other parameters are required in the calculation, namely, ϵ_0 and ϵ_∞. But these two parameters have not been measured so far in Cd_3P_2. Accordingly, instead of predicting the mobility of cadmium phosphide as a function of electron concentration at low temperatures, we will use, in turn, the available Cd_3P_2 mobility data at low temperatures in order to deduce the values of ϵ_0 and ϵ_∞. The static dielectric constant can be obtained at 4.2 K, in a manner similar to that followed in Ref. 45, from Eq. (9) only, if one assumes that scattering from charged centers is the limiting mechanism in electrical conduction at this temperature.[9] Unfortunately, no 4.2-K electron mobility data have been reported for Cd_3P_2 in the literature. It is nevertheless possible from the experimental measurements of Haacke and Castellion[9] to extrapolate with a reasonable accuracy to a very low-temperature mobility value of about 20 000 cm²/V sec for an undoped Cd_3P_2 single crystal containing an electron concentration of approximately 10^{18} cm^{-3}. If we then assume that there is one species of donor impurity and that it is singly ionized [i.e., $N=n$ in Eq. (9)], the resulting calculated electron mobility at this concentration fits exactly the estimated experimental value for $\epsilon_0 = 26$. Once ϵ_0 is known, the determination of ϵ_∞ can be undertaken. This is done most simply by calculating the overall electron mobility at liquid-nitrogen temperature from Eqs. (9)–(11), according to

$$\mu = (1/\mu_{cc} + 1/\mu_{ac} + 1/\mu_{op})^{-1} \qquad (14)$$

for different values of ϵ_∞, and by comparing the calculated mobility values with the available experimental data at this temperature.[49] These latter 77-K mobility data, gathered from the literature,[9-11,14,31,36] are plotted in Fig. 4 as a function of electron concentration, along with three theoretical curves obtained from Eq. (14) for three different values of the high-frequency dielectric constant, namely, $\epsilon_\infty = 14$, 17, and 20, respectively. In spite of the large scatter of the data, it appears that $\epsilon_\infty = 17$ would be a reasonable value.

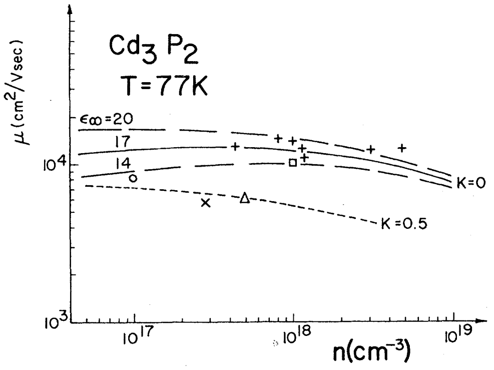

FIG. 4. Variation of the low-temperature mobility in Cd_3P_2 with electron concentration. Data at 77 K are taken from Refs. 9 (□), 10(×), 11 and 31 (+), 14 (○), and 36 (△). The three upper curves give the theoretical over-all electronic mobility at 77 K calculated for $\epsilon_0 = 26$ and $\epsilon_\infty = 14$, 17, and 20. The dotted line illustrates the effects of compensation with $K = 0.5$, $\epsilon_0 = 26$, and $\epsilon_\infty = 17$. For clarity, we have omitted here the 110-K mobility points of Blom and Burg (Ref. 12).

A few words must now be said concerning the two points which are well below the $\epsilon_\infty = 17$ curve. These latter should reflect a higher degree of compensation than the others as well as, possibly, an inferior crystal quality. In fact, it must be remembered that the curves of Fig. 4 assumed that compensation effects are negligible. Such an assumption is most likely no longer valid in the range of electron concentration below about $(5-6) \times 10^{17}$ cm^{-3}. If this is indeed the case, the mobility given by Eq. (9) must be multiplied by the factor $(1-K)/(1+K)$, where K is the compensation ratio, defined as the ratio of the concentration of acceptor-type ionized impurities to that of the donor-type ionized impurities. For example, for the Cd_3P_2 single crystal (sample number 1) of Żdanowicz and Bodnar,[36] which contains about 5×10^{17} electrons per cm³, the reported mobility is approximately 6000 cm²/V sec at 77 K, whereas the calculated overall mobility, using Eq. (14) with $\epsilon_0 = 26$ and $\epsilon_\infty = 17$ and assuming there is no compensation, is found to be about 12 600 cm²/V sec for this same concentration. In order to reproduce the measured electron mobility value, we have to assume a compensation ratio of $K \sim 0.50$, which is not an unreasonable value. The behavior of the mobility assuming this value of K is illustrated by the dashed line in Fig. 4. The same

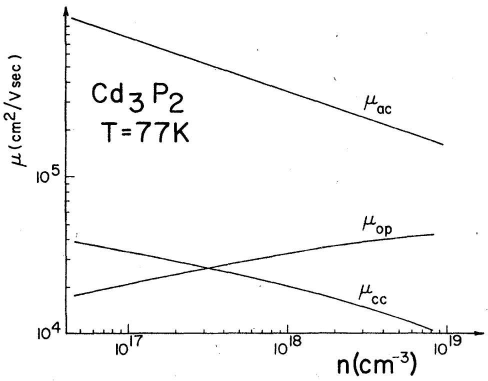

FIG. 5. Electron mobility in Cd_3P_2 at 77 K as a function of carrier concentration. The three solid-line curves show the theoretical mobilities for charged-center (μ_{cc}), polar-optical-phonon (μ_{op}), and acoustical-phonon (μ_{ac}) scattering mechanisms, calculated with $\epsilon_0 = 26$ and $\epsilon_\infty = 17$.

kind of considerations can be done for the low-concentration mobility point of Żdanowicz and Wojakowski.[16]

For the sake of completeness, we have illustrated in Fig. 5 the variation with electron concentration at 77 K and for $\epsilon_\infty = 17$ of the various contributions to the mobility due to charged centers (μ_{cc}), polar-optical phonons (μ_{op}), and acoustical phonons (μ_{ac}), respectively. As can be seen from Fig. 5, μ_{ac} is quite large as compared with μ_{cc} and μ_{op}, and does not play any primary role in the determination of the overall mobility versus concentration curve. This latter result is indeed satisfactory, since the acoustical deformation-potential constant E_d, being not known precisely, was chosen *a priori* somewhat arbitrarily in the calculations. It is worth mentioning that the value we obtain for ϵ_∞ is remarkably close to that reported for cadmium arsenide[39,46] and for the alloy $Cd_3As_{1.4}P_{0.6}$.[24]

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bond in Cd_3P_2 is close to that of III–V semiconductor compounds. As it will be shown in Sec. IIID, the value of 0.23 eV used in the present work has been determined directly from the interpretation of the recent low-temperature photoconductivity measurements on as-grown Cd_3P_2 crystals of Plenkiewicz *et al.* (Ref. 17).

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