ELECTRICAL PROPERTIES OF ZnGeP2 AND CdGeP2

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Résumé. — On a mesuré les propriétés électriques de cristaux de $ZnGeP_2$ et $CdGeP_2$, obtenus à partir d'une solution de plomb. $ZnGeP_2$ est de type p, il a une résistivité de $2{,}3 \times 10^3$ Ω.cm à température ambiante et une énergie d'activation (compensée) de l'accepteur de 0,21 eV. La mobilité de Hall est d'environ 10 $cm^2/V \cdot s$ et varie avec la température comme $T^{1.22}$. $CdGeP_2$ qui présente une transition de type p au type n à 284 K, a une résistivité de 10^6 Ω.cm et une énergie d'activation (compensée) de 0,2 eV. Les résultats ne sont pas typiques de ce qu'on peut attendre pour des propriétés de volume.

Abstract. — The electrical properties of $ZnGeP_2$ and $CdGeP_2$ crystals grown from lead solution were measured. $ZnGeP_2$ is p-type with a room temperature resistivity of 2.3×10^3 Ω-cm, and an acceptor activation energy (compensated) of 0.21 eV. Hall mobilities are about 10 $cm^2\ V^{-1}\ s^{-1}$ with a temperature dependence of $\mu \propto T^{1.22}$ $CdGeP_2$ shows a p-type to n-type transition at 284 K with a resistivity of 10^6 Ω-cm and an acceptor activation energy (compensated) of 0.20 eV. The results are not typical of the expected bulk properties.

1. **Introduction.** — $ZnGeP_2$ and $CdGeP_2$ are II-IV-V_2 compounds with relatively large band gaps. $ZnGeP_2$ is thought to be pseudo-direct or indirect with a room temperature band gap of ~ 2.0 eV, and $CdGeP_2$ is direct gap with a band gap of 1.7 eV. This paper describes the electrical properties of single crystals of these compounds grown from solution in molten lead. The results for $ZnGeP_2$ are in broad agreement with those obtained on crystals from different growth methods. $CdGeP_2$ crystals show a p-to n-type transition at 284 K ; analysis of results from this transition show that the behaviour is inconsistent with that to be expected from the bulk properties of this material.

2. **Crystal growth and sample preparation.** — Lead was chosen as the solvent, because no binary compounds have been found with Zn, Cd, Ge or P. The growth method employed the accelerated crucible rotation technique [1].

Stoichiometric amounts of the constituent elements were contained under vacuum in a silica ampoule 15 cm long and 2 cm diameter with enough lead to make a 20 mol % solution. The total charge was about 100 g. All materials were at least 5 N pure.

The ampoule was heated in a horizontal rocking furnace, with a temperature rise of 60 °C per hour to just below the melting point of the compound ($ZnGeP_2$ ~ 1 300 K, $CdGeP_2$ ~ 1 073 K). The furnace was rocked for a further two hours at this temperature before bringing to the vertical position to equilibrate. The best crystals were obtained with a 1.5 °C per hour cooling rate with a stirring rate of 4 cycles per minute and a 270° rotation on each cycle. The crystals nucleated from the walls of the ampoule, producing a mass of crystals from which platelets of up to $8 \times 6 \times 0.5$ mm^3 could be separated. Laue back reflection techniques showed that the largest faces were (112) with general growth direction along [111].

3. **Electrical measurements.** — Hall effect and electrical conductivity in the samples were measured by the Van der Pauw technique [2]. Crystals were ground with 6 μm and 1 μm diamond pastes to form plane parallel plates $5 \times 5 \times 0.2$ mm^3. The surfaces were cleaned by a 30 second etch in 5 concentrated HNO_3 : 5 concentrated HCl : 1 HF. Tin contacts were applied, and ohmic contacts were formed by a 200 V pulse between the contacts and the reverse face of the crystal. In the case of $CdGeP_2$ the sample was heated to 420 K to lower the bulk resistance during the forming process.

The results for $ZnGeP_2$ are shown in figure 1. The material was p-type with a room temperature carrier concentration of 2.4×10^{14} cm^{-3} and a resistivity of 2.3×10^3 Ω-cm. Assuming heavy compensation of the acceptors, because of the low carrier concentrations, the plot of $R_H\ T^{3/2}$ against carrier concentration gives an acceptor activation energy of ~ 0.21 eV.

Hall mobilities were of the order of 10 $cm^2\ V^{-1}\ s^{-1}$ and showed a temperature dependence $\mu \propto T^{1.22}$. Ionised flows give a $T^{1.5}$ dependence, and neutral centres give a mobility independent of temperature. Hence the mobility variation is consistent with a partially compensated system.

These results can be compared with previous work. Isomura and Masumoto [3] obtained melt grown crystals with resistivities of 10^6-10^7 Ω-cm with activa-

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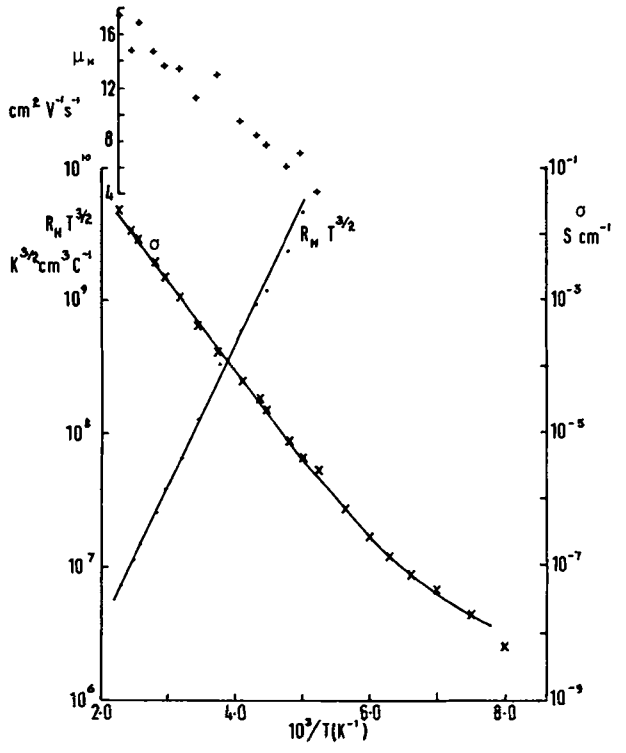

FIG. 1. — Temperature dependence of electrical properties of $ZnGeP_2$.

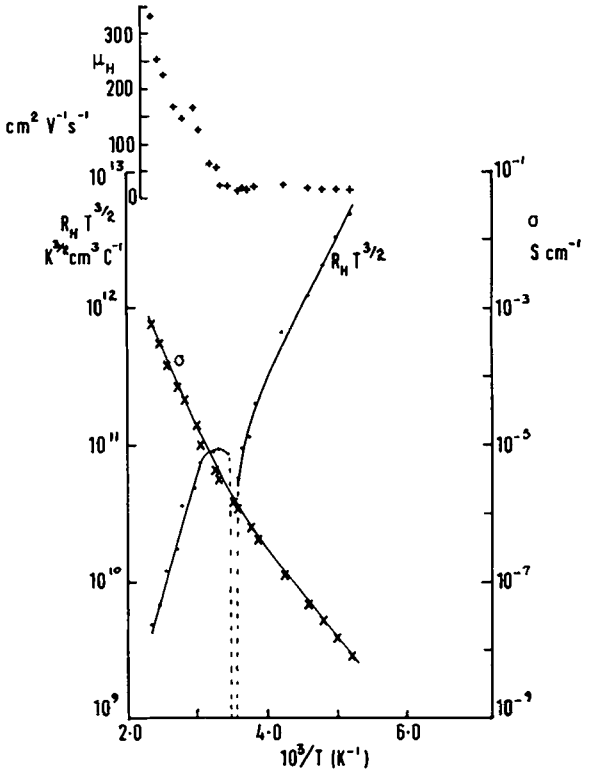

FIG. 2. — Temperature dependence of electrical properties of $CdGeP_2$.

tion energies of 0.55 eV. The Pb-Bi solution grown crystals of Somogyi and Bertoti [4, 5, 6] had resistivities of 10^4 Ω-cm and a compensated acceptor activation energy of 0.35 eV. Results quoted by Somogyi [7] on Bi solution grown crystals showed a Hall effect sign reversal for one sample. This will be considered in the final section.

The results for the $CdGeP_2$ sample show a p-to n-type transition at 284 K (Fig. 2). At low temperatures, the material is p-type and the compensated approximation yields an acceptor activation energy of 0.20 eV. However, the change of sign at 284 K means that the analysis for this activation energy cannot be carried to higher temperatures. The change of sign in the Hall coefficient is often observed in III-V compounds and marks the change from extrinsic to mixed conduction in materials where the electron mobility is significantly higher than the hole mobility. A typical case for GaSb is discussed by Leifer and Dunlap [8].

Analysis of results at the transition temperature can yield useful information regarding carrier mobilities and concentration. For mixed conduction, assuming a scattering constant of unity,

$$R_H = \frac{1}{e} \frac{(n\mu_n^2 - p\mu_p^2)}{(n\mu_n + p\mu_p)^2} \qquad (1)$$

so at the transition temperature where $R_H = 0$,

$$n\mu_n^2 = p\mu_p^2 . \qquad (2)$$

By extrapolating values of p and μ_p from low temperatures, and using the measured value of the conductivity at the transition temperature,

$$\sigma = e(n\mu_n + p\mu_p) \qquad (3)$$

values of n and μ_n can be obtained from (2) and (3).

The method is very sensitive to the accuracy of the extrapolation. For example, a simple extrapolation based on figure 2 leads to transition temperature values of $p = 2.63 \times 10^{11}$ cm^{-3} and $\mu_p = 18$ cm^2 V^{-1} s^{-1}, yielding $n = 4.78 \times 10^{10}$ cm^{-3} and $\mu_n = 42$ cm^2 V^{-1} s^{-1}. A more detailed study of the extrapolation (Fig. 3) indicates that $\mu_p = 30$ cm^2 V^{-1} s^{-1} might be more appro-

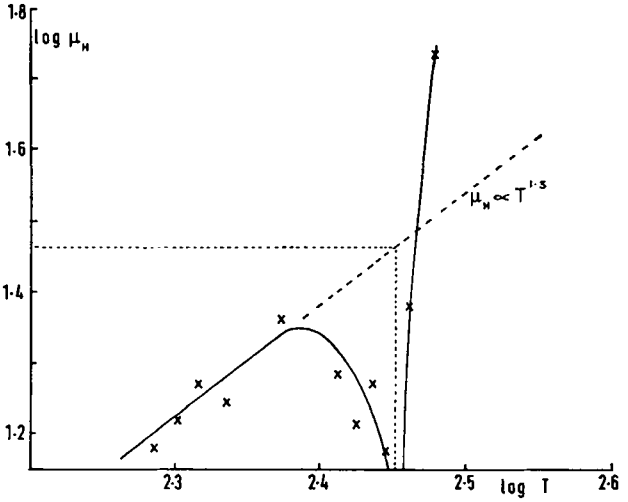

FIG. 3. — Hall mobilities in $CdGeP_2$.

priate, which leads to the values $n = 6 \times 10^7\ cm^{-3}$ and $\mu_n = 1\ 600\ cm^2\ V^{-1}\ s^{-1}$. The mobility values in the latter example are typical of those quoted for $CdGeP_2$ by Borchevskii *et al.* [9].

An order of magnitude check on the significance of these values may be made, by utilising another feature of the semiconductor properties at the transition temperature, which is that the measured conductivity is given by

$$\sigma = n_i\, e(\mu_n + \mu_p)$$

where n_i is the theoretical intrinsic concentration in pure material at the same temperature. If one assumes an arbitrary figure of $1\ 000\ cm^2\ V^{-1}\ s^{-1}$ for $(\mu_n + \mu_p)$ this gives $n_i \cong 7 \times 10^9\ cm^{-3}$.

A large anomaly exists between this value and the value for n_i calculated using the density of states effective masses [10, 11] $m_e^*/m = 0.085$ and $m_h^*/m = 0.56$, which together with an energy gap of 1.72 eV yields a value of $n_i \cong 1.7 \times 10^3\ cm^{-3}$ at 284 K. Thus it must be assumed that the p-n transition observed in $CdGeP_2$ is not typical of the bulk material, and is possibly due to higher conductivity surface states or some lack of homogeneity in the bulk material.

These results must cast some doubt upon other measurements made on high band gap II-IV-V_2 compounds, because it is a knowledge of the p-n transition that enables the order of magnitude check to be made. This transition has been observed in other materials, and table I shows order of magnitude calculations upon the results quoted for these materials. A comparison between the calculated and experimental values for n_i has been made, using the density of states effective masses quoted by Shay and Wernick [11] and assuming arbitrary mobility values of

$$(\mu_n + \mu_p) = 1\ 000\ cm^2\ V^{-1}\ s^{-1}\ .$$

The discrepancies are very large for $ZnGeP_2$ and $CdGeP_2$, but agreement is good for the lower band gap materials $CdGeAs_2$, $ZnSnAs_2$ and $CdSnAs_2$, when one considers the very arbitrary values of $(\mu_p + \mu_n)$ in the calculations.

It would appear that surface states or inhomogeneities in the high band gap materials are capable of shunting the normal bulk properties of the crystals. It has occurred with two materials grown by solution growth from molten metals, and a detailed study of these effects could be valuable for an understanding of the true bulk properties of these materials.

TABLE I

Order of magnitude calculations for intrinsic carrier concentrations at hall effect transition temperatures

Compound	Transition Temperature K	σ (Scm^{-1})	Energy gap at transition temperature (eV)	Density of states effective masses		$\mu_n + \mu_p$ (assumed value) $cm^2\ V^{-1}\ s^{-1}$	n_i (from σ) cm^{-3}	n_i (calculated) cm^{-3}	References
				$\frac{m_e^*}{m}$	$\frac{m_h^*}{m}$				
$CdGeP_2$ (Pb-solution)	284	10^{-6}	1.72	0.085	0.56	1 000	7×10^9	1.7×10^3	This paper [11]
$ZnGeP_2$ (Bi-solution)	235	3×10^{-7}	2.0	0.11	0.79	1 000	2×10^9	1.0×10^{-3}	[7, 11]
$CdGeAs_2$ (melt)	525	10	0.45	0.036	0.25	1 000	7×10^{16}	1.2×10^{16}	[11, 12, 13]
$ZnSnAs_2$ (melt)	670	14	0.58	0.05	0.35	1 000	9×10^{16}	2.7×10^{16}	[11, 14]
$CdSnAs_2$ (melt)	280	0.25	0.26	0.017	0.041	11 000 (quoted)	1.4×10^{14}	5×10^{14}	[11, 15]

References

[1] PAMPLIN, B. R., DRAPER, R. C. J. and HUMPHREYS, R. G., *Mater. Res. Bull.* (to be published).

[2] VAN DER PAUW, L. J., *Phillips Res. Rep.* **13** (1958) 1.

[3] ISOMURA, S. and MASUMOTO, K., *Phys. Stat. Sol.* (a) **13** (1972) 223.

[4] BERTOTI, I. and SOMOGYI, K., *Phys. Stat. Sol.* (a) **6** (1971) 439.

[5] SOMOGYI, K. and BERTOTI, I., *Japan J. Appl. Phys.* **11** (1972) 103.

[6] SOMOGYI, K., *Phys. Stat. Sol.* (a) **18** (1973) K 95.

[7] SOMOGYI, K., *Phys. Stat. Sol.* (a) **25** (1974) 141.

[8] LEIFER, H. N. and DUNLAP, W. C., *Phys. Rev.* **95** (1954) 51.

[9] BORCHEVSKII, A. S. *et al.*, *Sov. Phys.-Semicond.* **7** (1974) 1047.

[10] KILDAL, H., Ph. D. Thesis Stanford University, 1972.

[11] SHAY, J. L. and WERNICK, J. H., *Ternary Chalcopyrite Semiconductors* (Pergamon Press) 1974.

[12] EMELYANENKO, O. V. and POLUSHINA, I. K., *Phys. Stat. Sol.* **36** (1969) K 13.

[13] VAIPOLIN, A. A. *et al.*, *Izv. Akad. Nauk SSSRFiz.* **28** (1964) 1085.

[14] MASUMOTO, K. and ISOMURA, S., *J. Phys. Chem. Solids* **26** (1965) 163.

[15] POLYANSKAYA, T. A. *et al.*, *Sov. Phys. Solid State* **8** (1966) 1468.