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

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Abstract. — We verify the Vegard law for ZnSiAs$_{2-x}$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 $\Gamma_4 \rightarrow \Gamma_6$ = 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-V$_2$ 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 $\Gamma_3$ derives from the X$_1$ (0, 0, 2 p/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 ZnSiAs$_{2-x}$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.

ZnSiAs$_{2-x}$P$_x$ crystals of 0 ⩽ x ⩽ 2 were obtained by vapour phase transport from 5N elements with stoichiometric proportions. Mercuric chloride of concentration varying from 1 to 3 mg/cm$^3$ 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 × 2 × 0.5 mm$^3$, they were smaller than ZnSiAs$_2$ crystals (4 × 3 × 1 mm$^3$) and ZnSiP$_2$ crystals (5 × 2 × 0.5 mm$^3$). 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 ZnSiAs$_{2-x}$P$_x$ solid solution is the chalcopyrite one. The crystals are lengthened along the 111 axis and have natural facets (112) and (011). The solid solution lattice constants $a$ and $c$ (Table I) were determined by classical diffractometry measurements using CuK$_{\alpha1}$ 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.
Lattice parameters of the solid solution ZnSiAs$_{2-x}$P$_x$

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiAs$_2$</td>
<td>5.613 ± 0.001</td>
<td>10.887 ± 0.002</td>
<td>1.940</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.90}$P$</em>{0.10}$</td>
<td>5.559 ± 0.001</td>
<td>10.778 ± 0.002</td>
<td>1.939</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.75}$P$</em>{0.25}$</td>
<td>5.531 ± 0.001</td>
<td>10.714 ± 0.002</td>
<td>1.937</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.68}$P$</em>{0.32}$</td>
<td>5.506 ± 0.001</td>
<td>10.658 ± 0.003</td>
<td>1.936</td>
</tr>
<tr>
<td>ZnSiAs$<em>{0.60}$P$</em>{1.40}$</td>
<td>5.475 ± 0.002</td>
<td>10.590 ± 0.005</td>
<td>1.934</td>
</tr>
<tr>
<td>ZnSiP$_2$</td>
<td>5.399 ± 0.001</td>
<td>10.435 ± 0.002</td>
<td>1.933</td>
</tr>
</tbody>
</table>

Fig. 1. — Lattice parameters $a$ and $c$ of ZnSiAs$_{2-x}$P$_x$.

Fig. 2. — $c/a$ ratio variation versus $x$ of ZnSiAs$_{2-x}$P$_x$.

were natural facets (112) or (011) polished with diamond paste. At the rear face an ohmic contact was taken with tin or indium.

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 $I_{15} \rightarrow I_1$ 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

<table>
<thead>
<tr>
<th></th>
<th>$A \parallel (\perp)$ eV</th>
<th>$B \perp$ eV</th>
<th>$C \perp (\parallel)$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiAs$_2$</td>
<td>2.14 ± 0.02</td>
<td>2.24 ± 0.02</td>
<td>2.49 ± 0.03</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.90}$P$</em>{0.10}$</td>
<td>2.21 ± 0.02</td>
<td>2.31 ± 0.02</td>
<td>2.54 ± 0.03</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.75}$P$</em>{0.25}$</td>
<td>2.31 ± 0.02</td>
<td>2.40 ± 0.02</td>
<td>2.62 ± 0.03</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.68}$P$</em>{0.32}$</td>
<td>2.36 ± 0.02</td>
<td>2.46 ± 0.02</td>
<td>2.67 ± 0.03</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.50}$P$</em>{0.50}$</td>
<td>2.47 ± 0.02</td>
<td>2.57 ± 0.02</td>
<td>2.77 ± 0.03</td>
</tr>
<tr>
<td>ZnSiAsP</td>
<td>2.78 ± 0.02</td>
<td>2.88 ± 0.03</td>
<td>3.04 ± 0.03</td>
</tr>
<tr>
<td>ZnSiAs$<em>{0.50}$P$</em>{1.40}$</td>
<td>3.04 ± 0.04</td>
<td>3.17 ± 0.04</td>
<td>3.28 ± 0.04</td>
</tr>
<tr>
<td>ZnSiP$_2$</td>
<td>3.42 ± 0.02</td>
<td>(3.56)</td>
<td>3.63 ± 0.03</td>
</tr>
</tbody>
</table>
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-V$_2$ compounds J. E. Rowe and J. L. Shay [14] have shown that the quasicubic model can explain the splitting of the $\Gamma_{15}$ zincblende valence band under the combined action of the crystal field $\Delta_{df}$ and the spin-orbit splitting $\Delta_{so}$ (Fig. 5). The Hopfield theory [15] allows the calculation of $\Delta_{df}$ and $\Delta_{so}$ from the A, B, C transition energies

$$E_1 = E_A - E_B = \frac{1}{2} (\Delta_{so} + \Delta_{df}) - \frac{1}{2} \times$$

$$\times \left[ (\Delta_{so} + \Delta_{df})^2 - \frac{8}{3} \Delta_{so} \Delta_{df} \right]^{1/2}.$$  

These relations have allowed us (Fig. 6) to determine from our data the variations vs the concentration $x$ of $\Delta_{df}$ (Fig. 7) and $\Delta_{so}$ (Fig. 8). For ZnSiP$_2$ the values of the band C transition energies have been determined by extrapolation of their linear variation (Fig. 4).

![Figure 4](image_url)

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

![Figure 5](image_url)

**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 $\Delta_{df}$ is given by

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

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>
<thead>
<tr>
<th>Alloy</th>
<th>$\Delta_{so}$ (Hopfield) eV</th>
<th>$\Delta_{so(\Gamma_1)}$ eV</th>
<th>$\Delta_{df}$ (Hopfield) eV</th>
<th>$\Delta_{df} = \frac{3}{2} b \left( 2 - \frac{c}{a} \right)$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiAs$_2$</td>
<td>0.28</td>
<td>0.29</td>
<td>-0.13</td>
<td>-0.13 ($b = -1.4$)</td>
</tr>
<tr>
<td>ZnSiAs$_2$(ref. [3])</td>
<td>0.28</td>
<td>0.29</td>
<td>-0.13</td>
<td>-0.13 ($b = -1.8$)</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.90}$Po$</em>{0.10}$</td>
<td>0.26</td>
<td>0.28</td>
<td>-0.13</td>
<td>-0.13 ($b = -1.4$)</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.75}$Po$</em>{0.25}$</td>
<td>0.25</td>
<td>0.27</td>
<td>-0.12</td>
<td>-0.16 ($b = -1.8$)</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.68}$Po$</em>{0.32}$</td>
<td>0.24</td>
<td>0.26</td>
<td>-0.13</td>
<td>-0.16 ($b = -1.4$)</td>
</tr>
<tr>
<td>ZnSiAs$<em>{1.50}$Po$</em>{0.50}$</td>
<td>0.23</td>
<td>0.24</td>
<td>-0.13</td>
<td>-0.16 ($b = -1.4$)</td>
</tr>
<tr>
<td>ZnSiAsP</td>
<td>0.19</td>
<td>0.18</td>
<td>-0.13</td>
<td>-0.14 ($b = -1.4$)</td>
</tr>
<tr>
<td>ZnSiAs$<em>{0.60}$Po$</em>{1.40}$</td>
<td>0.14</td>
<td>0.14</td>
<td>-0.16</td>
<td>-0.14 ($b = -1.4$)</td>
</tr>
<tr>
<td>ZnSiP$_2$</td>
<td>0.09</td>
<td>0.07</td>
<td>-0.13</td>
<td>-0.14 ($b = -1.4$)</td>
</tr>
<tr>
<td>ZnSiP$_2$(ref. [18])</td>
<td>0.07</td>
<td>0.07</td>
<td>-0.13</td>
<td>-0.14 ($b = -1.4$)</td>
</tr>
</tbody>
</table>

**Table III**

*Theoretical and experimental values of the spin orbit splitting and the crystal field of ZnSiAs$_{2-x}$Po$_x$ alloys*
FIG. 6. — Graphic determination of $\Delta_{SO}$ and $\Delta_{CF}$ from the A, B, C transitions energies of ZnSiAs$_{2-x}$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].

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 $\Delta_{SO}$ is obtain from the K. Hübnner model [19]

$$\Delta_{SO} = \frac{1 - f(x)}{2} \left[ \frac{\Delta_{Zn} + \Delta_{Si}}{2} \right] +$$

$$+ \frac{1 + f(x)}{4} \left[ \Delta_{As}(2 - x) + \Delta_{P} x \right]$$

where $f(x)$ is the mean ionicity of the chemical bond of the compound. We have taken a linear law for $f(x)$ which gives the mean ionicity of ZnSiAs$_2$ and ZnSiP$_2$ [20]

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

$1 - f(x)$ is the valence electron probability to be found at the II — and IV — atom in the unit cell,

$1 + f(x)$ is the valence electron probability to be found at the V-atom in the unit cell,

$\Delta_{As}$, $\Delta_{Zn}$, $\Delta_{Si}$, $\Delta_{P}$ 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 $\Delta_{CF}$ and $\Delta_{SO}$ which are in good agreement with their experimental determination.

In conclusion we have reported that the variation vs $x$ of the ZnSiAs$_{2-x}$P$_x$ lattice parameters $a$ and $c$ follows the Vegard law. By following continuously the $I_{15} \rightarrow I_{14}$ 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.

References