INFLUENCE OF PRESSURE ON THE ELECTRICAL PROPERTIES OF Cd_3P_2

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(Received March 25, 1980; revised version received June 3, 1980)

For the first time the measurements of resistivity and the Hall coefficient as a function of pressure up to 1.2 GPa were performed for a number of as-grown and Cu-doped samples of Cd_3P_2. From the analysis of the data obtained for as-grown Cd_3P_2 the pressure coefficient of the energy gap was estimated as 45 meV/GPa, while the results obtained for the doped material have shown the existence of deep impurity levels with an activation energy also depending on pressure at the rate of 35 meV/GPa with respect to the conduction band edge.

PACS numbers: 72.20.-i, 71.25.Tn, 71.55.Dp, 71.30.+h

1. Introduction

Cd_3P_2 is one of members of $A_3^{II}B_2^{V}$ compounds having the tetragonal crystal structure. The method of preparation of this material and its semiconducting properties have been described first in [1, 2]. It was found that as-grown Cd_3P_2 is a degenerate n-type semiconductor with an energy gap of about 0.5 eV, electron concentrations in the range 10^{17}–10^{18} cm^{-3} and room temperature mobilities of 2000–3000 cm^2/Vs.

In recent years, considerable attention has been given to this semiconductor due to its attractive optical properties, in particular, the observation of laser emission [3].

The essential results concerning the band structure of Cd_3P_2 and its transport and optical properties have been reported in [4]. It was shown that almost all available experimental data can be interpreted within the Kane-type band structure model with an energy gap E_g of 0.575 eV, a matrix element P_{cv} of 6.9×10^{-8} eVcm and an electron effective mass at the conduction band edge m_0^* of 0.048 m_0.

Almost the same set of band parameters have been independently deduced from the last thermomagnetic and optical measurements of Cd_3P_2 [5, 6].

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This work was undertaken to examine the effect of high hydrostatic pressure on some transport properties of Cd_3P_2 as it was done earlier for other $A_3^{II}B_2^{V}$ compounds, i.e., for Cd_3As_2 [7] and for solid solutions of Cd_3As_2—Zn_3As_2 [8].

2. *Experimental*

Measurements were performed for several as-grown single crystals as well as for Cu-doped polycrystalline samples of Cd_3P_2. Doped crystals, with considerably lower free electron concentrations as compared to those in as-grown material, were obtained by the technique described in [6].

TABLE I

Sample	Electron concentration [cm^{-3}]	Electron mobility [cm^2/Vs]
1	3.7×10^{17}	1000
2	6.2×10^{17}	1100
3	5.8×10^{18}	2100
4	1.1×10^{19}	1800
5	2.7×10^{14}	300
6	7.0×10^{14}	340

The measurements of resistivity and the Hall coefficient as a function of pressure and temperature were carried out in a non-magnetic beryllium-copper chamber using high-purity gaseous hellium as a pressure transmitting medium.

The characteristics of the samples studied at normal pressure and at 300 K are shown in Table I.

3. *Results and discussion*

3.1. As-grown Cd_3P_2

The measured pressure dependences of resistivity ϱ and the Hall coefficient R_H for four as-grown single crystals of Cd_3P_2 are shown in Fig. 1. It can be seen that R_H for samples *2* and *3* is pressure independent indicating an extrinsic one-band mechanism of conductivity. Thus, a rise of ϱ with pressure observed for these samples is due only to a decrease of the electron mobility. A slightly higher change of ϱ observed for sample *1* with the lowest electron concentration is caused not only by a decrease of the mobility but also by a decrease in the electron concentration since R_H increases with pressure. On the other hand, the pressure dependences obtained for sample *4* with the highest electron concentration differ from those obtained for the others. Such a behaviour is, at present, unclear, and requires further studies.

Apart from sample *4*, the results obtained for other samples can be explained within the single Kane-type *s*-like conduction band model, which has been successfully applied

to Cd_3P_2 by others [4–6,9]. In particular, sample *3* is the most convenient for a more detailed analysis, since R_H in this sample is pressure independent and the electron concentration n is high enough to satisfy the strong degeneracy condition [9].

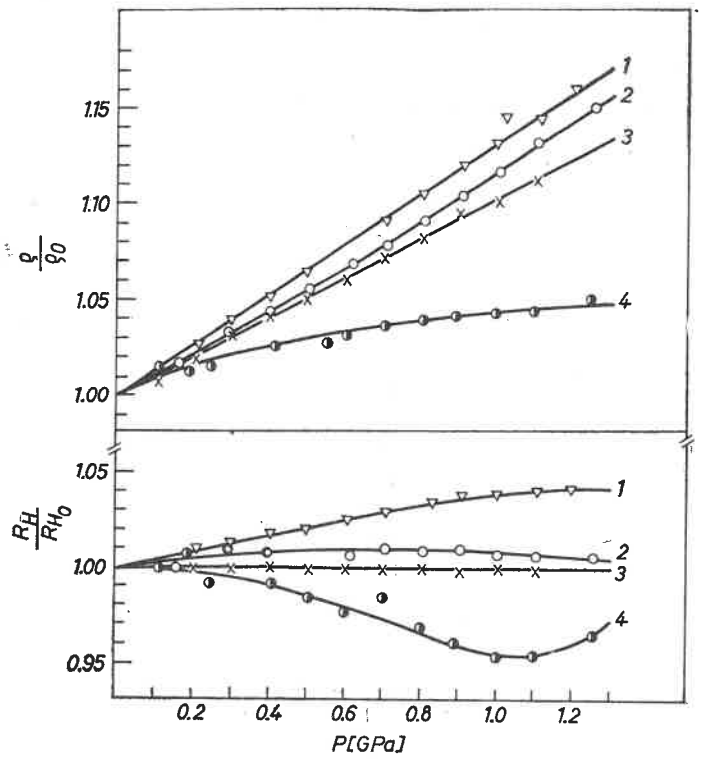

Fig. 1. Pressure dependence of resistivity and the Hall coefficient for as-grown samples of Cd_3P_2 at 300 K

It is known that for a degenerate semiconductor, ϱ can be expressed as [10]

$$\varrho = \sum_l \varrho_l = \sum_l \frac{1}{ne\bar{\mu}_l}, \tag{1}$$

where ϱ_l and $\bar{\mu}_l$ are a partial resistivity and an average mobility, respectively, associated with an l-th single scattering mechanism. The necessary expressions to calculate $\bar{\mu}_l$ have been derived by Zawadzki and co-workers [11] and have been used to describe the $\mu(n)$-dependence in Cd_3P_2 by Jay-Gerin et al. [4] and by Radautsan et al. [9]. It follows from these expressions that the pressure dependence of an l-th relative partial resistivity can be written in the following form, assuming all other parameters appearing in the formulas as pressure independent

$$\frac{\varrho_l(P)}{\varrho_l(0)} = \left[\frac{m^*(P)}{m^*(0)}\right]^2 \frac{F_l(P)}{F_l(0)}, \tag{2}$$

where m^* is the electron effective mass at the Fermi level and F_1 are rather complicated functions defined in the above references.

Calculations of relative partial resistivities according to Eq. (2) have been done under the following assumptions: (*i*) — spin-orbit splitting $\Delta \ll E_g(\Delta \sim 0.1$ eV [6]); (*ii*) — linear dependence of the energy gap on pressure: $E_g(P) = E_g(0)+\gamma P$ (where γ is a pressure coefficient); (*iii*) — electron effective mass at the bottom of the conduction band is proportional

TABLE II

Pressure [GPa]	$\frac{\varrho}{\varrho_0}$ (exper.)	γ [meV/GPa]	$\frac{\varrho_{ion}}{\varrho_{ion\,0}}$	$\frac{\varrho_{op}}{\varrho_{op\,0}}$	$\frac{\varrho_{ac}}{\varrho_{ac\,0}}$
0.5	1.051	40	1.030	1.046	1.070
		45	1.034	1.051	1.079
		50	1.037	1.057	1.087
1.0	1.102	40	1.061	1.093	1.143
		45	1.068	1.105	1.161
		50	1.076	1.116	1.180

to E_g: $m_0^*(P) = m_0^*(0)E_g(P)/E_g(0)$. According to Gelten et al. [6], the values of band parameters at 300 K and at normal pressure $E_g(0)$ and $m_0^*(0)$ have been taken as 0.53 eV and $0.045\,m_0$, respectively.

The relative partial resistivities associated with scattering on ionised impurities $\varrho_{ion}/\varrho_{ion\,0}$, optical phonons $\varrho_{op}/\varrho_{op\,0}$ and acoustical phonons $\varrho_{ac}/\varrho_{ac\,0}$, computed for several values of pressure coefficient γ and for $n = 5.8\times10^{18}$ cm^{-3}, are presented in Table II together with the experimental values of the relative total resistivity ϱ/ϱ_0 obtained for sample *3*.

It can be seen that the partial resistivities are almost linear with pressure and the pressure dependence is the smallest for $\varrho_{ion}/\varrho_{ion\,0}$ and the largest for $\varrho_{ac}/\varrho_{ac\,0}$. Thus, the value of the relative total resistivity ϱ/ϱ_0 should be somewhere between the $\varrho_{ion}/\varrho_{ion\,0}$ and $\varrho_{ac}/\varrho_{ac\,0}$. On the other hand, according to conclusions drawn in [5, 9], scattering on optical phonons is, at 300 K, dominant in Cd_3P_2 in the whole investigated range of electron concentrations. For these reasons, one can deduce, by comparing the calculated values with those obtained from experiment, that the energy gap in Cd_3P_2 increases with pressure at the rate γ of about 45 meV/GPa.

3.2. Cu-doped Cd_3P_2

The results of measurements of ϱ and R_H as a function of temperature and pressure are shown in Figs. 2 and 3. At normal pressure, similar temperature dependences have been obtained for the first time in [1] (ϱ vs $1/T$) and, quite recently, in [13] (ϱ and R_H vs $1/T$).

It can be seen from Fig. 2 that the logarithmic plots of ϱ and R_H vs $1/T$ change at normal pressure their slope as one passes from lower to higher temperatures, becoming straight lines in the range of 290–370 K at both normal pressure and $P = 1$ GPa. The

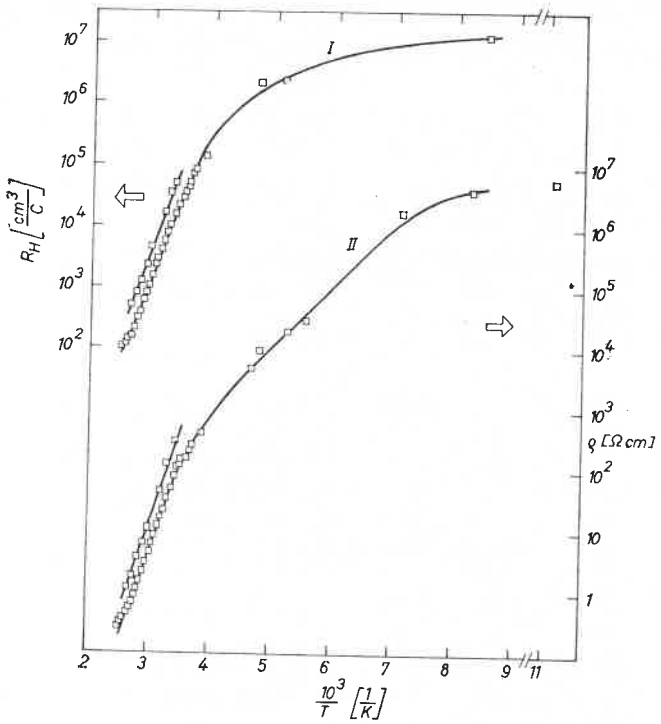

Fig. 2. Temperature dependence of resistivity and the Hall coefficient for Cu-doped sample 5 at normal pressure (I) and at 1 GPa (II)

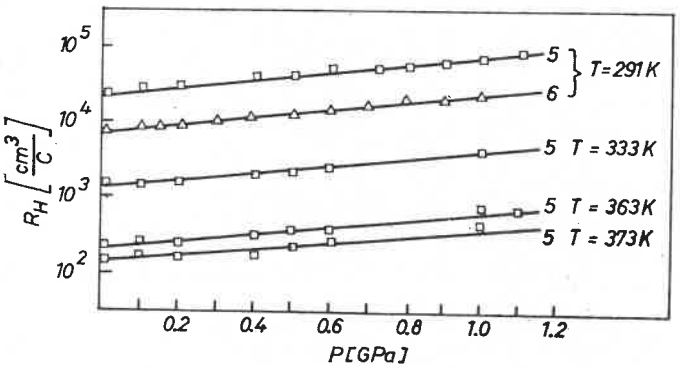

Fig. 3. Pressure dependence of the Hall coefficient for Cu-doped samples of Cd_3P_2 at different temperatures

linear parts of the curves allows us to determine an activation energy ΔE from the formula

$$\frac{1}{R_H e} \simeq n \sim \exp(-\Delta E/k_0 T). \tag{3}$$

Applying Eq. (3), one finds from Fig. 2 that ΔE is about 0.5 eV at normal pressure and slightly larger at $P = 1$ GPa.

The value of ΔE obtained cannot be attributed to a thermal activation energy of intrinsic conductivity, ΔE_0, since, in such a case, it should be doubled and give $e\Delta E_0 \simeq 1$ eV, while the real gap of Cd_3P_2 is 0.6 eV at low temperatures [14]. This means that ΔE can be associated with an excitation of electrons from deep Cu-levels (0.5 eV below the conduction band edge) to the conduction band. Such an interpretation is in very good agreement with the conclusion resulting from the analysis of photoconductivity measurements of Cu-doped Cd_3P_2 [15].

In order to check this supposition, one can use the electrical neutrality equation of a crystal assuming one donor and one acceptor level (a similar way has been used in [14]). In such a case, one can write that [16]

$$n+N_a+n_d = p+N_d+n_a \tag{4}$$

where N_a, N_d, n_a and n_d denote concentrations of acceptors, donors, unionised acceptors and unionised donors, respectively. In the temperature range investigated (290–370 K) the donors are completely ionised, thus $n_d = 0$; on the other hand, n and n_a can be written in the form [16]

$$n = N_c \exp(E_F/k_0T), \tag{5}$$

$$n_a = N_a/[1+0.5 \exp(E_F-E_a+E_g)/k_0T], \tag{6}$$

where N_c is the effective density of states in the conduction band, E_F is the Fermi level and E_a is the ionisation energy of acceptors. Using Eqs (4)–(6), one can write that

$$N_d-(n-p) = \frac{N_a n \exp[(E_g-E_a)/k_0T]}{2N_c+n \exp[(E_g-E_a)/k_0T]}. \tag{7}$$

In general, the above expression to calculate n is quite complicated, but making the reasonable simplification that $N_d \gg n-p$, one obtains

$$n \simeq \frac{2N_d}{N_a-N_d} N_c \exp[-(E_g-E_a)/k_0T]. \tag{8}$$

From comparison of this expression with Eq. (3) it follows that $\Delta E = E_g-E_a$. This means that ΔE is really associated with Cu-levels which act as traps for electrons at low temperatures, becoming a source of free carriers at higher temperatures.

The dependence of ΔE on pressure can be determined from the data shown in Fig. 3 based on Eq. (8) with

$$\Delta E(P) = \Delta E(0)+\gamma_i P \tag{9}$$

and taking into account the pressure dependence of the effective density of states N_c. The latter can be done as follows

$$N_c(P) \sim [m_0^*(P)]^{3/2} \sim [E_g(P)]^{3/2} = [E_g(0)]^{3/2}\left[1+\frac{\gamma P}{E(0)}\right]^{3/2}$$

$$\approx [E_g(0)]^{3/2} \exp\left[\frac{3\gamma P}{2E_g(0)}\right]. \tag{10}$$

The above approximation is quite good in the case of Cd_3P_2 since, for example, for $P = 1$ GPa, $\gamma = 45$ meV/GPa and $E_g(0) = 0.53$ eV, the last two terms of Eq. (10) differ by not more than 0.6%.

Using Eqs. (3), (8)–(10), finally, one obtains

$$R_H(P) = A \exp\left[\frac{\gamma_i}{k_0 T} - \frac{3\gamma}{2E_g(0)}\right] P, \tag{11}$$

where A depends on temperature and involves the normal pressure band parameters $E_g(0)$ and $m_0^*(0)$.

Using the values $E_g(0) = 0.53$ eV and $\gamma = 45$ meV/GPa in Eq. (11), one derives from the plots in Fig. 3 the values for the pressure coefficient γ_i equal to 35, 38, 39 and 38 meV/GPa at 291, 333, 363 and 373 K, respectively. The difference between the room temperature values of γ_i and those obtained at higher temperatures is probably due to larger experimental errors and fewer experimental points above $P = 0.6$ GPa in the range of 333–373 K. Thus, the room temperature value of $\gamma_i = 35$ meV/GPa, identical for both Cu-doped samples, is thought to be more credible than the others.

A comparison of this value with that found for the pressure coefficient of the energy gap ($\gamma \simeq 45$ meV/GPa) suggests that the Cu-levels in Cd_3P_2 move under the influence of pressure not only with respect to the conduction band but also with respect to the valence band. Verification of this supposition requires a more precise determination of both pressure coefficients, especially that of the energy gap.

4. Conclusions

When comparing the pressure coefficient of the energy gap obtained here for Cd_3P_2 ($\gamma \simeq +45$ meV/GPa) with that found for Cd_3As_2 ($\gamma = -57 \pm 10$ meV/GPa) [7] it follows that, according to the empirical rule [17], the symmetry of the conduction band in Cd_3P_2 is the same as the symmetry of the valence band in Cd_3As_2 and vice versa. Thus, Cd_3P_2 can be treated as an example of a tetragonal semiconductor with a small energy gap having the simple band structure (i.e., an s-like conduction band), while Cd_3As_2 can be an example of a tetragonal narrow-gap semiconductor with the inverted band structure (i.e., with a p-like conduction band) as was derived by Bodnar [18]. In order to recognize better the band structure of both compounds, in particular, the minima of their conduction bands, further studies are needed, especially on undoped good-quality single crystals with low free electron concentrations.

The authors are very indebted to Professor W. Żdanowicz for his continuous interest in this work and fruitful discussions.

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