

Absorption edge of Zn_3P_2

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The experimental data of the Zn_3P_2 absorption edge are analyzed for single crystals and thin films. The isotropic Kane band-structure model, with the introduction of a valence-level split-off due to crystal-field interaction is used to calculate the absorption coefficient. The best fit to the experimental data has been obtained for the following parameters: energy gap, $E_g = 1.51$ eV; spin-orbit splitting, $\Delta_{so} = 0.21$ eV; crystal-field splitting, $\Delta_{CF} = 0.04$ eV; momentum matrix element, $P = 4.7 \times 10^{-10}$ eV m; and heavy-hole effective mass, $m_{v1}^* = 0.22m_0$, at 300 K.

Zinc phosphide (Zn_3P_2) has been intensively investigated for the last four years as one of the most promising semiconductors for low-cost and high-efficiency solar-cell applications (for review see, e.g., Refs. 1 and 2). Comments on the Zn_3P_2 band-structure diagram have been published recently.³ However, there are no energy-structure calculations for the real (tetragonal) crystal structure of Zn_3P_2 so far.

Investigations of the Zn_3P_2 absorption coefficient over a wide temperature range of 5–300 K were performed in,⁴ and established the smallest energy gap of Zn_3P_2 as equal to 1.315 eV at 300 K, and 1.335 within the temperature range 80–5 K; this gap was ascribed to indirect transitions. The direct energy gap was estimated⁴ as equal to 1.515 eV at 300 K, 1.645 eV at 80 K, and 1.685 eV at 5 K. The direct energy-gap value was confirmed by an optical-absorption study (at 300 K) of thin films and bulk Zn_3P_2 (Refs. 5 and 6) and by photoluminescence measurements.⁷ Recent experiments on laser-excited photoluminescence emission of single Zn_3P_2 crystals⁸ have tended to confirm the interpretation of the lowest energy transition as well.

The absorption spectra for Zn_3P_2 single crystals⁴ and thin films⁶ measured under unpolarized light at 300 K are shown in Fig. 1 and will be used in the discussion given below. In order to best fit both sets of data, the curve for thin films was shifted up parallel to the absorption axis from the value of $\alpha = 1.05 \times 10^3 \text{ cm}^{-1}$ to $\alpha = 2.05 \times 10^3 \text{ cm}^{-1}$, at $\hbar\omega = 1.51$ eV, to provide a smooth fit within the range of $\alpha = (2.05 - 4.2) \times 10^3 \text{ cm}^{-1}$, shown in Fig. 2.

Using an isotropic three-level Kane band model⁹ one can calculate the absorption coefficient for each transition i from three valence levels (v_i) numbered from the top (v_1 , v_2 , and v_3) to one conduction level (c) from the well-known equation

$$\alpha_i = \frac{\pi e^2}{\epsilon_0 n c_0 m_0^2 \omega} M_i^2 \rho_i, \quad (1)$$

where $i = 1, 2$, and 3 for transitions v_1, v_2 , and

$v_3 \rightarrow c$, respectively, n is a refractive index, and for Zn_3P_2 , $n = 3.32$,⁶ ω is a frequency of the photon involved in the transition, ϵ_0 , c_0 , e , and m_0 are the dielectric permittivity, light velocity in vacuum, elementary charge, and free-electron mass, respectively. M_i is an optical matrix element and ρ_i is a joint density of states; both are described in detail below to derive the parameters used in the computations.

The optical matrix element is given by

$$M_i^2 = \frac{2m_0^2}{3\hbar^2} P^2 [(a_c d_i + d_c a_i)^2 + (a_c b_i + b_c a_i)^2], \quad (2)$$

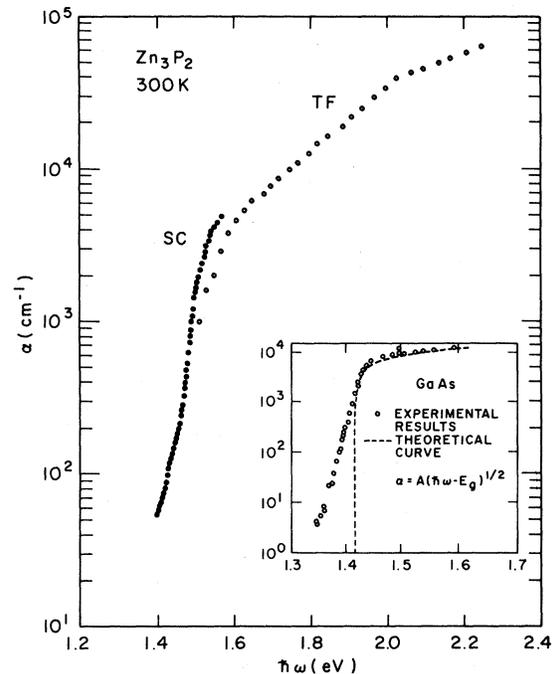


FIG. 1. Experimental data of Zn_3P_2 absorption near the fundamental absorption edge for single crystals (SC) after Ref. 4 and for thin films (TF) after Ref. 6. Only representative points are shown to clarify the figure. The insert shows the absorption edge of GaAs after Ref. 19.

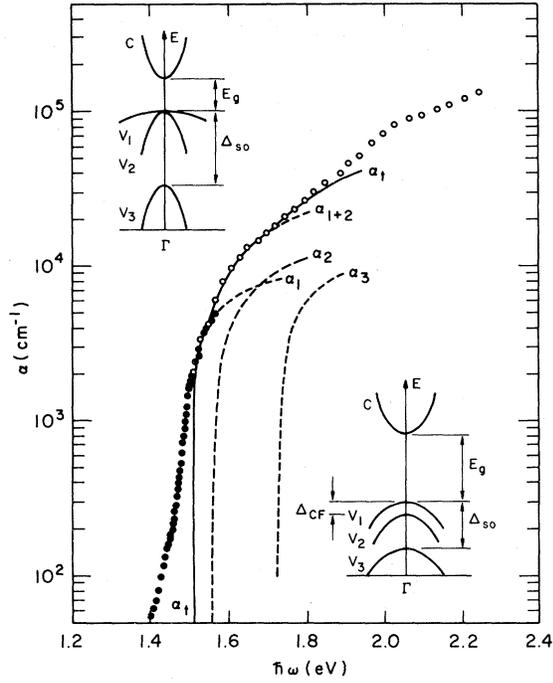


FIG. 2. A fit of the computed absorption plots $\alpha_i(\hbar\omega)$ and $\alpha_T(\hbar\omega)$ to the experimental data, for parameters given in Eq. (6). The original Kane model (Ref. 9) and that used in this work are shown as the upper and lower inserts, respectively. Not to scale.

where P is the momentum matrix element characterizing an interaction between conduction and valence bands, m_0 is the free-electron mass, and

$$\begin{aligned} a_{\Theta} &= kP(E'_{\Theta} + \frac{2}{3}\Delta_{so})N_{\Theta}^{-1}, \\ b_{\Theta} &= \frac{\sqrt{2}}{3}\Delta_{so}(E'_{\Theta} - E_g)N_{\Theta}^{-1}, \\ d_{\Theta} &= (E'_{\Theta} - E_g)(E'_{\Theta} + \frac{2}{3}\Delta_{so})N_{\Theta}^{-1}, \end{aligned} \quad (3)$$

where $\Theta = c, v_i$. For the parabolic v_1 level, $a(i=1)=0$, $b(i=1)=1$, and $d(i=1)=0$ (see below). N_{Θ} is a normalizing factor such that $a_{\Theta}^2 + b_{\Theta}^2 + d_{\Theta}^2 = 1$, and

$$E'_{\Theta} = E_{\Theta} - \frac{\hbar^2 k^2}{2m_0}. \quad (4)$$

E_{Θ} is an electron energy on the appropriate level (c, v_i), E_g is a fundamental energy gap (distance between v_1 and c), and Δ_{so} is a spin-orbit splitting (distance between v_3 and v_1 , which is double degenerate in the Γ point).

The joint density of states is given by the slopes of the $E(\vec{k})$ relations for each pair of levels (c, v_i) and for an isotropic model

$$\rho_i = k^2 / 2\pi^2 \left| \frac{dE_c}{dk} - \frac{dE_{v_i}}{dk} \right|, \quad (5)$$

where energies E_{Θ} are given by well-known solutions of the Kane secular equation⁹ and (in this model) refer to the conduction level (E_c) and either to the light-hole valence level (E_{v_2}) or the split-off valence level (E_{v_3}). The heavy-hole valence level (E_{v_1}) is assumed to be a simple parabolic level corresponding to the effective mass $m_{v_1}^*$, which is used as a fitting parameter.

The original Kane band-structure model is schematically shown as an upper insert in Fig. 2.

Absorption coefficients, α_i , for each transition i were computed separately for four parameters: energy band gap, E_g , spin-orbit splitting, Δ_{so} , momentum matrix element, P , and heavy-hole effective mass, $m_{v_1}^*$. The total interband absorption coefficient, α_T , was then determined by summing up the α_i values graphically. The resultant $\alpha_i(\hbar\omega)$ curves were next compared to the experimental data and computations were repeated for different parameters in order to improve the fit to experimental curves.

We began the computations with the following parameters: $E_g = 1.515$ eV,⁴ $\Delta_{so} = 0.11$,¹⁰ and momentum matrix element and heavy-hole effective mass taken as for the isomorphous Zn_3As_2 from Ref. 11: $P = 4 \times 10^{-10}$ eV m, and $m_{v_1}^* = 0.36m_0$. A large number of theoretical curves was generated for parameters in the following ranges: $E_g = 1.4-1.6$ eV, $\Delta_{so} = 0.1-0.5$ eV, $P = (2-10) \times 10^{-10}$ eV m, and $m_{v_1}^* = (0.1-1)m_0$. It was noticed that near the fundamental absorption edge a better fit to the experimental data was obtained by introducing into the calculations a small split-off between α_1 and α_2 curves. This is equivalent to a downward shift of the v_2 level (see inserts in Fig. 2) from the v_1 level, at the Γ point, and is understandable as a manifestation of the crystal-field interaction effect Δ_{CF} .¹⁰ This small shift of the v_2 level does not noticeably disturb the original Kane model in which the highest valence level is doubly degenerate in the Γ point. The same procedure has also been applied to the isomorphous compound, Zn_3As_2 in Ref. 11.

The best fit to the experimental results was obtained for the following set of parameters:

$$\begin{aligned} E_g &= 1.51 \text{ eV}, \quad \Delta_{so} = 0.21 \text{ eV}, \quad \Delta_{CF} = 0.04 \text{ eV}, \\ P &= 4.7 \times 10^{-10} \text{ eV m}, \quad m_{v_1}^* = 0.22m_0. \end{aligned} \quad (6)$$

These parameters are in reasonable correspondence with the values suggested in Ref. 10: $\Delta_{so} = 0.11$ eV and $\Delta_{CF} = 0.03$ eV. Also, the electron effective mass at the bottom of the conduction band, m_c^* , computed from the relation

$$\frac{m_0}{m_c^*} = 1 + \frac{2m_0P^2}{3\hbar^2} \left(\frac{2}{E_g} + \frac{1}{E_g + \Delta_{so}} \right) \quad (7)$$

and equal to $0.2m_0$ for the P , E_g , and Δ_{so} values estimated here, is in a relatively good agreement with

the m_c^* value from Ref. 12, $m_c^* = 0.128m_0$. It should be noted that no experimental evidence on the spin-orbit and crystal-field splitting has been published so far, except for the suggestions given in Ref. 5, $\Delta_{CF} = 0.1$ eV and $\Delta_{so} = 0.24$ eV, and in Ref. 13, $\Delta_{CF} = 0.03$ eV and $\Delta_{so} = 0.13$ eV, which were estimated from the spectral photoresponse of metal-Zn₃P₂ Schottky-type structures.

The P value estimated here is small compared with that of III-V compounds,¹⁴ and is also smaller than that for narrow-gap cadmium II-V compounds, Cd₃As₂ (Ref. 15) and Cd₃P₂ (Ref. 16). However, it is almost the same as the P value of the second wide-gap zinc II-V compound, Zn₃As₂, estimated in Refs. 11 and 17 as $P = 4 \times 10^{-10}$ eV m.

For direct transitions one expects no absorption below the energy gap, but in practice one usually finds a near-exponentially increasing absorption edge fulfilling the well-known Urbach rule¹⁸; for comparison see insert in Fig. 1 from Ref. 19, and the results for the isomorphous compound, Zn₃As₂ (Ref. 11). In the case of Zn₃P₂, however, in spite of some similarity with the GaAs and Zn₃As₂ absorption edges, we have the additional (indirect) optical transitions to the conduction-band minima shifted from the Γ point^{3,4} which is the main cause of the nonvanishing absorption below the fundamental absorption edge of Zn₃P₂. An Urbach edge, due to long-range potential fluctuations, cannot be excluded either.

The two main limitations of the Kane model used here are as follows:

- (1) The model is applicable to isotropic band-

structure semiconductors and is not strictly valid for tetragonal semiconductors. This problem has been discussed in Refs. 15 and 20 and the real crystal field was approximated by a cubic structure with tetragonal distortion; the anisotropic crystal potential was added to the Kane Hamiltonian. This procedure, however, requires more experimental data and will be applied when unambiguous data on Zn₃P₂ properties are known.

(2) The absorption formula in the Kane model is essentially valid for a perfect lattice at $T = 0$ K. Both the lattice dilatation and phonon interactions affect the $\alpha(\hbar\omega)$ shape. Better fitting could be obtained by taking into account low-temperature absorption data, but the absorption of thin Zn₃P₂ layers has not yet been measured at low temperatures and, on the other hand, the likely experimental errors (especially for thin films) seem to be much greater than those introduced by neglecting the effects mentioned above. Also, the Coulomb interaction, which gives a broadening of the absorption edge, can be neglected for the relatively low concentration of free carriers.

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