Band Structure of $ZnGeP_2$ and $ZnSiP_2$—Ternary Compounds with Pseudodirect Energy Gaps

J. L. Shay and B. Tell
Bell Telephone Laboratories, Holmdel, New Jersey 07733

and

E. Buehler and J. H. Wernick
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 8 February 1973)

We have observed electroreflectance structure in $ZnGeP_2$ at the pseudodirect energy gap, the direct energy gap derived from the indirect gap in GaP. The direct energy gap is also observed at higher energy. We also observe the direct energy gap of $ZnSiP_2$ some 1.0 eV above the absorption edge previously reported. The polarization selection rules observed at the direct gap in $ZnSiP_2$ are opposite to those found in all other II-IV-V_2 compounds investigated, and raise a fundamental question as to the physical origin of the crystal field splitting of the valence bands in these compounds.

As ternary analogs of GaP and AlP, the energy band structures of $ZnGeP_2$ and $ZnSiP_2$ are of special interest since theoretical considerations[1] suggest that they may have direct energy gaps although their binary analogs have indirect energy gaps. Earlier electroreflectance studies of II-IV-V_2 chalcopyrite crystals have not included these two compounds because they are usually semi-insulating as grown. In the present work, we report electrolyte electroreflectance studies of suitably doped, conducting crystals.

Because of the smaller Brillouin zone for the chalcopyrite structure relative to zinc blende, there is a four-to-one mapping of energy levels of the zinc-blende binary analog into the chalcopyrite Brillouin zone. One of the X points $(0, 0, 2\pi/a)$ in the zinc-blende zone maps to Γ, the center of the zone. Consequently the $\Gamma_{15} \rightarrow X_1$ indirect gap of GaP should map to a $\Gamma_{15} \rightarrow \Gamma_1$ direct energy gap in $ZnGeP_2$. Such energy gaps have been termed "pseudodirect"[2] since their strengths will depend upon the differences in the cation pseudopotentials. We report here the observations of pseudodirect transitions at the lowest energy gap in $ZnGeP_2$. We have also observed the direct energy gap in $ZnGeP_2$ corresponding to the direct energy gap in GaP. We find that the pseudodirect transitions are ~20 times weaker than the direct transitions. Both the pseudodirect and the direct transitions display a fine structure with the same splittings since they both originate on the same set of valence bands. The ordering and splittings of these valence bands result from the simultaneous influences of spin-orbit splitting and the built-in lattice compression (2%). At higher photon energies many new transitions are observed corresponding to the E_1 and $E_1 + \Delta_1$ transitions in GaP. Assignment of these transitions to specific regions of the Brillouin zone cannot be made at this time, and must await full zone calculations of the energy band structure and optical properties.

The electroreflectance spectrum of $ZnSiP_2$ reported here came to us as a great surprise. Whereas the band gap of $ZnSiP_2$ has often been quoted as ~2.0 eV and has been thought to be direct,[3] we find that the lowest direct band gap with an appreciable oscillator strength lies at 2.96 eV, far above the absorption edge[3] and luminescence features[4] previously studied. Of more consequence however, is our observation that transitions at this lowest band gap are strongest for light polarized $\vec{E} \perp \vec{Z}$, in contrast to all other II-IV-V_2 crystals investigated.[5] If this band gap is derived from the $\Gamma_{15} \rightarrow \Gamma_1$ band gap of GaP, then the crystal field splitting of the p-like valence bands is opposite to that observed in the other II-IV-V_2 crystals even though all crystals studied manifest a built-in compression. The crystal field anomaly reported for $ZnSiP_2$ is especially disturbing in comparison with $ZnSiAs_2$ for which the normal ordering of the valence bands was observed.[2] One would intuitively expect that any "chemical" effects associated with the difference between the cation species Zn and Si would be independent of the anion (As or P) in the ternary compound.

The resistivity of $ZnGeP_2$ crystals grown from the melt[6] was typically $>10^4$ Ω cm. Diffusion of Ga at 700°C under a slight P overpressure re-

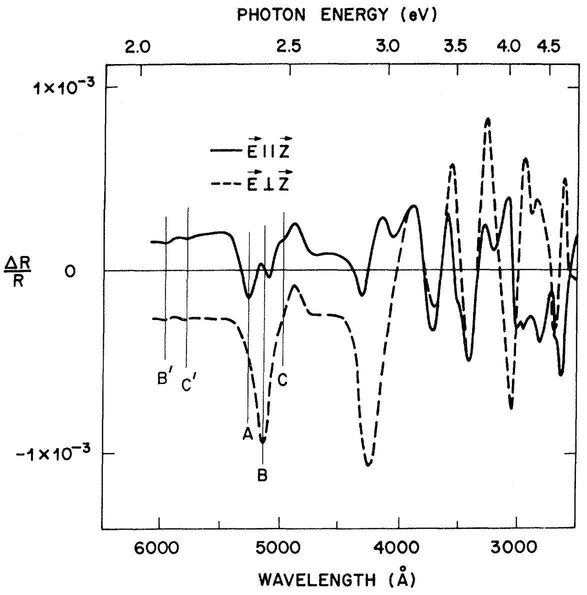

FIG. 1. Room-temperature electrolyte electroreflectance spectrum for $ZnGeP_2$. Since the orientation was approximately (112), $\vec{E} \parallel \vec{Z}$ is only nominal.

duced the resistivity to ~10-Ω-cm *p* type, which was adequate for electrolyte electroreflectance experiments. Crystals of $ZnSiP_2$ grown by iodine transport were also semi-insulating as grown, but could be rendered conducting (*n* type) by diffusion of In in a slight P overpressure. Measurements were also performed on 10-Ω-cm *n*-type $ZnSiP_2$ crystals grown from Sn solution.

The room-temperature electroreflectance spectrum of $ZnGeP_2$ is shown in Fig. 1. The direct energy gap of $ZnGeP_2$ has been previously reported between 1.8 and 2.25 eV depending upon the interpretation of absorption spectra.[7] We see in Fig. 1 that the lowest direct energy gap with appreciable oscillator strength (labeled *A*) occurs at 2.34 eV. Together with the *B* and *C* transitions at 2.40 and 2.48 eV, these are attributed to the direct energy gaps in $ZnGeP_2$ related to the $\Gamma_{15} \rightarrow \Gamma_1$ energy gap in GaP (a spin-orbit-split doublet at 2.74 and 2.84 eV[8]).

In the theoretical band structure for $ZnGeP_2$ shown in Fig. 2, the Γ_3 and $T_1 + T_2$ conduction bands are derived from X_1 in GaP, Γ_2 is derived from X_3, and Γ_1 is derived from Γ_1. The valence bands Γ_4 and Γ_5 result from a crystal field splitting of the Γ_{15} valence band in GaP, and spin-orbit interaction lifts the double degeneracy of Γ_5 (not shown in Fig. 2). The *A*, *B*, and *C* structures in Fig. 1 are therefore assigned to $(\Gamma_4, \Gamma_5) \rightarrow \Gamma_1$ transitions.

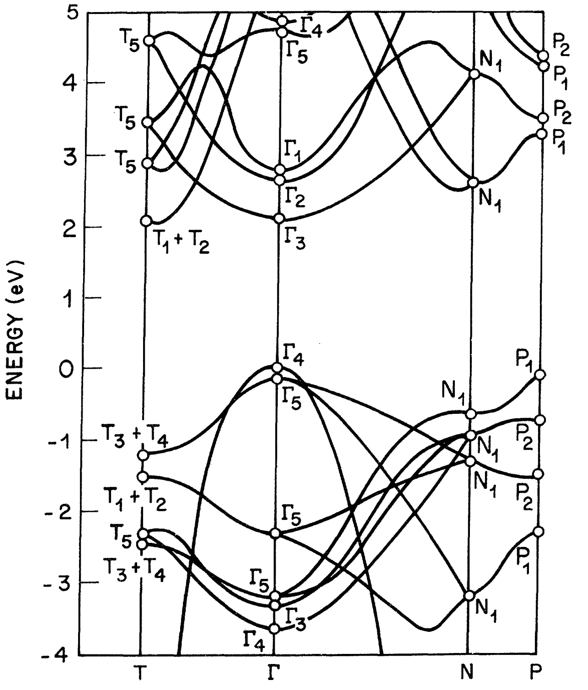

FIG. 2. Theoretical energy band structure for $ZnGeP_2$ obtained by imbedding the band structure of GaP into the chalcopyrite Brillouin zone (after Ref. 10).

The weaker structures *B'* and *C'* at 2.05 and 2.11 eV in Fig. 1 are attributed to the spin-orbit-split pseudodirect transition $\Gamma_5 \rightarrow \Gamma_3$ in Fig. 2. The expected *A'* structure is too weak to be observed since the $\Gamma_4 \rightarrow \Gamma_3$ transition becomes allowed only when spin-orbit interaction is included. The energy separation between the *B'* and *C'* structures is approximately the same as between *B* and *C*, since they are due to transitions from the same valence bands. Those pseudodirect transitions in $ZnGeP_2$ are close in energy to the indirect gap in GaP at 2.26 eV.[9] These assignments are consistent with the low-temperature thermoreflectance and wavelength-modulated absorption measurements of Shileika.[10]

In the 3- to 4.5-eV photon energy range only the E_1 and $E_1 + \Delta_1$ transitions are observed in the electroreflectance spectrum of GaP. It is evident in Fig. 1 that considerably more structure is observed in $ZnGeP_2$ in the same energy region. Possible explanations for this multiplicity have been discussed elsewhere.[11] Assignment of this structure observed in $ZnGeP_2$ to specific regions of the chalcopyrite Brillouin zone must await full zone calculations of energy bands and optical

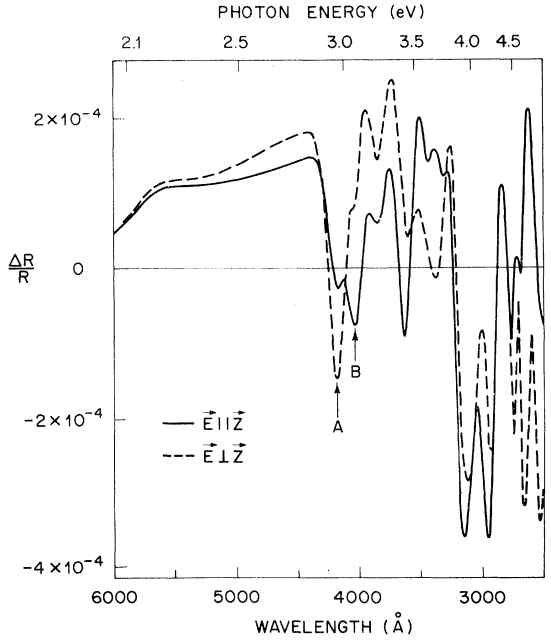

FIG. 3. Room-temperature electrolyte electroreflectance spectrum for $ZnSiP_2$. The orientation was (112), so $\vec{E} \parallel \vec{Z}$ is only nominal.

properties.

Whereas the direct band gap for $ZnSiP_2$ is usually quoted as ~2.0 eV, we find that the first direct transition with appreciable oscillator strength occurs at 2.96 eV (*A* in Fig. 3) followed by another strong transition, *B*, at 3.06 eV. It is clear therefore from these electroreflectance data that the absorption edge[3] and luminescence[4] observed near 2.0 eV do not result from energy bands derived from the $\Gamma_{15} \rightarrow \Gamma_1$ transition in GaP as previously thought.[3]

Of greater consequence however is the observation that the lowest strong transition (*A*) in $ZnSiP_2$ is strongest for light polarized $\vec{E} \perp \vec{Z}$ in contrast to all other II-IV-V_2 crystals investigated.[5] If the *A* and *B* structures in Fig. 3 result from $(\Gamma_4, \Gamma_5) \rightarrow \Gamma_1$ transitions, then the polarization selection rules imply that the Γ_5 valence band lies above Γ_4 whereas just the opposite has been observed in all other II-IV-V_2 crystals. The crystal field splitting of the Γ_5 and Γ_4 valence bands has been attributed to the built-in lattice compression on the basis that the observed splittings vary approximately linearly with $2-c/a$, the built-in compression,[5] and the proportionality coefficient has the same sign and magnitude as the (001) uniaxial deformation potential measured for several III-V compounds. Consequently either the ordering of the valence bands implied by the polarization dependences of the *A* and *B* structures in Fig. 3 are completely anomalous, or these structures are not derived from $\Gamma_{15} \rightarrow \Gamma_1$ transitions in III-V compounds.

This dilemma could be resolved if the lowest conduction band level had the symmetry Γ_{15} rather than Γ_1. The lowest direct energy gap in $ZnSiP_2$ would then be derived from $\Gamma_{15} \rightarrow \Gamma_{15}$ transitions in III-V compounds rather than $\Gamma_{15} \rightarrow \Gamma_1$ as observed for all other II-IV-V_2 compounds. If the conduction-band crystal field splitting were such that Γ_5 was below Γ_4, then *A* would be assigned to $\Gamma_4 \rightarrow \Gamma_5$ ($\perp$), *B* to $\Gamma_5 \rightarrow \Gamma_5$ ($\parallel$), and the weaker structure near 3.2 eV would be assigned to $\Gamma_5 \rightarrow \Gamma_4$ transitions. This suggestion seems tenuous however since the $\Gamma_{15} \rightarrow \Gamma_{15}$ energy gaps in GaP and AlP (the binary analogs) are 4.8 and 4.6 eV, respectively,[12] i.e., ~1.7 eV above the energy of the *A* and *B* transitions in Fig. 3.

We conclude that the direct energy gaps in both $ZnGeP_2$ and $ZnSiP_2$ are well above the absorption edges previously observed. Hence the absorption edges in both crystals result from indirect and pseudodirect energy gaps derived from the $\Gamma_{15} \rightarrow X_1$ energy gap in GaP. The strength of the electroreflectance structure observed at the pseudodirect gap in $ZnGeP_2$ is ~20 times weaker than the structure observed at the direct gap, considerably weaker than might have been expected on the basis of the large difference in the Zn and Ge pseudopotentials. Finally, the polarization dependence of the direct energy gap in $ZnSiP_2$ is opposite to that observed in all other ternary phosphides and arsenides. If the direct energy gap in $ZnSiP_2$ involves the same energy bands as produce the direct gap in other crystals (i.e., $\Gamma_{15} \rightarrow \Gamma_1$), the observed polarization dependences raise a fundamental question as to the physical origin of the crystal field splitting of the uppermost valence bands in these compounds.

We are grateful to A. Shileika and Y. Petroff for discussions of their studies of the absorption edge structure of $ZnGeP_2$, to R. Humphreys for samples of solution-grown $ZnSiP_2$, to R. L. Barns for determination of lattice constants, and to L. M. Schiavone and Mrs. A. A. Pritchard for their able technical assistance.

---

[1] G. F. Karavaev and A. S. Poplavnoi, Fiz. Tverd. Tela 8, 2143 (1966) [Sov. Phys. Solid State 8, 1704 (1967)]; G. F. Karavaev, A. S. Poplavnoi, and V. A. Chaldyshev,

Fiz. Tekh. Poluprov. 2, 113 (1968) [Sov. Phys. Semicond. 2, 93 (1968)]; V. A. Chaldyshev and V. N. Pokrovskii, Izv. Viz. Fiz. SSSR 2, 173 (1960), and 5, 103 (1963).

[2] J. L. Shay, E. Buehler, and J. H. Wernick, Phys. Rev. B 3, 2004 (1971).

[3] N. A. Goryunova, S. S. Grigor'yan, and L. B. Zlatkin, Izv. Akad. Nauk SSSR, Neorg. Mater. 2, 2125 (1966).

[4] J. L. Shay, R. F. Leheny, E. Buehler, and J. H. Wernick, J. Lumin. 1, 851 (1970); R. E. Nahory, J. Shah, R. C. C. Leite, E. Buehler, and J. H. Wernick, Phys. Rev. B 1, 4677 (1970).

[5] J. L. Shay, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972,* edited by The Polish Academy of Sciences (PWN—Polish Scientific Publishers, Warsaw, 1972).

[6] E. Buehler and J. H. Wernick, J. Cryst. Growth 8, 324 (1971).

[7] B. Ray, A. J. Payne, and G. J. Burrell, Phys. Status Solidi (b) 35, 197 (1969).

[8] M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1969).

[9] P. J. Dean and D. J. Thomas, Phys. Rev. 150, 690 (1966).

[10] A. Shileika, in Proceedings of the First International Conference on Modulation Spectroscopy, Tucson, Arizona, 23–26 November 1972 (to be published).

[11] J. L. Shay, Phys. Rev. Lett. 29, 1008 (1972).

[12] J. A. Van Vechten, Phys. Rev. 187, 1007 (1969).

Investigation of the Spin Dependence in the Deuteron-Nucleus Interaction

L. D. Knutson and W. Haeberli
*University of Wisconsin, Madison, Wisconsin 53706**
(Received 22 January 1973)

Measurements of the cross section, the vector analyzing power, and the three tensor analyzing powers have been made for deuteron elastic scattering from ^{90}Zr at 5.5 MeV. The measurements are explained by an optical-model potential whose spin-dependent parts are calculated from the nucleon-nucleus potential. The predicted spin-orbit potential, which is considerably different from the potentials used in previous phenomenological analyses, also gives excellent agreement with the vector analyzing power at 9 MeV.

The optical model has been used to describe deuteron elastic scattering from a wide range of target nuclei. Watanabe[1] has suggested that the deuteron-nucleus potential might be calculated from the empirically known nucleon-nucleus optical potentials. In this so-called folding model, the deuteron potential is taken to be the sum of the neutron-nucleus and proton-nucleus potentials, averaged over the internal motion of the deuteron.

The purpose of the present Letter is to investigate whether the folding model correctly predicts the spin-dependent parts of the deuteron optical-model potential. Phenomenological spin-dependent potentials have shown some resemblance to the folding-model predictions,[2,3] but no systematic investigation of the accuracy of the spin-dependent potentials has been made.

When the nucleon-nucleus potentials are made up of central and spin-orbit terms, the deuteron potential will likewise contain a central and a spin-orbit term.[1] In addition, the folding-model potential will contain a tensor potential of the form

$$V_T(\vec{r}) = F(r)T_r \tag{1}$$

provided that the effects of the deuteron D state are included.[4] In Eq. (1), r is the deuteron-nucleus separation and the tensor operator, T_r, is defined by

$$T_r = (\vec{s}\cdot\hat{r})^2 - \tfrac{2}{3}, \tag{2}$$

where $\vec{s}$ is the deuteron spin.

The spin-dependent potentials predicted[5] from the folding model for 5.5-MeV deuterons incident on ^{90}Zr are shown in Fig. 1. These potentials were calculated using formulas given by Raynal.[6] The tensor potential is complex because the central nucleon-nucleus potentials are complex. The spin-orbit potential results from the neutron and proton spin-orbit potentials and is thus purely real.

The spin-orbit and tensor potentials have only a small effect on the elastic scattering cross section, but do affect the analyzing powers[7] (i.e., cross section for polarized incident deuterons).