# Temperature dependence of electron concentration in cadmium arsenide

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From measurements of the temperature dependence of the electron concentration in $Cd_3As_2$, we found values for the conduction-band parameters that are in good agreement with those recently reported by Aubin, Caron, and Jay-Gerin. However, in contrast with these authors we found no small overlap, but a relatively large gap of 26 meV between the heavy-hole band maximum and the conduction-band minimum.

In two recent papers[1,2] Aubin, Caron, and Jay-Gerin proposed an electronic-energy-band structure of $Cd_3As_2$. By gathering the literature values of electron effective masses from electrical transport studies and interpreting these data in Kane's model for the $\alpha$-Sn type inverted structure, these authors deduced the dispersion relation for the conduction band. The available data on the optical gap were used to determine the position and shape of the heavy-hole band, resulting in band schemes at 300 and 77 K as shown in Fig. 4 of Ref. 1 and Fig. 4 of Ref. 2, respectively. The ever present high degeneracy of this material (a characteristic electron concentration of about $2\times10^{18}$ cm$^{-3}$ corresponding to a Fermi energy of about 0.15 eV) excluded up to now the determination of both conduction- and valence-band parameters from transport measurements only.

We prepared $Cd_3As_2$ samples with net donor concentrations almost an order of magnitude lower than those reported in the literature.[3] Samples with initial concentrations of about $2\times10^{18}$ cm$^{-3}$ were subjected to various heat treatments in either cadmium or arsenic atmospheres. Reduction of net donor concentrations was found to be most effective by applying a two-stage annealing procedure in arsenic vapor. The samples were first annealed during 1 week at 250 °C, followed by a much longer annealing time (2–4 months) at 100 °C. Substantial decrease in net donor concentration with time only started during the second stage of the treatment. A time of over 2 months is needed before a minimum value is achieved. Once the samples are stabilized in this way, their electron concentrations remain constant with time when maintained in air at room temperature.

In these samples the degeneracy is partly lifted, and measurements of the electron concentration $n$ as function of temperature can be used to obtain numerical values for some important band parameters of the above mentioned model. The $n$-$T$ dependences of four samples in the temperature range from 4.2 to 360 K are given in Fig. 1. The net donor concentrations ($N_D - N_A$) of the samples are $2.30\times10^{17}$, $3.95\times10^{17}$, $4.75\times10^{17}$, and $7.70\times10^{17}$ cm$^{-3}$, respectively. For each net donor concentration $n(T)$ can be calculated by solving simultaneously the equations

$$n - p = N_D - N_A , \tag{1}$$

$$n = \frac{1}{3\pi^2}\left(\frac{k_0T}{P}\right)^3 {}^0K_0^{3/2}(\eta, \beta, \Delta/k_0T) , \tag{2}$$

$$p = \frac{1}{2\pi^2}\left(\frac{2m_d^* k_0 T}{\hbar^2}\right)^{3/2} F_{1/2}(E_t/k_0T - \eta) . \tag{3}$$

In Eqs. (1)–(3) $n$, $p$, $N_D$, and $N_A$ are the concentrations of electrons, heavy holes, donors, and

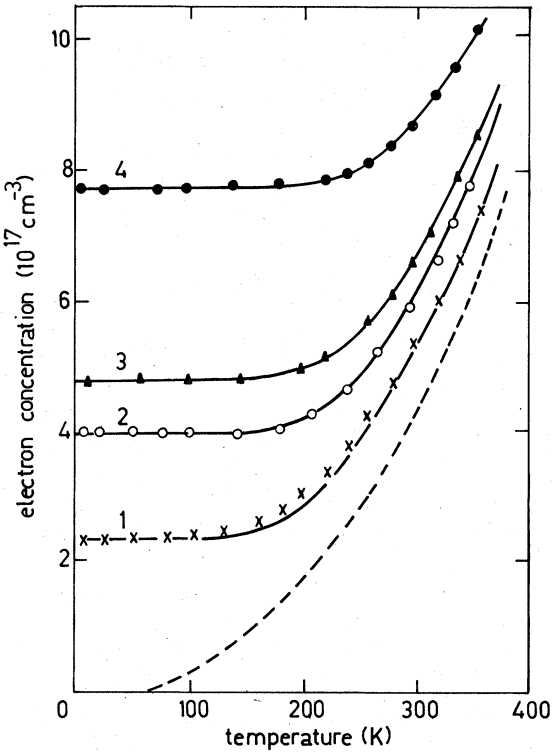


FIG. 1. Electron concentration as function of temperature for various net donor concentrations (2.30, 3.95, 4.75, and 7.70) $\times10^{17}$ cm$^{-3}$ for samples 1, 2, 3, 4 respectively. The dashed curve represents the corresponding intrinsic concentration..

 

acceptors, respectively. The symbol ${}^0K_0^{3/2}(\eta, \beta, \Delta/k_0T)$ represents a generalized ${}^nL_k^m(\eta,\beta)$ integral,[5] by fully taking into account the free-electron term $\hbar^2k^2/2m_0$ as well as finite spin-orbit splitting $\Delta$. $F_{1/2}(E_t/k_0T-\eta)$ is a Fermi-Dirac integral of order $\frac{1}{2}$. It should be noticed that the band model we use here is essentially that of Aubin, Caron, and Jay-Gerin (Fig. 4 of Ref. 1), apart from the fact that we make no assumptions about the position of the maximum of the heavy-hole band in $k$ space. The conduction band is described by the largest root of the secular equation for the three-band Kane model for the $\alpha$ – Sn type structure.[4] Due to the lack of information about higher-lying bands in $Cd_3As_2$, corrections due to these bands can not be included. The $K$ integral in Eq. (2) is similar to the integral introduced by Ermolovich and Kravchuk[6] for the InSb type structure. These authors define a four-parameter integral, in which the effective mass at the bottom of the conduction band acts as the fourth parameter. However, expressing this quantity in terms of the Kane matrix element $P$ reduces this four-parameter integral to our three-parameter $K$ integral, multiplied by a constant factor containing $P$.

For the heavy-hole band we assume an isotropic parabolic band with a thermal energy gap $E_t$ between its top and the conduction-band minimum. The zero of energy is taken at the bottom of the conduction band, thus a positive $E_t$ would signify an overlap between the heavy-hole and conduction bands. If the heavy-hole band maximum is displaced from $\Gamma$ as has been suggested by some authors,[1,2,7] Eq. (3) still holds. Due to the introduction of the density-of-states effective mass in Eq. (3), this equation remains valid regardless of the number of equivalent extrema associated with the heavy-hole band.

Adopting temperature-independent values for $\Delta$ of 0.30 eV,[8] and for the Kane matrix element $P$ of $7.0\times10^{-8}$ eV cm,[9] a computer fitting of the experimental $n(T)$ data yielded the following numerical results (in the temperature range from 100 to 400 K):

$$E_0 = 0.12 + 3.3\times10^{-4}T \text{ eV}; \quad E_t = -26 \text{ meV};$$
$$m_d^* = 0.50m_0.$$

The positive sign of $E_0$ is caused by the fact that in the secular equation we used for the $\alpha$-Sn structure,[4] $E_0$ represents the absolute energy separation between $\Gamma_6$ and $\Gamma_8$. Comparing the above numerical results with those given in Refs. 1 and 2, we have to distinguish between the bands originating from the third-order secular equation (light-electron, light-hole, and split-off valence band) and the heavy-hole band. The magnitude of the direct gap $E_0$ at $\Gamma$ as well as the sign and magnitude of its temperature coefficient are in good agreement with the values reported by Aubin *et al.* Since the values of $P$ and $\Delta$ are also nearly the same, we may conclude that positions and shapes of the light-electron band, light-hole, and split-off valence bands are well established now and that they exhibit the $\alpha$-Sn type ordering. Recent analysis by Bodnar[10] of Shubnikov–de Haas and de Haas–van Alphen effects in terms of a band model which takes into account the tetragonal field splitting, also give strong evidence for an $\alpha$-Sn like structure.

Considering the numerical data for the heavy-hole band, we conclude that remarkable differences with the work by Aubin *et al.* are found. Whereas these authors deduce from the few available optical data that there should exist a zero indirect gap or even a small overlap, our analysis of $n(T)$ gives a negative value of $E_t$. Secondly, our value of the effective mass is much higher than $0.12m_0$, the value obtained by Aubin *et al.* as well as by Haidemenakis *et al.*[11] from low-temperature magneto-optical experiments. Concerning our results it has to be remarked that in the fitting procedure $E_t$ and $m_d^*$ are highly correlated. This is illustrated in Fig. 2, which shows that the combination $m_d^*/m_0 = 0.50$, $E_t = -26$ meV is not the unique one leading to a good fit to the experimental results of Fig. 1. Smaller values of $m_d^*$ result in smaller—but strongly temperature dependent—values of $E_t$, and conversely. For instance, a value of $m_d^* = 0.12m_0$ requires $E_t$ to vary from about −10 meV at 100 K to an overlap of 30 meV at 300 K. On the other hand, regarding $E_t$ as fixed at zero gives

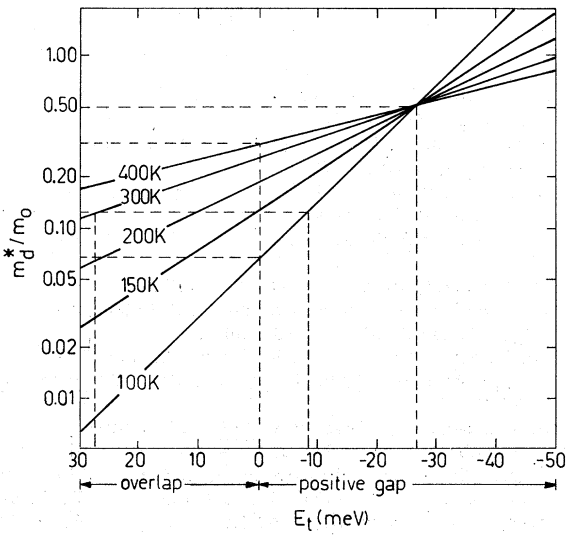


FIG. 2. Correlation between $m_d^*$ and $E_t$ for the same set of values for $E_0$, $P$, and $\Delta$ as in Fig. 1.

rise to an $m_d^*$ increasing from $0.07m_0$ at 100 K to $0.22m_0$ at 300 K. For the given values of $E_0$, $P$, and $\Delta$, the only set of temperature-independent values of $E_t$ and $m_d^*$, which gives a good fit to the experimental results over the whole temperature and concentration ranges, is the combination $E_t = -26$ meV and $m_d^* = 0.50m_0$. The fact that $E_t$ and $m_d^*$ may be expected to have only very small temperature coefficients, because they are influenced only by bands far away, makes this set of values the more reliable.

Aubin *et al.* proposed a complex heavy-hole band with off-axis maxima and a smoothing out towards $\Gamma$ with a residual gap $E_r$ (see Fig. 4 of Ref. 1). From the above given analysis of the experimental data it is not possible to decide whether $E_t$ is a direct or an indirect gap. Therefore we also tried to fit our data by assuming a quartic model for the heavy-hole band,[12] involving two sets of electrons and one set of holes. However, we could not obtain a definite answer, also because of the fact that interpretation in this model requires the introduction of some extra fitting parameters, such as the effective mass of the heavy electrons. Conclusive evidence for the Aubin model of the heavy-hole band should come from optical data on low-concentration samples. We started optical absorption measurements on very thin samples with electron concentrations of about $5\times10^{17}$ cm$^{-3}$. The absorption coefficient was calculated assuming direct transitions from a heavy-hole band described by a quartic model to the conduction band. This quartic model gives a much better agreement with the experimental optical data than a simple parabolic heavy-hole band at $\Gamma$. With $E_t = -26$ meV a value of $4\times10^6$ cm$^{-1}$ was found for the wave number corresponding to the heavy-hole band maximum. More extensive absorption measurements and calculations for geometrically more complex heavy-hole band forms are necessary.

Regarding the large difference between our value of $m_d^* = 0.50m_0$ and that of $0.12m_0$ from the literature[1,11] one has to realize that in our case we are dealing with the density-of-states effective mass. For a heavy-hole band exhibiting a number of equivalent extrema ($N_v$), the relation $m_d^{*3/2} = N_v m^{*3/2}$ should be applied. This leads to a value of $N_v$ of about 8, a result which is not unreasonable in view of the band-structure calculations by Lin-Chung.[7] Concerning our value of $m_d^*$ it has to be clearly stated that this type of curve fitting of transport coefficients versus temperature can result in a nonphysical value. Both Fermi surface and optical data are necessary before final conclusions about the phenomenological band structure may be drawn.

Finally we comment on the conclusion by Aubin *et al.* that, if the shape of the heavy-hole band does not depend on temperature, the overlap with the conduction band increases as the temperature is lowered. This is in disagreement with our results, as can be seen in Fig. 2. For a constant $m_d^*$ smaller than $0.50m_0$, $E_t$ always decreases ("overlap" decreases) with decreasing temperature. This also means that the absolute value of the residual $E_r$ should increase with lowering temperature, in contradiction to the suggestion in Ref. 2.

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[9]This value is obtained by reinterpreting previous results [F. A. P. Blom and J. Th. Schrama, Phys. Lett. A 30, 245 (1969)] without simplifying the secular equation. The introduction of a weak temperature dependence of $P$, which was reported in Ref. 1, has no significant effect on the confidence limits of the band parameters. The same conclusion has been drawn for HgSe by S. L. Lehoczky, J. G. Broerman, D. A. Nelson, and C. R. Whitsett, Phys. Rev. B 9, 1598 (1974).
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