Calculated Band Structure and Reflectivity Spectra of ZnGeP$_2$†

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(Received 26 January 1973)

The imaginary part of the dielectric function, the energy band structure, and the reflectivity of the ternary compound ZnGeP$_2$ are calculated using the empirical pseudopotential method. A critical point analysis in the Brillouin zone is discussed in detail to explain prominent optical structure. Spin-orbit corrections to the band structure were calculated at a few points in the Brillouin zone.

There has been much interest recently in the structure of the reflectivity and modulated reflectivity spectra of II-IV-V$_2$ materials that crystallize in the chalcopyrite structure. Being the closest analogs of the III-V zinc-blende crystals, with electronic and optical properties close to those of the zinc-blende analogs, chalcopyrite crystals show considerably more structure in the experimental reflectivity and electroreflectance spectrum[1] than to the III-V compounds.

The chalcopyrite real-space unit cell can be thought of as composed of two zinc-blende unit cells stacked and compressed along the c axis. The two cations of the II-IV-V$_2$ crystal are in alternating positions along the c axis substituting for the cation in the III-V crystal. The anion is slightly displaced from its original position closer to the group-IV cation (except in the ZnSn compounds). Using this real-space structure, the zinc-blende Brillouin zone (BZ) can be multiply mapped four times completely into the smaller chalcopyrite BZ.

Using a quasicubic model, transitions between the valence and conduction band of a chalcopyrite crystal have been divied by Shay[2] into two categories: direct transitions—those originating from direct transitions in a zinc-blende crystal; pseudodirect transitions—those originating from indirect transitions in a zinc-blende crystal. It is important to determine if the reflectivity peaks are caused by direct or pseudodirect transitions and to what extent the band structure of a II-IV-V$_2$ crystal is only a slight perturbation of the band structure of its cubic analog.

We report here the first calculation of the reflectivity $R(\omega)$ as a function of photon energy ω for a II-IV-V$_2$ crystal in the chalcopyrite structure. The main purpose of this work is to identify the regions in the BZ responsible for the main structure in the measured[1] reflectivity and electroreflectance spectrum common to most of these compounds. The crystal we have considered is ZnGeP$_2$, the analog of GaP; its crystal parameters are $a = 5.46$ Å, $c = 10.71$ Å, and $u = 0.2582$ (all at room temperature). The method used to calculate the energy bands and dipole matrix elements is the empirical pseudopotential method.[3] No attempt is made to fit the pseudopotential form factors $V(q)$ to experiment.

We define symmetric, antisymmetric, and antisymmetric-cation pseudopotential form factors in the following way: $V_S = \frac{1}{4}(V_{\mathrm{Ge}} + V_{\mathrm{Zn}} + 2V_{\mathrm{P}})$, $V_A = \frac{1}{4}(V_{\mathrm{Ge}} + V_{\mathrm{Zn}} - 2V_{\mathrm{P}})$, and $V_A{}^C = \frac{1}{2}(V_{\mathrm{Zn}} - V_{\mathrm{Ge}})$. Our starting point was the form factors of GaP[4] and Ge[5]; it is assumed that $V_S = V_S{}^{\mathrm{GaP}}$, $V_A = V_A{}^{\mathrm{GaP}}$, and $V_A{}^C = V_{\mathrm{Ga}} - V_{\mathrm{Ge}}$. For large wave vector $\vec{q}$ the pseudopotential curves for GaP and Ge were freehand extrapolated. For $q^2 < 4(2\pi/a)^2$ the pseudopotential curves were extrapolated to agree with $V_{\mathrm{Zn}}(q=0) - V_{\mathrm{Ge}}(q=0) = V_{\mathrm{P}}(q=0) = -\frac{2}{3}\epsilon_{\mathrm{F}}$, where ϵ_{F} is the Fermi level appropriate to the total number of valence electrons in this crystal. The method of calculation has been described elsewhere,[3] hence we just give the parameters particular to this calculation. The wave functions were expanded in a set of 69–84 plane waves; 244 additional plane waves were used through the perturbation scheme developed by Löwdin.[6] The energies and wave functions were calculated in $\frac{1}{16}$ of the BZ at 288 grid points, and the $\epsilon_2(\omega)$ integration over k space was performed by the method developed by Gilat and Raubenheimer[7] in what we call the practical Brillouin zone (PBZ). The PBZ was chosen in the following way: It can easily be shown that the region in k space surrounded by the planes $k_z = 0$, $k_z = 2\pi/c$, $k_x = k_y$, $k_y = 0$, and $k_z = \pi/a$ is completely equivalent to the usual irreducible part of the BZ (i.e., $\frac{1}{16}$ of the full BZ).

Spin-orbit corrections were carried out at a few points in the BZ by extending the zinc-blende calculation.[8] The fact that we are dealing with three kinds of atoms and a total of eight atoms in the primitive cell presents no problem, but the ratios of the cation spin-orbit contribution to the anion spin-orbit contribution have to be evaluated[9]; this leaves us with one spin-orbit parameter which we choose to be that of Ge. The procedure now would be to fit this parameter to the spin-orbit splitting $\Delta_{\mathrm{s.o.}}$ at the Γ point of the BZ. Since not much is known about $\Delta_{\mathrm{s.o.}}$ for $ZnGeP_2$, the parameter we choose was the one that gives the correct spin-orbit splitting for Ge in the diamond structure. The eigenvalues of the spin-orbit Hamiltonian involve the diagonalization of a 138×138 matrix and the large amount of computer time involved prohibits calculations over the entire BZ.

The point group of the chalcopyrite structure is $D_{2d}{}^{12}$ and the notation for symmetry points we use is that of Zak.[10] Inside square parentheses we will show the symmetry in the zinc-blende BZ from the quasicubic model; e.g., $X_1[\Sigma_2]$ denotes a wave function with symmetry X_1 originating from a Σ_2 wave function in the zinc-blende case.

In Fig. 1 we show the calculated band structure for $ZnGeP_2$ along some important symmetry directions. As one would expect from a quasicubic model for $ZnGeP_2$, this band structure shows that the most important deviations from the band structure of a zinc-blende material (when folded into the chalcopyrite BZ) are at points where two bands with the same symmetry in the $D_{2d}{}^{12}$ representation are degenerate in the latter band structure.

There is some controversy about the structure of the first gap of $ZnGeP_2$. Bendorius *et al.*[11] find an absorption edge of 2 eV with a hydrostatic pressure coefficient of $dE_{\mathrm{gap}}/dP = 1.2\times10^{-6}$ eV/bar; this indicates[12] that the first absorption edge of $ZnGeP_2$ is a pseudodirect gap $\Gamma_5[\Gamma_{15}]$

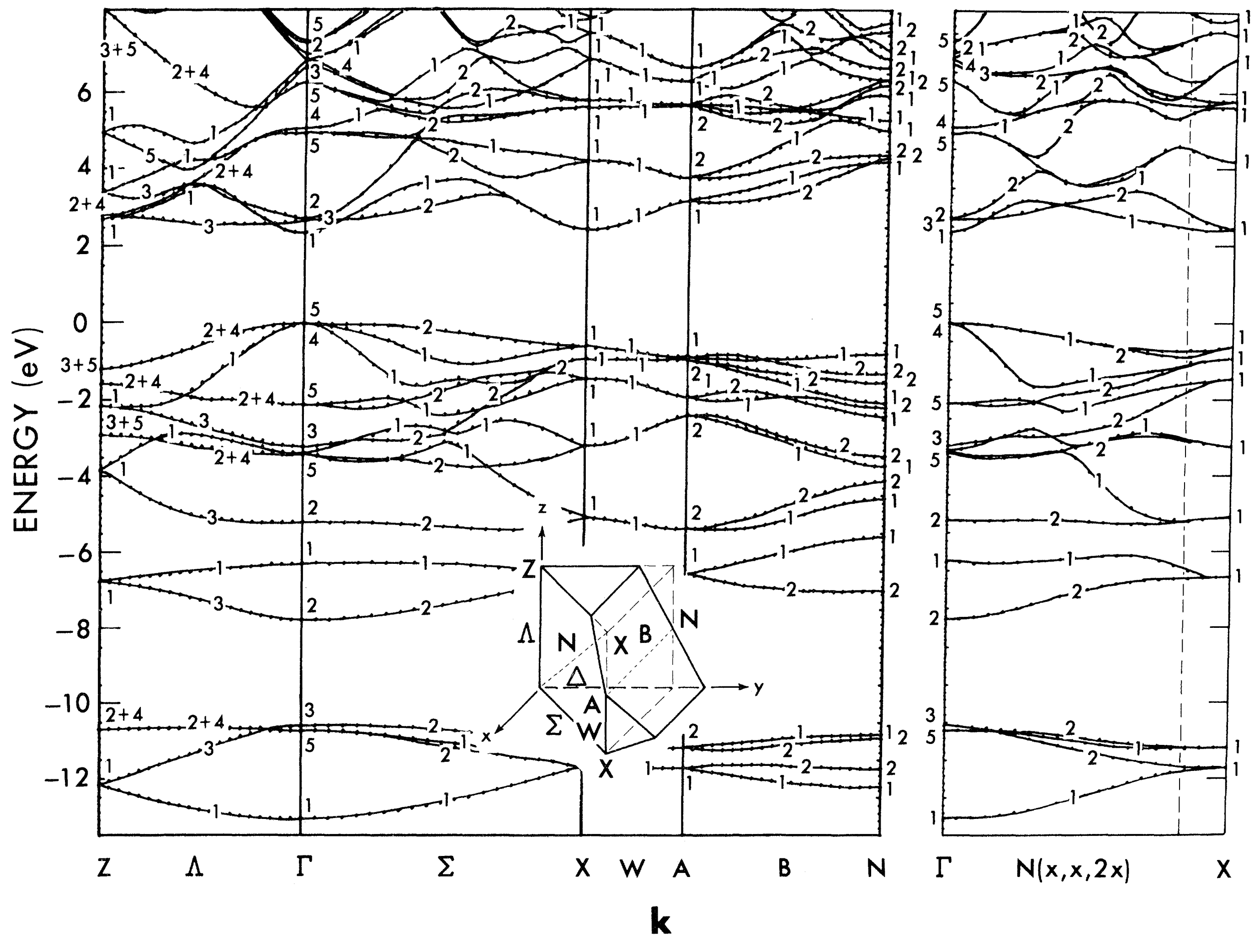

FIG. 1. Band structure of $ZnGeP_2$ along principal symmetry directions, irreducible part of the BZ and PBZ (dotted lines) showing the notation for symmetry points used in this work.

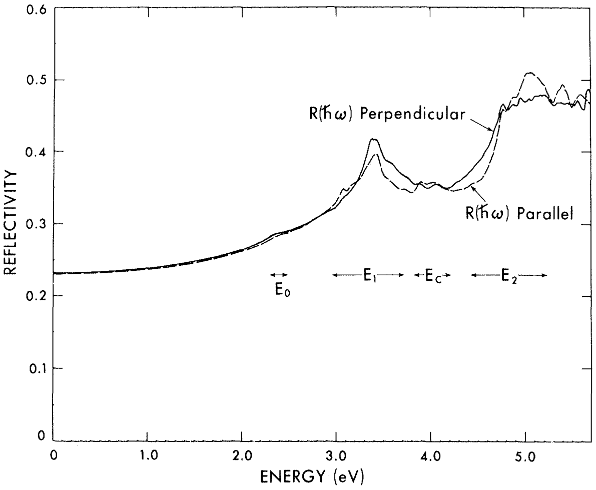

FIG. 2. Calculated reflectivity spectrum for $ZnGeP_2$ in the parallel and perpendicular polarizations.

$\rightarrow \Gamma_3[X_1]$ with small mixing of X_1 with Γ_1. But values as different as 1.81 and 2.25 eV[13] have been reported for the first absorption edge; the present calculation predicts that $ZnGeP_2$ has a direct energy gap followed by a pseudodirect gap ~0.3 eV higher in energy. Some reports indicate that the first direct gap is around 2.5 eV with a crystal field splitting Δ_{cryst} of -0.08 eV[14]; our calculated value is $\Delta_{\text{cryst}}=0.03$. First-order perturbation theory predicts that crystal field splitting depends only on the tetragonal compression of the crystal, and therefore it depends only on the slopes of the pseudopotential curves near the reciprocal lattice vectors (2, 0, 0), (2, 2, 0), and (3, 1, 2). It would be easy to adjust the pseudopotential curves to give the observed crystal splitting. Calculated matrix elements for pseudodirect transitions $\Gamma_{15}-X_1$ are too weak to be observed in the reflectivity spectrum.

Recently much attention has been concentrated on the E_1 region of the II-IV-V_2 reflectivity spectrum. In the zinc-blende materials this region contains two spin-orbit-split peaks E_1 and $E_1+\Delta_1$. In the II-IV-V_2 crystals there is much more structure. Stokowski[1] has examined $ZnSiAs_2$, $CdSiAs_2$, $CdSnAs_2$, and $CdSnP_2$. He suggests that the spectra are similar in the E_1 region and he labels the peaks $E_1(1)$, $E_1(2)$, $E_1(3)$, and $E_1(4)$. He also finds some structure at higher energies E_{C1}, E_{C2}, and E_{C3} but these do not appear in all the crystals. At this point our calculations yield information on only part of the E_1 region (see Fig. 2). The low-energy part [the first two peaks which may be $E_1(1)$ and $E_1(2)$ for small spin-orbit splitting] come from transitions in the N plane[10] in the $(x, x, 2x)$ direction, and we get two peaks when spin-orbit splitting is included. We agree with Stokowski that the four peaks cannot arise from two spin-orbit-split bands.[11] Analysis of dipole matrix elements shows the $E_1(1)$ peak to be stronger in parallel polarization, in agreement with experiment. We find two more pieces of structure above $E_1(1)$ and $E_1(2)$ which may be associated with $E_1(3)$ and $E_1(4)$, but further analysis is necessary before we can make definite assignments. From our critical point analysis, we conclude that the additional structure of the E_1 peak is mainly the result of strong mixing in the N plane $[(x, x, z)]$ originating at the crossing point of the Γ-Σ and W-L conduction bands on the $(x, x, 0)$ line, and also from strong mixing at the point X of the chalcopyrite BZ. For most zinc-blende materials, the Σ_2 valence band at $(\frac{1}{2}, \frac{1}{2}, 0)$ is almost degenerate with the L_3 valence band.[5] In the chalcopyrite structure these two points map into X; $X(L_3)$ is fourfold degenerate and $X_1(\Sigma_2)$ twofold degenerate; the tetragonal compression splits the $X(L_3)$ level into two doubly degenerate levels. When the antisymmetric cation potential is turned on, the interaction between these levels is quite strong, allowing all three transitions to the bottom of the conduction band $X_1[L_1]$. Calculations in the E_C (3.9–4.1 eV) region yield a peak which is caused by one of these transitions $X_1[L_3+\Sigma_2]\rightarrow X_1[L_1]$ between bands 11, 12 and 17, 18. This transition is allowed in both parallel and perpendicular polarization, but stronger in parallel polarization.

Most of the contribution to the E_2 structure comes from direct transitions in the Δ and Σ directions of the analog. The Δ direction folds into the Δ, Λ, and $(x, 0, 1)$ directions of the chalcopyrite BZ while the Σ direction is folded into the Σ, $(x, 0, x)$, and $(1-x, 0, 1-2x)$ directions. Partial summation over k space in these directions shows that in effect the E_2 peak is mainly a Δ, Σ peak. Additional structure in the E_2 peak comes from direct and pseudodirect transitions around the point $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ $\{[\frac{1}{4}, \frac{1}{4}, \frac{3}{4}]$ in the cubic BZ$\}$. This point is threefold degenerate in the absence of crystal field splitting and an antisymmetric cation potential, therefore the mixing is quite large. It is interesting to notice that $k=(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ is the representative k point for calculating the charge density[15] for tetragonal body-centered structures.

The intensity of the E_2 peak is considerably reduced when compared with the intensity of the

E_2 peak for zinc-blende crystals, but it is still higher than the measured E_2 peak which is smaller in magnitude than the E_1 peak for most chalcopyrites.

After this calculation was completed, Petroff *et al.*[16] did a reflectivity and wavelength-modulation experiment for $ZnGeP_2$. Their results show an E_1 and E_2 peak of the same intensity and are otherwise similar to our theoretical results. In fact, if the entire theoretical spectra is shifted to lower energies by around 0.3 eV, the agreement between theory and experiment for almost all the optical structure is very good. This is encouraging since no experimental data (except for structure constants) for $ZnGeP_2$ were used in our calculations. This result suggests that small changes in the pseudopotential form factors could give theoretical spectra in excellent agreement with experiment.

We would like to thank Dr. Y. Petroff for stimulating discussions. We would like to thank Dr. John P. Walter for discussions and help in formulating this problem in its early stages. Part of this work was done under the auspices of the U. S. Atomic Energy Commission.

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*Work supported in part by the National Science Foundation under Grant No. GH 35688.

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