PHYSICAL REVIEW B VOLUME 12, NUMBER 4 15 AUGUST 1975

Band structure and optical spectrum of AlP†

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(Received 6 January 1975)

The band structure of AlP is calculated using the empirical pseudopotential method. The pseudopotential form factors are deduced from those of Si and GaP. The band structure obtained is found to be in good agreement with recent experimental data. Based on the calculated band structure the electronic density of states, the dielectric constant, and the reflectivity spectrum are also calculated.

I. INTRODUCTION

The optical properties of AlP were paid relatively less attention in the past than those of other more commonly known III-V compound semiconductors. This is mainly due to the difficulty of growing the crystal in sufficiently pure form and its instability in a humid atmosphere.[1] Recently, Lorenz *et al.*[2] have reported the fundamental absorption edge of an AlP single crystal, which was synthesized and grown using a modified Bridgeman two-zone technique. Monemar[3] has reported absorption measurements on AlP crystals for temperatures between 4 and 300 °K, and photon energies below 3.1 eV. Also reported[4] very recently by Monemar was the measurement of the photoluminescence spectra of AlP. In both works by Monemar, the AlP crystals were grown by a synthesis technique. All the above, as well as earlier experimental results, indicate that AlP has an indirect minimum band gap, with the lowest conduction state occuring at the X point of the Brillouin zone. The values of the minimum band gap reported,[2-7] however, range from 2.50 to 2.52 eV at 4 °K, and from 2.41 to 2.7 eV at room temperature. Little is known about other critical-point band gaps, except that a weak structure near 3.6 eV in the photoluminescence excitation spectrum was observed,[4] which, because of its similarity to that in the corresponding spectra of GaP, was assigned the $\Gamma_{15v} \rightarrow \Gamma_{1c}$ exciton transition. Several calculations[8-10] of the band structure of this crystal exist in the literature. They are at variance with one another, as well as with the experimental data.

II. METHOD

In this paper, we present a calculation based on the empirical pseudopotential method.[11] It is a common practice to determine the pseudopotential form factors of a crystal by fitting salient experimental features of its optical spectrum. In the case of AlP, however, there are not sufficient experimental data to fit for the three symmetric and three antisymmetric form factors normally required for a zinc-blende type crystal, such as AlP. To get around this difficulty, we use the following procedure. First, one notices that AlP is the isoelectronic nearest neighbor to Si in the periodic table. The lattice constant of AlP is 5.42 Å,[12] which is within 0.2% of that of Si (5.45 Å). Since the symmetric form factors are the average of those of the constituent atoms, in the unit cell, i.e., Al and P, we expect that it can be well approximated by the form factors of Si. Therefore we have

$$V^S_{\mathrm{AlP}}(\underset{\sim}{G}) \equiv \tfrac{1}{2}[V_{\mathrm{Al}}(\underset{\sim}{G}) + V_{\mathrm{P}}(\underset{\sim}{G})] \approx V_{\mathrm{Si}}(\underset{\sim}{G}),$$

where $V_{\mathrm{Al(P)}}$ is the Fourier transform of the pseudopotential of Al (P) and is defined as

$$V_{\mathrm{Al(P)}}(\underset{\sim}{G}) = \frac{1}{\Omega}\int_{\mathrm{cell}} v_{\mathrm{Al(P)}}(\underset{\sim}{r}) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{r}}\, d\underset{\sim}{r},$$

where Ω $(=a^3/4)$ is the volume of the primitive cell. $v_{\mathrm{Al(P)}}(\underset{\sim}{r})$ is the pseudopotential of Al (P). The antisymmetric form factors are defined as

$$V^A_{\mathrm{Al}}(\underset{\sim}{G}) \equiv \tfrac{1}{2}[V_{\mathrm{Al}}(\underset{\sim}{G}) - V_{\mathrm{P}}(\underset{\sim}{G})].$$

What is needed to determine $V^A_{\mathrm{AlP}}(\underset{\sim}{G})$ is either $V_{\mathrm{Al}}(\underset{\sim}{G})$ or $V_{\mathrm{P}}(\underset{\sim}{G})$, and from this $V^A_{\mathrm{AlP}}(\underset{\sim}{G})$ can be

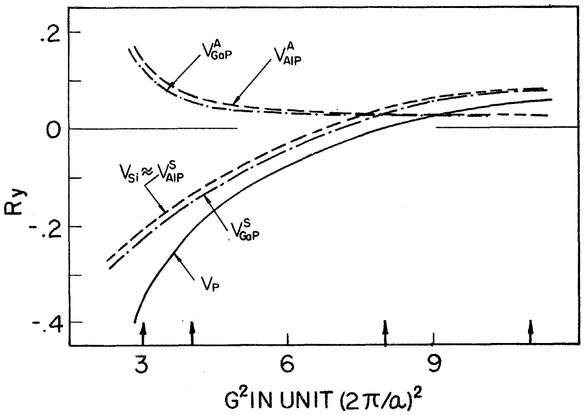

FIG. 1. Fourier transforms of the pseudopotentials for AlP, GaP, etc. The arrows on the abscissa indicate the values of q^2 at which values of the form factors are needed for the band-structure calculation.

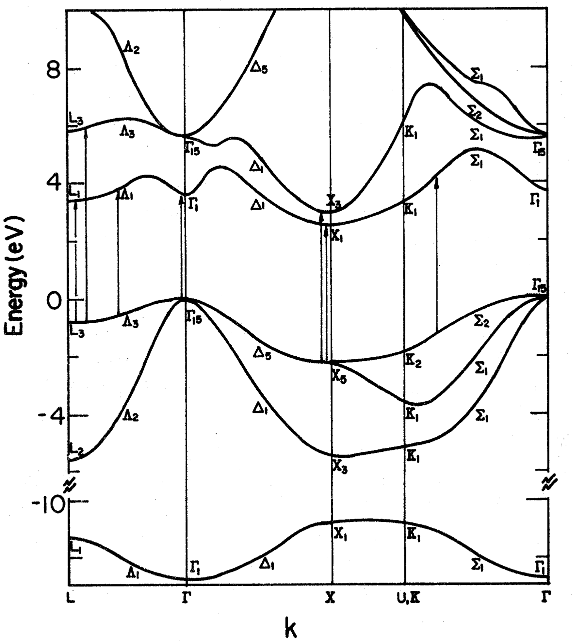

FIG. 2. $E-\vec{k}$ diagram at and on points or lines of high symmetry. The top valence states occur at Γ points of the Brillouin zone. The lowest conduction states occur at X point. The arrows indicate direct transitions believed to be mainly responsible for structures in the optical spectrum.

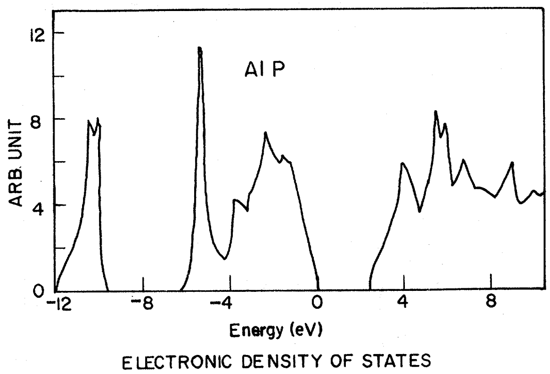

FIG. 3. Electronic density of states. The zero of the energy scale is placed at the top of the valence band.

found in the following way: We take the pseudopotential form factors of GaP, as determined by Cohen and Bergstresser,[13] and plot them as a function of G^2. A polynomial is then interpolated through these points for $V^S_{\text{GaP}}(\underset{\sim}{G})$ and $V^A_{\text{GaP}}(\underset{\sim}{G})$, respectively, as shown in Fig. 1. We refer to the curves obtained as $V^S_{\text{GaP}}(q^2)$ and $V^A_{\text{GaP}}(q^2)$. By taking the difference between the two curves, we obtain the curve $V_{\text{P}}(q^2)$, which is the Fourier transform of the atomic pseudopotential of P. We next do the same for the Si form factors[13] and take the curve obtained as an approximation to $V^S_{\text{AlP}}(q^2)$. The differences between $V^S_{\text{AlP}}(q^2)$ and $V_{\text{P}}(q^2)$ gives $V^A_{\text{AlP}}(q^2)$. The values of which at $q^2=3$, 4, and 11, as read from the curve $V^A_{\text{AlP}}(q^2)$, are 0.13, 0.08, and 0.03 Ry, respectively. We thus arrive at the following sets of pseudopotential form factors for AlP:

$$V^S(3)=-0.21,\quad V^S(8)=0.04,\quad V^S(11)=0.08,$$

$$V^A(3)=0.13,\quad V^A(4)=0.08,\quad V^A(11)=0.03.$$

Volume renormalization in this particular case affects the major band gaps on the order of only a few meV and are neglected in the present calculation. When the above form factors are used to calculate the band structure of AlP, it turns out that the indirect minimum gap, $\Gamma_{15v}\rightarrow X_{1c}$, is 2.23 eV and the lowest direct gap, $\Gamma_{15v}\rightarrow\Gamma_{1c}$ is 3.35 eV. In order to bring the calculated minimum band gap into closer agreement with the experimental results, we reduce the value of $V^A_{\text{AlP}}(11)$ by 0.015 Ry. With this minor modification the minimum gap now becomes 2.49 eV, in excellent agreement with Monemar's value of 2.505±0.01 eV. Furthermore, the smallest direct gap, $\Gamma_{15v}\rightarrow\Gamma_{1c}$, which we make no effort to fit, now has the value 3.60 eV, in very good agreement with 3.63±0.02 eV, also obtained by Monemar.

TABLE I. Experimental data of energy gaps of AlP.

$\Gamma_{15v}\rightarrow\Gamma_{1c}$ (eV)	$\Gamma_{15v}\rightarrow X_{1c}$ (eV)	Type of measurement	Source of data
•••	2.6 ~ 2.7 (300 °K)	extrapolated from absorption edge of $Ga_{1-x}Al_xP$	Ref. 7
•••	2.52 at 0 °K 2.45 at 300 °K	absorption edge	Ref. 2
•••	2.41 ± 0.04 at 300 °K	absorption edge	Ref. 3
•••	2.42 at 300 °K	reflectivity and absorption	Ref. 5
•••	2.48 at 300 °K	absorption edge of $Al_xGa_{1-x}P$	Ref. 6
3.63 ± 0.02 at 4 °K	2.505 ± 0.01 at 4 °K	photo-luminescence	Ref. 4

III. RESULTS

The $E-\underset{\sim}{k}$ diagram at selected higher symmetry

TABLE II. Comparison of important transition energies in AlP obtained by various band-structure calculations.

Transitions	(Ref. 8)	(Ref. 9)	(Ref. 10)	Present calculation
$\Gamma_{15v}\rightarrow X_{1c}$	2.14	2.4	2.3; 2.7	2.49
$\Gamma_{15v}\rightarrow\Gamma_{1c}$	3.27	~4.0	3.7; 4.6	3.60
$\Gamma_{15v}\rightarrow\Gamma_{15c}$	4.79	~5.3	5.2; 5.2	5.6
$X_{5v}\rightarrow X_{1c}$	4.22	~4.8	4.3; 4.6	4.75
$X_{5v}\rightarrow X_{3c}$	4.96	~5.6	5.1; 5.2	5.25
$L_{3v}\rightarrow L_{1c}$	3.75	~4.4	4.1; 4.4	4.15
$L_{3v}\rightarrow L_{3c}$	6.08	~6.0	6.3; 6.3	6.65

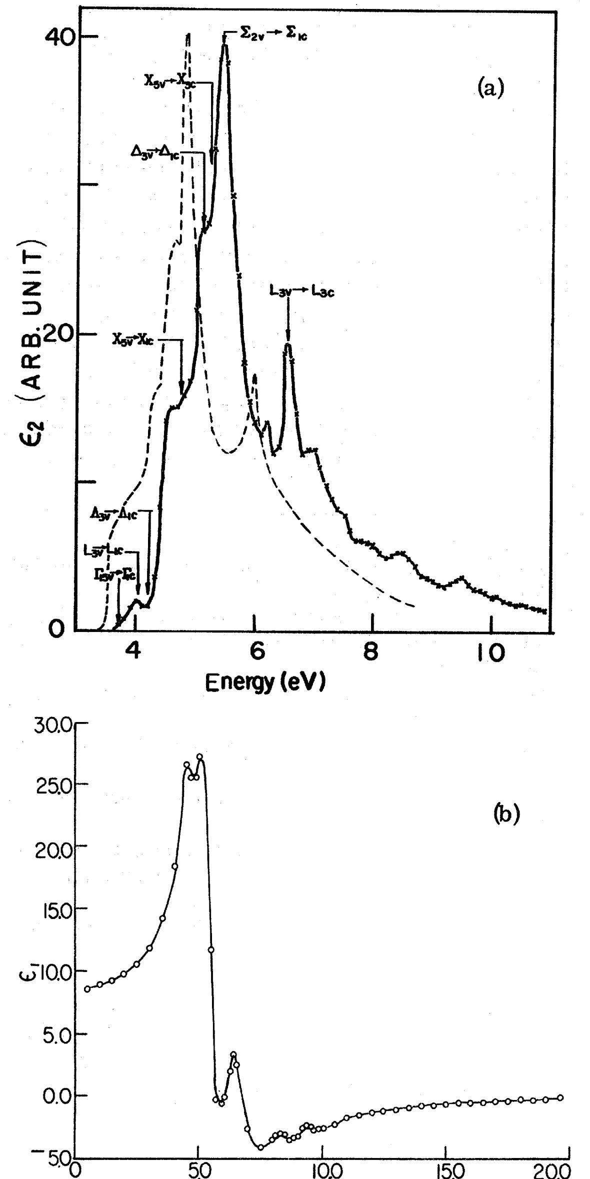

FIG. 4. (a) ϵ_2 versus photon energy. The full line is the result of the present calculation. The features in the spectrum are assigned based on the $E-\vec{k}$ diagram in Fig. 2. The dashed line is the result from Stukel and Euwema (Ref. 8). (b) ϵ_1 versus photon energy obtained from ϵ_2 by Kramer-Kronig transformation (see text for details).

points and lines is plotted in Fig. 2. No experimental data for transitions other than $\Gamma_{15v}\rightarrow X_{1c}$ and $\Gamma_{15v}\rightarrow\Gamma_{1c}$ are available at the present time. If such data were available, a more extensive judgement could be made on the accuracy of the calculated band structure. However, because of the fact that the pseudopotential form factors are obtained systemmatically from reasonable assumptions, with only one minor adjustment, we believe that the result of the present calculation is a relatively more accurate description of the band structure of AlP. Also listed in Table I are the energies of several important transitions obtained from the present calculation, along with those of previous calculations.

Very recently the total valence-band density of states for a number of common semiconductors have become available[14] from x-ray photo-electron emission experiments, which for the first time determine accurately the energies of deep-lying valence states. This information has been found very useful in judging the accuracy of a particular band-structure calculation. Figure 3 shows the density of states of AlP based on the present band structure. Numerically, we sample a uniform bcc mesh of 74 points in the irreducible wedge of the Brillouin zone, followed by a linear interpolation, which generates eigenvalues at more than 100,000 k points in the Brillouin zone. The density-of-states function obtained by these numerical procedures has a resolution essentially identical to that of those obtained by Chelokowsky *et al.*[15] for other III-V compounds, where more than four times as many sampling points were used.

We next calculate the imaginary part of the dielectric constant, $\epsilon_2(\omega)$, due to direct interband transitions. By time-dependent perturbation theory, one can show

$$\epsilon_2(\omega)=\frac{e^2\hbar^2}{3\pi m^2\omega^2}\sum_{c,v}\int\delta(E_c(\underset{\sim}{k})-E_v(\underset{\sim}{k})-\hbar\omega)\times M_{v,c}(\underset{\sim}{k})d\underset{\sim}{k},$$

where

$$M_{v,c}(\underset{\sim}{k})=|\langle U_{\underset{\sim}{k},v}|\nabla|U_{\underset{\sim}{k},c}\rangle|^2 .$$

$U_{\underset{\sim}{k},v}$ and $U_{\underset{\sim}{k},c}$ are, respectively, the periodic parts of the valence and conduction-band wave functions. In actual calculation, the integration

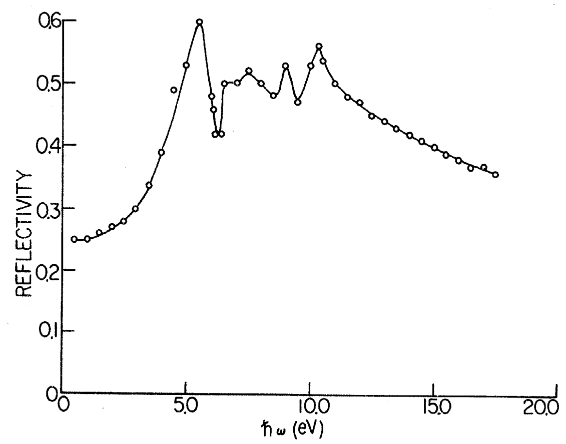

FIG. 5. Reflectivity versus photon energy (see text for details).

over $\underset{\sim}{k}$ in Eq. (2) is replaced by summation over a mesh of $\underset{\sim}{k}$ points in the irreducible part of the Brillouin zone. The numerical techniques used in the present calculation are similar to those described in the literature.[11] Figure 4 shows the calculated ϵ_2 spectrum in which the salient features have been assigned based on the band structure shown in Fig. 2. Also shown in Fig. 4 is the ϵ_2 spectrum calculated by Stukel *et al.* It is seen that the present calculated result is very similar to that of Stukel *et al.*, except for a shift of about 0.6 eV towards higher energy of the $\Sigma_{2v} \rightarrow \Sigma_{1c}$ and $L_{3v} \rightarrow L_{3c}$ peaks, although the assignments of some of the structures are different. The reflectivity, which is a more desirable quantity for direct comparison with experimental results, is given by

$$R = \frac{(\epsilon_1^2+\epsilon_2^2)^{1/2} - [2\epsilon_1 + 2(\epsilon_1^2+\epsilon_2^2)^{1/2}]^{1/2} + 1}{(\epsilon_1^2+\epsilon_2^2)^{1/2} + [2\epsilon_1 + 2(\epsilon_1^2+\epsilon_2^2)^{1/2}]^{1/2} + 1} ,$$

where ϵ_1, the real part of the dielectric constant, can be obtained from ϵ_2 by a Kramer-Kronig transformation. To do this, one needs the value of ϵ_2 over all frequencies. Since ϵ_2 can only be calculated for a limited range of energy, we attach a structureless tail of the form[11] $\beta\omega/(\omega^2+\gamma^2)^2$ to the calculated ϵ_2 spectrum given in Fig. 4. γ is set equal to 4.5 eV. β is determined by continuity. The ϵ_1 spectrum obtained is also shown in Fig. 4(b). Figure 5 shows the calculated reflection spectrum. To our knowledge no experimental reflectivity data over this range of photon energies are yet available for comparison with the theoretical result.

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*Present address: NRC Post-doctoral resident research associate at AFCRL.

†Supported in part by Air Force Cambridge Research Laboratories under Contract No. F19628-72-C-0286.

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