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To cite this version:
R. Humphreys, B. Pamlin. OPTICAL ABSORPTION IN ZnSiP2. Journal de Physique Colloques, 1975, 36 (C3), pp.C3-159-C3-162. <10.1051/jphyscol:1975329>. <jpa-00216299>

HAL Id: jpa-00216299
https://hal.archives-ouvertes.fr/jpa-00216299
Submitted on 1 Jan 1975

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OPTICAL ABSORPTION IN ZnSiP$_2$

R. G. HUMPHREYS and B. R. PAMPLIN

School of Physics, Bath University, U. K.

Résumé. — On a étudié le coefficient d'absorption de ZnSiP$_2$ au voisinage de sa bande interdite pour les deux polarisations. On a trouvé trois singularités pour $E \perp c$ qui sont attribuées à des transitions pseudo-directes. L'absorption pour $E \parallel c$ est attribuable principalement à des transitions indirectes. Une courbe théorique a été ajustée aux résultats expérimentaux à l'aide des intensités relatives des transitions pseudo-directes calculées à partir du modèle quasi cubique. Ceci conduit pour l'énergie de liaison de l'exciton à une valeur approximative de 22 meV, et pour l'élément de matrice des transitions pseudo-directes à une valeur à peu près mille fois plus petite que celle des transitions directes dans les composés III-V. Les différences d'énergie entre les bandes de valence donnent des valeurs pour l'énergie du couplage spin-orbite de 0,056 eV et pour l'énergie du champ cristallin de — 0,130 eV. La bande interdite de ZnSiP$_2$ à la température ambiante est de 2,082 eV après avoir tenu compte de l'énergie de liaison de l'exciton.

Abstract. — The polarised absorption coefficient of ZnSiP$_2$ near the fundamental absorption edge has been studied. Three singularities were found for $E \perp c$ which are attributed to pseudodirect transitions. The absorption for $E \parallel c$ is mainly due to indirect transitions. A theoretical curve was fitted to the experimental results with the aid of the relative theoretical intensities for pseudodirect transitions calculated from the quasicubic model. This yields approximate values for the exciton binding energy of 22 meV, and for the matrix element for pseudodirect transitions about a thousand times smaller than that for direct transitions in III-V compounds.

The splittings of the valence bands give values for the spin-orbit splitting of 0.056 eV and of the crystal field splitting of — 0.130 eV. The lowest band gap in ZnSiP$_2$ is pseudodirect at 2.082 eV at room temperature after making allowance for the exciton binding energy.

1. Introduction. — By analogy with the III-V compounds, ZnSiP$_2$ is expected to have a pseudodirect band gap. This has been confirmed by wavelength modulated absorption measurements [1] and measurements of the pressure dependence of the absorption edge [2, 3]. In this paper we report the first detailed measurements of the absorption due to the pseudodirect gap in ZnSiP$_2$.

A pseudodirect gap arises in a ternary chalcopyrite semiconductor whose III-V analogue is indirect. When the band structure of an indirect gap III-V compound is embedded in the chalcopyrite Brillouin zone to give a first approximation to the band structure of its II-IV-V$_2$ analogue the (001) conduction band minimum maps back to the zone centre [4], while the (100) and (010) minima map to T. Transitions from the valence band maximum at $\Gamma$ to the conduction band minimum which maps back to $\Gamma$ are allowed without the participation of a phonon, and are called pseudodirect [5] since their strength depends on the difference between the pseudopotentials of the cations.

It has been shown [6] that the (001) minimum in GaP decreases in energy relative to those at (100) and (010) under a uniaxial strain parallel to c. Since the chalcopyrite structure is slightly compressed in this direction, the pseudodirect gap is expected to be lowest in energy and the indirect one slightly higher. The magnitude of this splitting can be estimated assuming that the tetragonal compression is the sole cause of the splitting and that the deformation potential is the same as that measured for GaP [6]. On these assumptions this splitting is estimated as 0.23 eV.
The degeneracy between the light and heavy hole bands in III-V compounds is lifted in the chalcopyrite structure by the crystal field, and the resulting valence bands are only spin degenerate.

The band structure of ZnSiP$_2$ at $\Gamma$ is summarised in figure 1 with the selection rules [7] for optical transitions. All three transitions are allowed for $E \perp c$, and one also for $E \parallel c$. The three transitions are labelled $A'$, $B'$ and $C'$ in order of increasing energy.

2. Experimental. — The crystals used in this work were grown from solution in zinc by an accelerated crucible rotation technique [8]. Single crystals 0.2-0.8 mm thick and oriented as (112) or (101) platelets were used.

The absorption measurements were carried out using a Leiss double prism monochromator, a quartz-halogen source chopped at 800 Hz, and an S 20 response photomultiplier. The signal was amplified and detected with a phase sensitive detector. Both transmission and reflection measurements were made and the absorption coefficient calculated correcting for multiple reflections in the usual way [9]. No attempt was made to correct for surface absorption or for stray light, which was below one part in $10^5$, and could not be detected above the noise.

The orientation of the crystals used was such that it was not possible to measure the absorption coefficient for $E \parallel c$ exactly. The orientation of the crystals was determined using Laue back-reflection photographs and a polarising microscope, and the angle $\theta$ between the $c$ axis and the plane of the crystal calculated. The absorption coefficient for $E \parallel c$ was then obtained from [10]

$$\alpha(\text{measured}) = \alpha_\parallel \cos^2 \theta + \alpha_\perp \sin^2 \theta$$

where $\alpha(\text{measured})$ was determined for $E$ parallel to the projection of $c$ in the plane of the crystal. The uncertainty in the measurements of $\alpha_\parallel$ is thus considerably greater than that in the measurements of $\alpha_\perp$ since $\alpha_\parallel$ is rather sensitive to errors in the measurements of the angle $\theta$.

3. Results and discussion. — The absorption coefficient showed three singularities for $E \perp c$, and possibly one for $E \parallel c$. This structure was more distinct at low temperatures and its clarity varied from crystal to crystal. The curves shown in figure 2 have the best defined structure found, and were obtained from a crystal which was 100 ohm-cm n-type and bright red in colour, and was oriented as a (101) platelet.

The three singularities were attributed to pseudodirect transitions between the three valence bands and the lowest conduction band minimum. All three were polarised $E \perp c$ in agreement with the selection rules. It is possible that the $B'$ transition was also observed for $E \parallel c$ as is allowed by the selection rules, although this could be due to errors in correcting for the orientation of the crystal. Similar singularities have been observed in the absorption of ZnSiP$_2$ by Gorban et al. [11] who attributed them to different levels of the same exciton.

At higher energies the absorption coefficient rises steadily, but less steeply at low temperatures than at room temperature. This is qualitatively the behaviour expected of indirect transitions.

The absorption curves are therefore interpreted as due to indirect transitions similar to those observed at the absorption edge of indirect gap III-V compounds with pseudodirect transitions added. The absorption coefficient for $E \parallel c$ is almost entirely due to indirect transitions. The difference between the absorption coefficients for the two polarisations varies relatively little with temperature except for the shift of the band gap and the increased broadening of the structure at room temperature. It was therefore assumed that the indirect absorption was approximately independent of polarisation, and that the difference between the absorption coefficients may be taken as a fairly good approximation to the pseudodirect absorption alone.

Hopfield's quasicubic model [12] yields eigenfunctions which can be used to predict the relative magnitudes of the matrix elements for the three transitions for $E \perp c$. The matrix elements $M$ for the $A'$ and $C'$ transitions are given by:

$$M_{1,2}^{12} = \frac{p^{12}}{1 + \frac{1}{2} \left(2 + \frac{3E_{1,2}}{\hbar^3} \right)^2}$$

where $p^{12}$ is given by

$$\frac{m^2_p}{\hbar^2} p^{12} = < C | p_x | X >^2 = < C | p_y | Y >^2$$

and $E_{1,2}$ are the energies of the two $I_2$ valence bands relative to the $\Gamma_6$ valence bands, and $\hbar$ is the spin-orbit splitting, C is the conduction band wave function and X and Y are valence band basis functions which have the symmetry of atomic p-functions. $E_{1,2}$ can be
estimated from the relative positions of the singularities, and calculated from

$$E_{1,2} = -\frac{1}{2} (\delta + \Delta) \pm \frac{1}{2} \left( \delta + \Delta \right)^2 - \frac{8}{3} \delta \Delta \right)^{1/2}$$

(2)

where $\delta$ is the crystal field splitting.

The matrix elements for the transitions $A'$, $B'$ and $C'$ are calculated to be in the ratio 0.029 : 1 : 0.97. The absorption coefficient due to a direct exciton at the band gap is related to the matrix elements by [13]

$$a_0 = \frac{1}{2} \frac{(2 m_0)^{-1/2} e^2 R^{1/2} M^2}{n \epsilon_0 e^2 h^4 E_g}$$

(3)

where $m_0$ is the electron-hole reduced mass, $R$ the exciton binding energy, $n$ the refractive index and $E_g$ the band gap.

Using the electron effective masses calculated by a pseudopotential method [7] and hole effective masses from $k \cdot p$ theory [14] the reduced effective mass is estimated to vary little between different valence bands with a value of $m_0 = 0.17 m_0$. On a hydrogenic model this gives a value of $R = 19$ meV if $\epsilon = 11$ [15].

The experimental curve for the difference between the absorption coefficients in the two polarisations was fitted to the theoretical curve for the absorption due to two excitons. The theoretical ratio of intensities was assumed, and the lowest energy exciton was neglected as being too weak to be significant. Theoretical curves have been calculated by Sell and Lawaetz [16] for the spectral dependence of the absorption due to a Wannier exciton broadened by Lorentzians of several different widths. Curves for broadening parameters intermediate between those given were obtained by interpolation. The resulting curve is shown in figure 3 with representative experimental points.

![Fig. 3. — Theoretical fit to the difference between the absorption coefficients for the two polarisations at 124 K. Representative experimental points are marked by circles. The fall-off in the experimental results at high energies is due to stray light.](image)

This fit was obtained for $R = 22$ meV, $a_0 = 49$ cm$^{-1}$, band gaps at 2.252 eV and 2.294 eV, and broadening parameters of 0.75 and 1.0. Since the fit was performed by hand it is not expected to be the best possible, but the agreement with experiment is fairly good. The value obtained for $R$ is close to that calculated from the theoretical effective masses. The theoretical and experimental curves diverge somewhat at higher energies. A similar discrepancy in GaP [16] was attributed to non-parabolicity of the bands. In the present case further errors may arise due to polarisation dependent indirect transitions.

From the value of $a_0$ obtained from the fit, the $a_0$ for the $A'$ transition was estimated as 1.5 cm$^{-1}$. This is of similar magnitude to that observed experimentally, which cannot be determined with any accuracy due to the weakness of the transition.

A similar fit was performed to the room temperature results assuming a constant value of $E_2$, $a_0$ and $R$. A reasonable fit was obtained for broadening parameters of 1.0 and 1.5. The structure is much less well defined and the fitting process is therefore more approximate than at low temperature. The shift in energy gap with temperature is in agreement with that obtained for the $A'$ transition.

The value of $a_0$ can be substituted into eq. (3) to obtain an estimate of the matrix element $P'$ for pseudo-direct transitions. With $n = 3.1$ [17], $m_0 = 0.17 m_0$, $R = 22$ meV, the matrix element was estimated as

$$E_p = \frac{2 m_0}{h^2} P'^2 = 0.015 \text{ eV}.$$  

This can be compared to the matrix elements for direct transitions in the III-V compounds for which the mean value of $E_p$ is 20 eV [18], so that pseudo-direct transitions in ZnSiP$_2$ are about a thousand times weaker than direct transitions in the III-V compounds. While the value obtained here is only approximate, the conclusion may be drawn that pseudo-direct matrix elements are probably sufficiently small to be negligible in calculating effective masses.

**TABLE I**

<table>
<thead>
<tr>
<th>Band Gap Energies in ZnSiP$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ = 290 K (eV)</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>A'</td>
</tr>
<tr>
<td>B'</td>
</tr>
<tr>
<td>C'</td>
</tr>
</tbody>
</table>

The values of the energy gaps obtained from the curve fitting are listed in table I. The spin-orbit and crystal field splittings calculated by substituting these values into eq. (2) are $\delta = 0.056$ eV and $\delta = -0.130$ eV. The spin-orbit splitting may be compared with that calculated by Hübner and Unger [19] of 0.07 eV. The crystal field splittings of II-IV-V$_2$ compounds have been explained by Shay et al. [20] as being
predominately due to the tetragonal compression. They suggested that
\[ \delta = -1.5 b(2 - c/a) \]
where \( b \) is the deformation potential of the III-V analogue. On the assumption that \( b = 1.0 \), the value predicted for \( \text{ZnSiP}_2 \) is \(-0.117\), in good agreement with this result. These splittings are summarised in table II together with the results of reference [1] for comparison.

Table II

<table>
<thead>
<tr>
<th>( \delta ) (eV)</th>
<th>Expt.</th>
<th>Theory</th>
<th>Ref. [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A ) (eV)</td>
<td>0.056</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>( R ) (eV)</td>
<td>0.022</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>( E_p ) (eV)</td>
<td>0.015</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The agreement found here with the quasicubic model in both the intensities of the transitions and the magnitudes of the valence band splittings is reassuring in view of the electroreflectance results of Shay et al. [21], which appeared to cast doubt on the validity of this theory applied to \( \text{ZnSiP}_2 \). The lowest transition seen in electroreflectance was reported as being polarised perpendicular to \( c \) in contrast to all the other II-IV-V\(_2\) compounds for which data are available. It seems most likely that this transition occurs away from the zone centre, and that the A transition is higher in energy, as might be expected from a consideration of the lowest direct band gaps in the III-V analogues.

4. Conclusion. — The absorption coefficient of \( \text{ZnSiP}_2 \) can be understood in terms of pseudodirect and indirect transitions. On the assumption that the indirect absorption is approximately polarisation independent, the experimental results have been fitted to theory and several parameters obtained. The valence band splittings are in good agreement with the predictions of theory. The exciton binding energy estimated from the absorption curves is fairly large (22 meV) and is close to that calculated using reasonable effective masses. The matrix element which has been obtained for pseudodirect transitions is at best approximate, but is so small as to permit the conclusion that the pseudodirect matrix element can be neglected in estimating effective masses by k.p theory.

The lowest band gap in \( \text{ZnSiP}_2 \) is pseudodirect with \( E_g = 2.082 \) eV after allowance has been made for the exciton binding energy. The mean temperature coefficient of the band gap between room temperature and liquid nitrogen temperature is \( 3.1 \times 10^{-4} \) eV/K.

Acknowledgment. — This work was supported by Honeywell Inc.

References