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ELECTROREFLECTANCE AND BAND STRUCTURE OF $\text{ZnSiAs}_{2-x}\text{P}_x$ ALLOYS

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Résumé. — L'étude de la solution solide $\text{ZnSiAs}_{2-x}\text{P}_x$ montre que la variation des paramètres a et c en fonction de la composition suit la loi de Vegard. L'étude de cette solution solide par électroréflectance, à température ambiante, a permis d'établir l'évolution des transitions directes en fonction de la composition et de déterminer le gap de ZnSiP_2 : $\Gamma_7 \rightarrow \Gamma_6 = 3,42$ eV. Les valeurs expérimentales du champ cristallin et de l'éclatement spin-orbite obtenues à partir du modèle quasi cubique sont en bon accord avec les valeurs théoriques.

Abstract. — We verify the Vegard law for $\text{ZnSiAs}_{2-x}\text{P}_x$ solid solution. We follow by electroreflectance the $\Gamma_{15} \rightarrow \Gamma_1$ transitions in the entire range of composition and give the direct threshold $\Gamma_7 \rightarrow \Gamma_6 = 3.42$ eV for ZnSiP_2 . From the quasicubic model we obtain the crystal field and the spin-orbit splitting which are compared with theory.

For the II-IV-V₂ chalcopyrite semiconductors, experimental [1] and theoretical [2] results give two models of band structure. They may have direct energy gap derived from the zincblende $\Gamma_{15} \rightarrow \Gamma_1$ levels or a pseudodirect gap: in the last case the minimum of the conduction band Γ_3 derives from the X_1 (0, 0, $2\pi/a$) point of the zincblende. ZnSiAs_2 and ZnSiP_2 have such a pseudodirect gap [1].

The direct edge of ZnSiAs_2 has been extensively studied [3-5]. In the case of ZnSiP_2 the nature of the fundamental edge is not well understood. Several authors [6-8] have studied this edge by different technics; the experimental values of the direct gap are not in good agreement. Particularly recent electroreflectance (E. R.) measurements by J. L. Shay *et al.* [9] show an interesting result the structure observed near 3 eV cannot derive from a $\Gamma_{15} \rightarrow \Gamma_1$ transition and the direct transition seems to be at higher energy.

We have performed E. R. experiments on the $\text{ZnSiAs}_{2-x}\text{P}_x$ solid solution which allowed us to follow continuously the direct transitions $\Gamma_{15} \rightarrow \Gamma_1$ from ZnSiAs_2 to ZnSiP_2 . At our knowledge the only optical results previously reported on this compound were based upon absorption measurements [10] which cannot give in this case information about such a transition.

$\text{ZnSiAs}_{2-x}\text{P}_x$ crystals of $0 \leq x \leq 2$ were obtained by vapour phase transport from 5N elements with stoichiometric proportions. Mercuric chloride of concen-

tration varying from 1 to 3 mg/cm³ was used as silicon carrier. The quartz ampule of 15 cm long and 16 mm in diameter was put in a linear temperature gradient (1 120 °C-1 050 °C). The temperature setting up stands at 530 °C to obtain ZnP_2 and goes to higher temperature with a slow heating rate of 20 °C per hour in order to ensure the complete reaction of the group V elements.

The transport duration is included between 4 and 8 days. Mixed crystals were about $3 \times 2 \times 0.5$ mm³, they were smaller than ZnSiAs_2 crystals ($4 \times 3 \times 1$ mm³) and ZnSiP_2 crystals ($5 \times 2 \times 0.5$ mm³). The crystals are homogeneous within the electron microprobe uncertainty which is typically 0.02 atomic fraction. In the ampule according to the temperature deposition we obtain different crystals. The phosphorus rich alloys are grown in the coldest part of the tube.

The habit of growth of the $\text{ZnSiAs}_{2-x}\text{P}_x$ solid solution is the chalcopyrite one. The crystals are lengthened along the 111 axis and have natural facets ($\bar{1}\bar{1}2$) and (0 $\bar{1}1$). The solid solution lattice constants a and c (Table I) were determined by classical diffractometry measurements using $\text{Cu}_{K\alpha}$ X ray. Their variation versus x is reported in figure 1. They are consistent with the Vegard law which does not agree with previous results [11]. We can notice in figure 2 the small linear variation of the c/a ratio.

Electroreflectance spectra have been obtained at 300 K by the electrolyte method (KCL N/10) with linearly polarized light. Our experimental set up has been described elsewhere [12]. Light reflecting faces

(*) Associé au C. N. R. S.

TABLE I

Lattice parameters of the solid solution $\text{ZnSiAs}_{2-x}\text{P}_x$

	a (Å)	c (Å)	c/a
ZnSiAs_2	5.613 ± 0.001	10.887 ± 0.002	1.940
$\text{ZnSiAs}_{1.50}\text{P}_{0.50}$	5.559 ± 0.001	10.778 ± 0.002	1.939
$\text{ZnSiAs}_{1.25}\text{P}_{0.75}$	5.531 ± 0.001	10.714 ± 0.002	1.937
$\text{ZnSiAs}_{1.02}\text{P}_{0.98}$	5.506 ± 0.001	10.658 ± 0.003	1.936
$\text{ZnSiAs}_{0.67}\text{P}_{1.33}$	5.475 ± 0.002	10.590 ± 0.005	1.934
ZnSiP_2	5.399 ± 0.001	10.435 ± 0.002	1.933

FIG. 1. — Lattice parameters a and c of $\text{ZnSiAs}_{2-x}\text{P}_x$. FIG. 2. — c/a ratio variation versus x of $\text{ZnSiAs}_{2-x}\text{P}_x$.

were natural facets $(\bar{1}\bar{1}2)$ or $(0\bar{1}1)$ polished with diamond paste. At the rear face an ohmic contact was taken with tin or indium.

FIG. 3. — Room temperature E. R. spectra of $\text{ZnSiAs}_{2-x}\text{P}_x$. Alloys for light polarized relative to the optic axis.

Typical E. R. spectra are reported on figure 3 for different concentrations. The ZnSiAs_2 and ZnSiP_2 spectra are similar to those previously reported by Shay *et al.* [3-9]. When the phosphorus concentration is more important than the arsenic one, an apparent modification of the selection rules appears for the first structure in the E. R. spectra; this effect has been observed by Shay *et al.* [9] in ZnSiP_2 and can be explained by a pseudodirect transitions mixing. When the arsenic concentration is more important than the phosphorus one the three transitions (A, B, C) associated with the direct threshold $\Gamma_{15} \rightarrow \Gamma_1$ are well resolved with the same selection rule than ZnSiAs_2 . The A, B, C transitions observed are given in table II. Within the experimental uncertainty we can give a linear interpretation of the variation vs the concentration x of the direct transition (Fig. 4). We can notice

TABLE II

Energies transitions associated with the zincblende $\Gamma_{15} \rightarrow \Gamma_1$ levels of $\text{ZnSiAs}_{2-x}\text{P}_x$

	A $\parallel (\perp)$ eV	B $\perp$ eV	C $\perp (\parallel)$ eV
ZnSiAs_2	2.14 ± 0.02	2.24 ± 0.02	2.49 ± 0.03
$\text{ZnSiAs}_{1.90}\text{P}_{0.10}$	2.21 ± 0.02	2.31 ± 0.02	2.54 ± 0.03
$\text{ZnSiAs}_{1.75}\text{P}_{0.25}$	2.31 ± 0.02	2.40 ± 0.02	2.62 ± 0.03
$\text{ZnSiAs}_{1.68}\text{P}_{0.32}$	2.36 ± 0.02	2.46 ± 0.02	2.67 ± 0.03
$\text{ZnSiAs}_{1.50}\text{P}_{0.50}$	2.47 ± 0.02	2.57 ± 0.02	2.77 ± 0.03
ZnSiAsP	2.78 ± 0.02	2.88 ± 0.03	3.04 ± 0.03
$\text{ZnSiAs}_{0.60}\text{P}_{1.40}$	3.04 ± 0.04	3.17 ± 0.04	3.28 ± 0.04
ZnSiP_2	3.42 ± 0.02	(3.56)	3.63 ± 0.03

FIG. 4. — Energies of the $\Gamma_{15} \rightarrow \Gamma_1$ transitions vs composition x of $\text{ZnSiAs}_{2-x}\text{P}_x$ at room temperature.

for the first time that the value of the $\Gamma_7 \rightarrow \Gamma_6$ direct threshold of ZnSiP_2 is 3.42 eV at 300 K. This value is in good agreement with the mean energy gap theoretically obtained by L. P. Pasemann [13] (3.9 eV at 0 K) and is 1 eV at less above the previous experimental results [6-9]. The B, C transitions become nearer when x increases and are not separable for ZnSiP_2 .

In the II-IV-V₂ compounds J. E. Rowe and J. L. Shay [14] have shown that the quasicubic model can explain the splitting of the Γ_{15} zincblende valence band under the combined action of the crystal field Δ_{cf} and the spin-orbit splitting Δ_{so} (Fig. 5). The Hopfield theory [15] allows the calculation of Δ_{cf} and Δ_{so} from the A, B, C transition energies

$$E_1 = E_A - E_B = \frac{1}{2}(\Delta_{so} + \Delta_{cf}) - \frac{1}{2} \times \left[(\Delta_{so} + \Delta_{cf})^2 - \frac{8}{3} \Delta_{so} \Delta_{cf} \right]^{1/2}$$

$$E_2 = E_C - E_B = \frac{1}{2}(\Delta_{so} + \Delta_{cf}) + \frac{1}{2} \times \left[(\Delta_{so} + \Delta_{cf})^2 - \frac{8}{3} \Delta_{so} \Delta_{cf} \right]^{1/2}$$

These relations have allowed us (Fig. 6) to determine from our data the variations vs the concentration x of Δ_{cf} (Fig. 7) and Δ_{so} (Fig. 8). For ZnSiP_2 the values of the band C transition energies have been determined by extrapolation of their linear variation (Fig. 4).

FIG. 5. — Band structure and selection rules at $k = (000)$ in zincblende and chalcopyrite for light polarized relative to the optic axis. Polarizations in parentheses are allowed only when spin orbit interaction is included.

The theoretical variation of Δ_{cf} is given by

$$\Delta_{cf} = \frac{3}{2} b \left(2 - \frac{c}{a} \right)$$

where b is the deformation potential describing the splitting of the valence bands in the zincblende under uniaxial stress. From the ZnSiAs_2 results we have taken $b = -1.4$ eV. This experimental value is in good agreement with those of GaAs (-1.75 eV) [15] and

TABLE III

Theoretical and experimental values of the spin orbit splitting and the crystal field of $\text{ZnSiAs}_{2-x}\text{P}_x$ alloys

	Δ_{so} (Hopfield) eV	$\Delta_{so(f_1)}$ eV	Δ_{cf} (Hopfield) eV	$\Delta_{cf} = \frac{3}{2} b \left(2 - \frac{c}{a} \right)$ eV
ZnSiAs_2	0.28	0.29	-0.13	-0.13 ($b = -1.4$)
ZnSiAs_2 (ref. [3])	0.28	0.29	-0.13	-0.16 ($b = -1.8$)
$\text{ZnSiAs}_{1.90}\text{P}_{0.10}$	0.26	0.28	-0.13	
$\text{ZnSiAs}_{1.75}\text{P}_{0.25}$	0.25	0.27	-0.12	
$\text{ZnSiAs}_{1.68}\text{P}_{0.32}$	0.24	0.26	-0.13	
$\text{ZnSiAs}_{1.50}\text{P}_{0.50}$	0.23	0.24	-0.13	
ZnSiAsP	0.19	0.18	-0.13	
$\text{ZnSiAs}_{0.60}\text{P}_{1.40}$	0.14	0.14	-0.16	
ZnSiP_2	0.09	0.07	-0.16	-0.14 ($b = -1.4$)
ZnSiP_2 (ref. [18])	0.07	0.07	-0.13	-0.14 ($b = -1.4$)

FIG. 6. — Graphic determination of Δ_{so} and Δ_{cf} from the A, B, C transitions energies of $\text{ZnSiAs}_{2-x}\text{P}_x$ for : 1, $x = 0$; 2, $x = 0.1$; 3, $x = 0.25$; 4, $x = 0.32$; 5, $x = 0.5$; 6, $x = 1$; 7, $x = 1.4$; 8, $x = 2$. ● G. Babonas value [18].

FIG. 7. — Variation of the crystal field splitting vs x of $\text{ZnSiAs}_{2-x}\text{P}_x$ full line theory with $b = -1.4$ eV. ● Our experimental values. ○ G. Babonas value [18]. ★ J. L. Shay value [13].

GaP (-1.5 eV) [17]. This value is used in the entire range of composition of the solid solution and gives for ZnSiP_2 $\Delta_{cf} = -0.13$ eV which is the result obtained by G. Babonas [18] from wavelength modulated absorption measurements. The theoretical variation of Δ_{so} is obtain from the K. Hübner model [19]

$$\Delta_{so} = \frac{1 - f_i(x)}{2} \left[\frac{\Delta_{Zn} + \Delta_{Si}}{2} \right] + \frac{1 + f_i(x)}{4} [\Delta_{As}(2 - x) + \Delta_P x]$$

FIG. 8. — Variation of the spin orbit splitting versus x of $\text{ZnSiAs}_{2-x}\text{P}_x$ full line theoretical variation. ● Our experimental values. ○ G. Babonas value [18]. ★ J. L. Shay value [13].

$f_i(x)$ is the mean ionicity of the chemical bound of the compound. We have taken a linear law for $f_i(x)$ which gives the mean ionicity of ZnSiAs_2 and ZnSiP_2 [20]

$$f_i(x) = 0.279 + 0.033 x$$

$\frac{1 - f_i(x)}{2}$ is the valence electron probability to be found at the II — and IV — atom in the unit cell,

$\frac{1 + f_i(x)}{4}$ is the valence electron probability to be found at the V-atom in the unit cell,

Δ_{As} , Δ_{Zn} , Δ_{Si} , Δ_P are the atomic spin orbit splitting given by F. Herman *et al.* [21].

On figures 7 and 8 we have reported the theoretical variation of Δ_{cf} and Δ_{so} which are in good agreement with their experimental determination.

In conclusion we have reported that the variation vs x of the $\text{ZnSiAs}_{2-x}\text{P}_x$ lattice parameters a and c follows the Vegard law. By following continuously the $\Gamma_{15} \rightarrow \Gamma_1$ transitions from ZnSiAs_2 to ZnSiP_2 we have shown that the direct gap of ZnSiP_2 associated to the $\Gamma_7 \rightarrow \Gamma_6$ levels is 3.42 eV. We have observed that the valence band splittings are explained by the quasicubic model and are in good agreement with theory.

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