

SEMICONDUCTING PROPERTIES OF Zn_3P_2 — Cd_3As_2 SOLID SOLUTIONS

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It is shown that semiconducting compounds Cd_3As_2 and Zn_3P_2 (both of identical crystal structure) form continuous series of pseudobinary four-components solid solutions over the whole range of compositions. The results were examined by X-ray analysis and dilatometric measurements. The Hall coefficient and resistivity were measured between 300° and 800°K. The samples are found to be semiconducting, of *n*-type when less than 50% mole of Zn_3P_2 were present in their compositions. At higher concentrations of Zn_3P_2 the samples were always *p*-type.

1. Introduction

As was reported earlier, cadmium arsenide — Cd_3As_2 , which belongs to the isomorphic of $A_3^II B_2^V$ intermetallic semiconducting compounds forms complete solid solutions with Zn_3As_2 [1, 2] and Cd_3P_2 [3]. In this paper some results of our investigations on pseudobinary four-components solid solutions of Zn_3P_2 — Cd_3As_2 are presented.

The semiconducting properties of Cd_3As_2 have been investigated quite well. This compound is always an *n*-type semiconductor with the concentration of degenerated electrons never less than $n = (1.6-2) \times 10^{18} \text{ cm}^{-3}$ with the mobility of electrons at room temperature $\mu_H = 1 \times 10^4 = 1.5 \times 10^4 \text{ cm}^2/\text{V s}$, $\sigma = 10^4 (\Omega \cdot \text{cm})^{-1}$, and $m_n^* = 0.05 m_0$ [4, 5]. There are considerable differences between the widths of the forbidden band reported by various authors ($\Delta E = 0.14-0.6 \text{ eV}$) [4, 5, 6, 7].

Zn_3P_2 is always a *p*-type semiconductor, with low conductivity $\sigma = 10^{-5} (\Omega \cdot \text{cm})^{-1}$ at 300°K, with $\Delta E = 1.15 \text{ eV}$ and very low mobility of holes [8, 9]. In view of identical crystal structures and very different electrical and thermal properties of both these compounds some interesting properties can be expected from this system.

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2. Preparation of the sample

Various alloys of the system $Zn_3P_2 - Cd_3As_2$ were prepared directly from highly purified compounds Zn_3P_2 and Cd_3As_2 in fused quartz ampoules. The compounds synthesized from pure elements (99.999% pure) were additively purified by sublimation in vacuum. The compounds put into ampoules in required quantity were melted, then slowly cooled slightly below their melting point and then annealed at this temperature during some days or even weeks. The inside surface of the ampoules were carbon-coated by pyrolysis of benzene.

3. X-ray analysis and dilatometric measurements

In order to carry out X-ray analysis, the samples were pulverized and mixed with about 20 per cent NaCl ($a = 5.6392 \text{ \AA}$) internal standard. The X-ray diagrams were obtained with a Guinier focussing camera and CuK_α ($\lambda = 1.54051 \text{ \AA}$) radiation, or with the DRON-1 diffractometer.

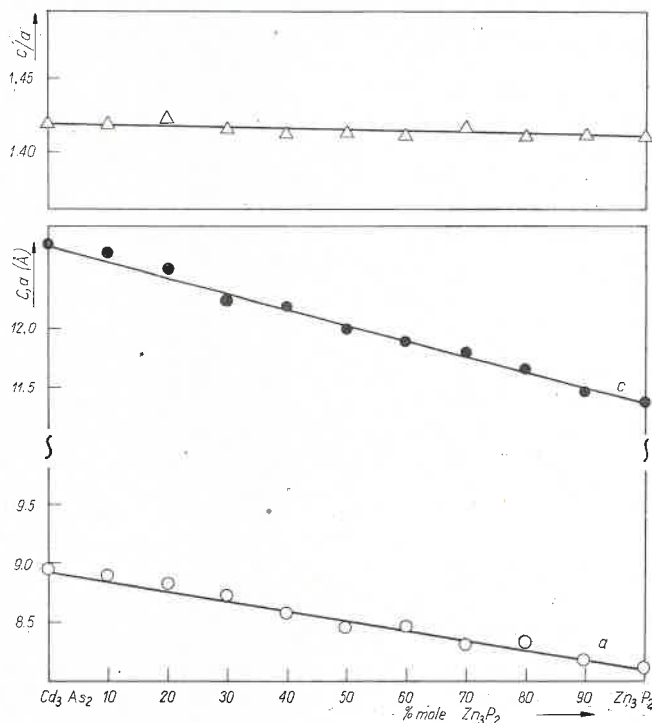


Fig. 1. Lattice constants of the system $Zn_3P_2 - Cd_3As_2$ as versus concentration

The lattice constants were calculated by means of the least squares method with an accuracy of 0.02 per cent. The calculations were performed on the Elliot 803 digital computer.

The reflection lines were always sharp and no doubling was observed for the investigated compositions. The lattice constants of Cd_3As_2 assumed in the present calculations

are $a = 8.963 \text{ \AA}$ and $c = 12.68 \text{ \AA}$ and for Zn_3P_2 $a = 8.097 \text{ \AA}$ and $c = 11.45 \text{ \AA}$ according to Ref. [10].

Fig. 1 represents the variation of the tetragonal lattice constant in the Cd_3As_2 lattice by the addition of Zn_3P_2 . It can be seen that the lattice constants vary almost in accordance with Vegard's law.

An additional data about $\text{Zn}_3\text{P}_2 - \text{Cd}_3\text{As}_2$ system was received by the supplied dilatometric method. Thermal expansion was measured by the use of a Leitz-Wetzlar optical

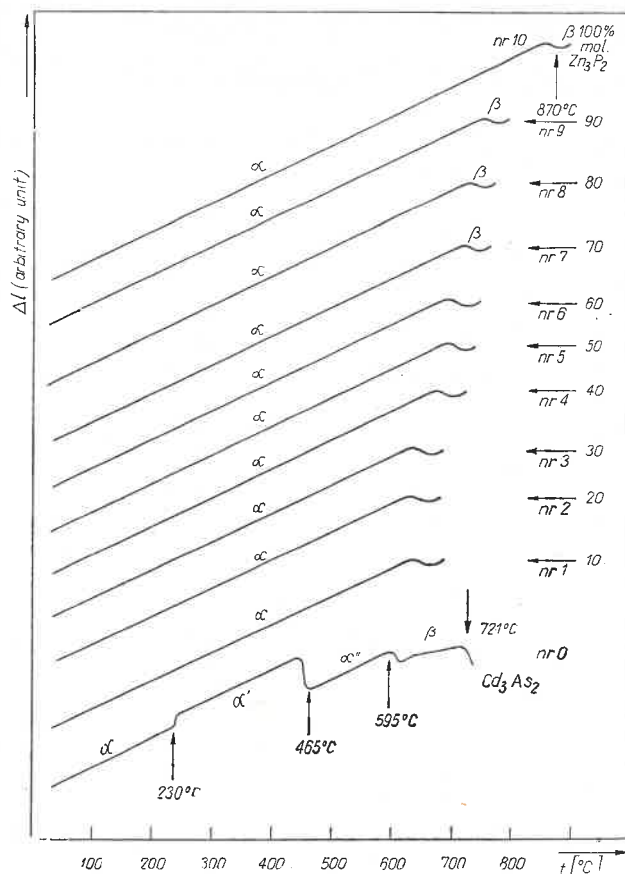


Fig. 2. Dilatometric curves for Zn_3P_2 , Cd_3As_2 and their solid solutions

dilatometer. Cylindrical samples 4.5 mm long were obtained by cooling of the melt in a graphite tube sealed in a quartz tube filled with argon. Dilatation Δl was measured with respect to chronine. The temperature was determined by a Pt-PtPd thermocouple. Dilatometric measurements of the $\text{Zn}_3\text{P}_2 - \text{Cd}_3\text{As}_2$ alloys were carried out for 9 different compositions with the molar contents of Zn_3P_2 increased in 10 per cent stops. The results of measurements are given in Fig. 2. In all ranges of temperature (20–100°C) and concentra-

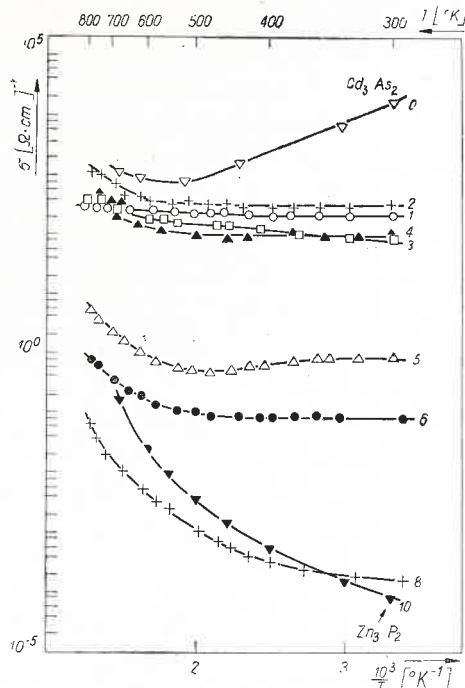


Fig. 3. Temperature dependence of the conductivity samples 0 — Cd_3As_2 , 1 — 10% mole Zn_3P_2 — 90% mole Cd_3As_2 , 2 — 20% mole Zn_3P_2 — 80% mole Cd_3As_2 , 3 — 30% mole Zn_3P_2 — 70% mole Cd_3As_2 , 4 — 40% mole Zn_3P_2 — 60% mole Cd_3As_2 , 5 — 50% mole Zn_3P_2 — 50% mole Cd_3As_2 , 6 — 60% mole Zn_3P_2 — 40% mole Cd_3As_2 , 7 — 70% mole Zn_3P_2 — 30% mole Cd_3As_2 , 8 — 80% mole Zn_3P_2 — 20% mole Cd_3As_2 , 9 — 90% mole Zn_3P_2 — 10% mole Cd_3As_2 , 10 — Zn_3P_2

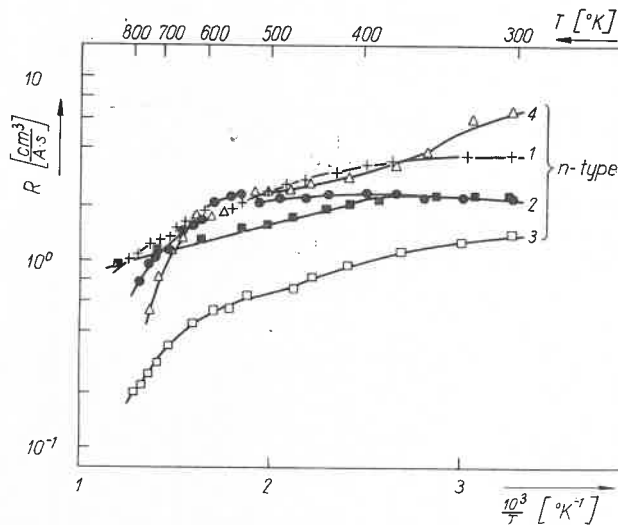


Fig. 4. Dependence of the Hall coefficient on $\frac{1000}{T}$ for *n*-type Zn_3P_2 — Cd_3As_2 samples

tions of the investigated solid solutions only one high temperature reversible phase transitions $\alpha \rightarrow \beta(\alpha''/\beta - \text{Cd}_3\text{As}_2 - 595^\circ\text{C}$, $\alpha/\beta - \text{Zn}_3\text{P}_2 - 880^\circ\text{C}$) [2,11] is observed.

Therefore, from the above measurements it may be concluded that the pseudobinary four-component system $\text{Zn}_3\text{P}_2 - \text{Cd}_3\text{As}_2$ consists of a continuum of solid solutions.

4. Electrical measurements

The resistivity and the Hall coefficient of individual samples, polished to the size of $1.5 \times 4 \times 12 \text{ mm}^3$ were made by taking the voltage-drop by means of a d. c. potentiometer. The electrodes were soldered to the samples with tin.

Fig. 3 shows the temperature dependence of the conductivity of some *n*-type [1-4]

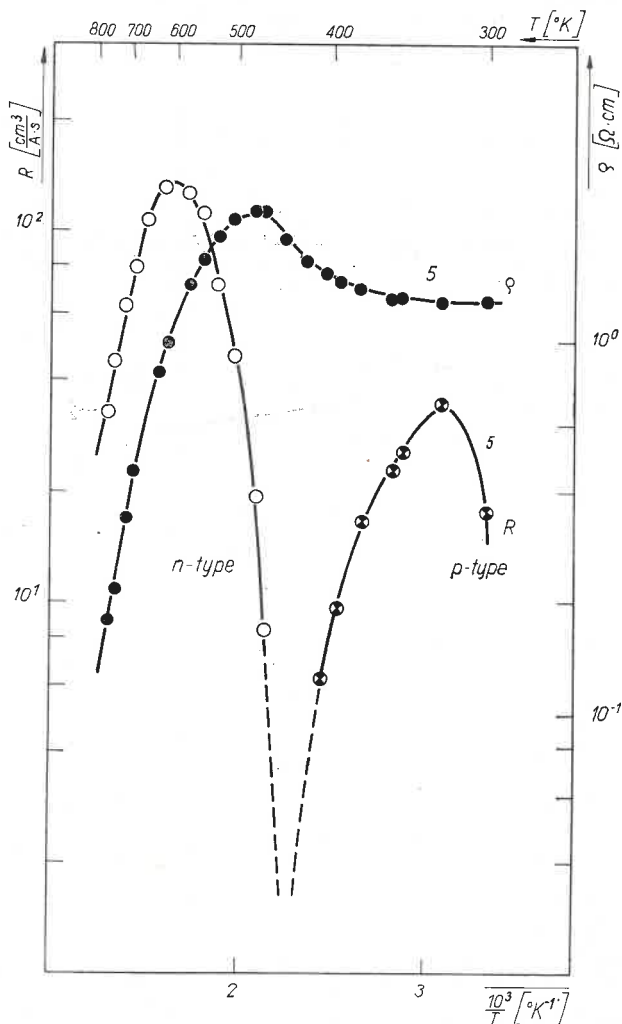


Fig. 5. Temperature dependence of the Hall coefficient and resistivity for No 5 *p*-type sample ($\text{Zn}_{1.5}\text{Cd}_{1.5}\text{AsP}$)

and *p*-type [5, 6, 8] samples between 300 and 800°K. The conductivity of the investigated samples at $T = 300^\circ\text{K}$ varies from about $4000 (\Omega \cdot \text{cm})^{-1}$ for Cd_3As_2 to about $10^{-4} (\Omega \cdot \text{cm})^{-1}$ for Zn_3P_2 [4]. Fig. 4 shows the results of the temperature measurements of the Hall coefficients R_H for *n*-type samples.

The concentration of the current carriers $N_D - N_A$ calculated from the formula $n = N_D - N_A = -1/eR$ at $T = 300^\circ\text{K}$, varied for all *n*-type samples very slightly, with the addition of Zn_3P_2 to Cd_3As_2 , and did not differ distinctly from the *n*-concentration in Cd_3As_2 .

Because of a lack of stability and reproducibility it was impossible to measure the temperature dependence of the very small Hall coefficient for samples [6, 7, 8, 9] and [10].

Fig. 5 represents the results of Hall and resistivity temperature measurements obtained for *p*-type sample No 5. The inversion point lies at about 430°K . From the relation $\frac{R_{\max}}{R_s} = \frac{b^2}{4(b-1)}$ where R_{\max} — the maximum value of the Hall coefficient, R_s — Hall coefficient in the extrinsic region, it was found that for the sample No 5 $b = \mu_n/\mu_p = 19$.

Fig. 6 shows the temperature dependence of the Hall mobility $\mu_H = R \cdot \sigma$ the investi-

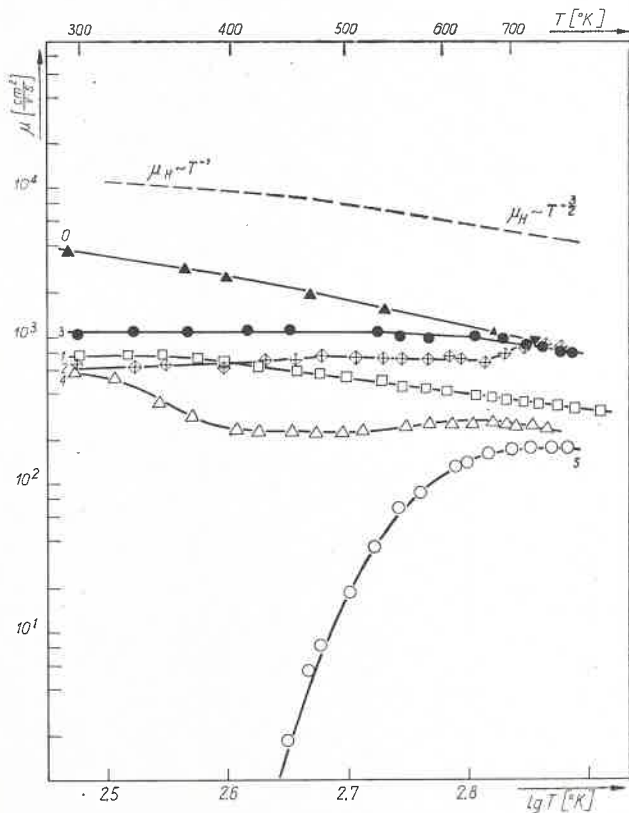


Fig. 6. Temperature dependence of the Hall mobility of electrons and holes in Zn_3P_2 - Cd_3As_2 samples

gated samples of *n*-type. For Cd_3As_2 and for sample No 1 (*n*-type) above room temperature, the mobility is determined by scattering on lattice vibrations ($\mu_H \sim T^{-3/2}$).

For samples with higher concentration of Zn_3P_2 [2, 3, 4] the mobility is almost constant, which shows that electrons are scattered mainly by ionized impurities.

The width of the forbidden bands (ΔE_0) of the investigated solid solutions have been calculated from the temperature dependence of R_H and σ in the intrinsic range. Fig. 7

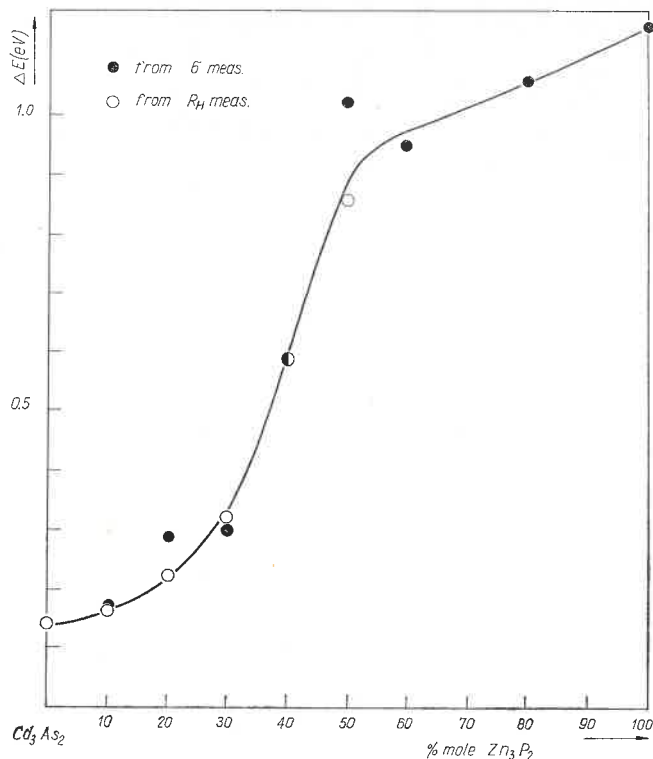


Fig. 7. Dependence of the forbidden bands ΔE_0 in Zn_3P_2 - Cd_3As_2 samples on the concentration of Zn_3P_2

represents values of ΔE_0 for *n*- and *p*-type Zn_3P_2 - Cd_3As_2 samples deduced by means of the relations

$$\Delta E_{0H} = 0.397 \cdot \frac{\Delta \log (RT^{3/2})}{\Delta \left(\frac{1000}{T} \right)}$$

$$\Delta E_{0\sigma} = 0.397 \cdot \frac{\log \sigma}{\Delta \left(\frac{1000}{T} \right)}$$

For the *n*-type samples the ΔE_0 values are in good agreement with ΔE_{0H} values. For *p*-type samples (more than 50% Zn_3P_2) it was possible to calculate ΔE_0 only from σ measurements.

REFERENCES

- [1] L. Żdanowicz, W. Żdanowicz, *Phys. Status Solidi*, **6**, 227 (1964).
- [2] W. Żdanowicz, K. Łukaszewicz, W. Trzebiatowski, *Bull. Acad. Polon. Sci., Sér. Sci. Chim.*, **12**, 169 (1964).
- [3] K. Masumoto, S. Isomura, *Transactions of National Research Institute for Metals*, **9**, 287 (1967).
- [4] W. Żdanowicz, *Proc. Intern. Conf. Semicond. Phys.*, Prague 1960, p. 1095.
- [5] W. J. Turner, A. S. Fischer, W. E. Réese, *Phys. Rev.*, **121**, 759 (1961).
- [6] L. Żdanowicz, *Acta Phys. Polon.*, **31**, 1021 (1967); *Phys. Status Solidi*, **20**, 473 (1967).
- [7] G. J. Goncharenko, V. Shevchenko, *Phys. Status Solidi*, **41**, K. 117 (1970).
- [8] W. Żdanowicz, Z. Henkie, *Bull. Acad. Polon. Sci., Sér. Sci. Chim.*, **12**, 729 (1964).
- [9] J. Lagrenaudie, *J. Phys. Radium*, **16**, 234 (1955).
- [10] M. V. Stackelberg, P. Paulus, *Z. physik. Chem.*, **28 B**, 427 (1935).
- [11] J. Berak, Z. Pruchnik, *Roczniki Chemii*, **43**, 1141 (1969), (in Polish).