Electronic Band Structure and Related Properties of Cubic AlP

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A first-principles self-consistent orthogonalized-plane-wave energy-band calculation has been carried out for cubic AlP using a nonrelativistic formalism and Slater's free-electron-exchange approximation. These are the first fully convergent, fully self-consistent energy-band solutions reported for AlP. The imaginary part of the dielectric constant, spin-orbit splitting, effective masses at $k=0$, and the x-ray form factors (Fourier transforms of the electron charge density) have been calculated. Since little is known experimentally about AlP, no comprehensive comparison can be made with experimental data.

I. INTRODUCTION

VERY little study, either experimental or theoretical has been given during the past few years to the cubic III–V compound, AlP. This compound, like most semiconducting compounds and alloys of aluminum, is difficult to prepare and study because of its high melting point ($>2000°C$) and its instability in a humid atmosphere.[1,2]

The purpose of this paper is to report for AlP a theoretical calculation of the band structure, the imaginary part of the dielectric constant ϵ_2 derived from the theoretical bands, spin-orbit splitting, effective masses at $k=0$, and the form factors (the Fourier transforms of the electron charge density).

In the past couple of years a great deal of success has been attained in calculating the energy-band structures of group III-V, II-VI, and IV compounds using a first-principles self-consistent orthogonalized-plane-wave (SCOPW) model developed here at ARL. The SCOPW programs used to calculate the electronic band structure have given surprisingly good one-electron band energies for compounds such as CdS,[3] ZnS and ZnSe,[4] GaAs,[5] and Si.[6] For ZnS, GaAs, and Si, where relativity is not important, the unadjusted band energies fit all known experimental facts when Slater's exchange is used.[7]

II. SELF-CONSISTENT OPW CALCULATIONS

The orthogonalized plane-wave method of Herring[8] is used to calculate the electron energies. In the SCOPW model,[3,4] the electronic states are divided into tightly bound core states and loosely bound valence states. The core states must have negligible overlap from atom to atom. They are calculated from a spherically symmetrized crystalline potential.

The valence states must be well described by a modified Fourier series:

$$\psi_{k_0}(\mathbf{r}) = \sum B_\mu \Big[(1/\sqrt{\Omega_0}) e^{i\mathbf{k}_\mu \cdot \mathbf{r}} - \sum_a e^{i\mathbf{k}_\mu \cdot \mathbf{R}_a} \sum_c A_{c\mu}{}^a \psi_c(\mathbf{r} - \mathbf{R}_a) \Big],$$

where $\mathbf{k}_\mu = \mathbf{k}_0 + \mathbf{K}_\mu$, $\mathbf{k}_0$ locates the electron within the first Brillouin zone, $\mathbf{K}_\mu$ is a reciprocal lattice vector, R_a is an atom location, ψ_c is a core wave function, and Ω_0 is the volume of the crystalline unit cell. The coefficients $A_{c\mu}{}^a$ are determined by requiring the $\psi_{k_0}(\mathbf{r})$ be orthogonal to all core-state wave functions. The variation of B_μ to minimize the energy then results in the valence one-electron energies and wave functions.

The dual requirements of no appreciable core overlap and the convergence of the valence-wave-function expansion with a reasonable number of OPWs determines the division of the electron states into core and valence states. For Al and P the $3s$ and $3p$ states are taken as the valence states. Very good convergence is obtained when 229 OPWs are used in the series expansion.

The calculation is self-consistent in the sense that the core and valence wave functions are calculated alternately until neither changes appreciably. The Coulomb potential due to the valence electrons and the valence charge density are both spherically symmetrized about each inequivalent atom site. With these valence quantities frozen, new core wave functions are calculated and iterated until the core wave functions are mutually self-consistent. The total electronic charge density is calculated at 650 crystalline mesh points covering $1/24$ of the unit cell, and the Fourier transform $[\rho(\mathbf{r})]^{1/3}$ is calculated. The new crystal potential is calculated from the old valence charge distribution and the new core charge distribution. Then new core-valence orthogonality coefficients $A_{c\mu}{}^a$ are calculated. The iteration cycle is then completed by the calculation of new valence energies and wave functions. The iteration process is continued until the valence one-electron energies change less than 0.02 eV from iteration to iteration.

The appropriate charge density to use for both the self-consistent potential calculation and the form-

[1] O. Madelung, *Physics of III–V Compounds* (John Wiley & Sons, Inc., New York, 1964).

[2] R. J. Stirn (private communication).

[3] R. N. Euwema, T. C. Collins, D. G. Shankland, and J. S. DeWitt, Phys. Rev. **162**, 710 (1967).

[4] D. J. Stukel, R. N. Euwema, T. C. Collins, F. Herman, and R. K. Kortum, Phys. Rev. **179**, 740 (1969).

[5] T. C. Collins, D. J. Stukel, and R. N. Euwema, Phys. Rev. (to be published).

[6] D. J. Stukel and R. N. Euwema (to be published).

[7] D. J. Stukel, R. N. Euwema, T. C. Collins, and V. Smith, Phys. Rev. (to be published).

[8] C. Herring, Phys. Rev. **57**, 1169 (1940).

TABLE I. Self-consistent energy eigenvalues for cubic AlP based on Slater's and Kohn-Sham's exchange and on a four-point (Γ, X, L, W) zone sampling. 229 OPW's were used at Γ, and a comparable number of OPW's at X, L and W. The zero of energy has been placed at the top of the valence band (Γ_{15v}). All entries are in eV.

Level	Slater exchange	Kohn-Sham exchange
Γ_{15c}	4.79	4.22
Γ_{1c}	3.27	3.30
Γ_{15v}	0.0	0.0
Γ_{1v}	-11.45	-11.66
X_{3c}	2.88	1.98
X_{1c}	2.14	0.97
X_{5v}	-2.08	-2.33
X_{3v}	-5.32	-5.68
X_{1v}	-9.15	-8.98
X_{3c}-X_{5v}	4.96	4.31
X_{1c}-X_{5v}	4.22	3.30
L_{1c}	8.75	7.57
L_{3c}	5.29	4.44
L_{1c}	2.96	2.58
L_{3v}	-0.79	-0.85
L_{1v}	-5.45	-5.97
L_{1v}	-9.80	-9.75
L_{3c}-L_{3v}	6.08	5.29
L_{1c}-L_{3v}	3.75	3.43
W_{1c}	6.05	5.81
W_{4c}	4.85	3.97
W_{4v}	-2.70	-3.19
W_{2v}	-3.03	-3.54
W_{1v}	-4.99	-5.22
W_{3v}	-9.10	-8.88
W_{4c}-W_{4v}	7.55	7.16

factor calculation is the average charge density of all the electrons in the Brillouin zone. In the present self-consistent calculations, this average is approximated by a weighted average over electrons at the Γ, X, L, and W high-symmetry points of the Brillouin zone shown in Fig. 1. The weights are taken to be proportional to the volumes within the first Brillouin zone closest to each high-symmetry point. The adequacy of this approximation has been tested and the error in the energy eigenvalues has been shown to be less than 0.2 eV.[4]

In order to calculate the absorptive part of the dielectric constant ϵ_2, a pseudopotential fit is made to the relevant energy levels at the Γ, X, L, and W points. The pseudopotential technique is then used to calculate energy differences and transition matrix elements throughout the Brillouin zone.[9] In our experience, this procedure gives the ϵ_2 peaks at the correct energies, although the relative peak heights do not match experiment.

One way of taking relativistic effects into account within the framework of nonrelativistic band calculations is with first-order perturbation theory. The perturbing Hamiltonian obtained for the spin-orbit split-
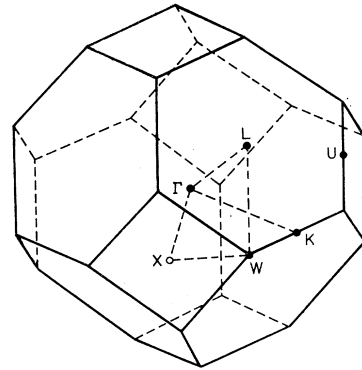

FIG. 1. The zinc blende Brillouin zone with high-symmetry points labeled.

ting is

$$\hat{H}_{so} = -\tfrac{1}{4}iq^2\boldsymbol{\sigma}\cdot[\boldsymbol{\nabla} V(\mathbf{r})\times\boldsymbol{\nabla}],$$

where $V(\mathbf{r})$ is the potential, σ is the Pauli spin operator, and q is the fine-structure constant. The Γ_{15v} SCOPW valence functions are used in this calculation.

III. RESULTS

The SCOPW model contains no adjustable parameters. However, one must supply the lattice constant. In these calculations the lattice constant used was 5.42 Å.[10] Since the accuracy of the lattice constant is not known, the dependence of the band energies upon uncertainties of the lattice constant has been estimated by making self-consistent calculations with two different lattice constants. A change of 0.2% in the lattice constant caused a shift of 0.05 eV in the band gap.

The energy bands based on Slater's exchange are shown in Fig. 2. The energy eigenvalues resulting from the self-consistent calculation using the Slater and the Kohn-Sham exchange are given in Table I. The Kohn-Sham results are shown only because they give
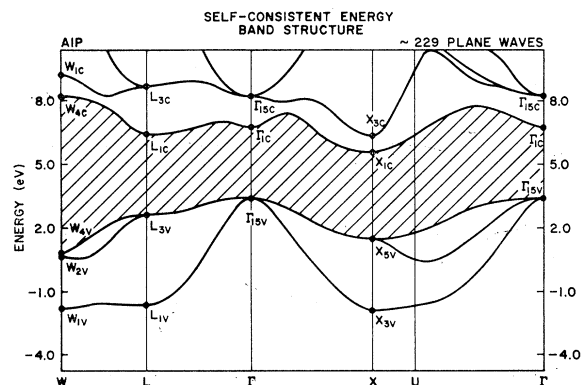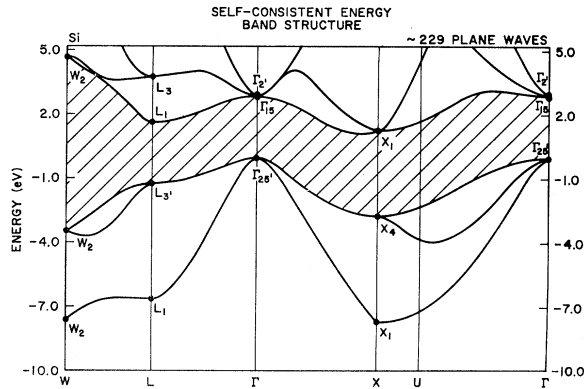

FIG. 2. SCOPW energy-band structure of AlP. The solid dots denote SCOPW energy levels. The solid lines were obtained by fitting a pseudopotential type of interpolation scheme to the SCOPW energy levels.

[9] R. N. Euwema, D. J. Stukel, T. C. Collins, J. S. DeWitt, and D. G. Shankland, Phys. Rev. **178**, 1419 (1969).

[10] R. W. G. Wycoff, *Crystal Structures* (Wiley–Interscience, Inc., New York 1951), Vol. **2**.

FIG. 3. SCOPW energy-band structure of Si. The solid dots denote SCOPW energy levels. The solid lines were obtained by fitting a pseudopotential type of interpolation scheme to the SCOPW energy levels.

one an idea of the effect of varying the exchange constant. The results obtained using Slater's exchange are the significant results for comparisons with experiment. It has been shown for group II-VI, III-V, and IV compounds that the results obtained using Slater's exchange match experiment much more closely than those obtained using the Kohn-Sham exchange.[3-7] The opposite conclusion would hold if a non-self-consistent atomic potential had been used.

The calculated indirect bandgap $X_{1c}-\Gamma_{15v}$ is 2.14 eV. Experimentally, the correct value for the bandgap is unresolved. In 1956 Hrostowski reported 3.0 for the bandgap of AlP based on the color of material.[11] Grimmeiss et al. have reported a bandgap of 2.42 eV at 20°C determined from reflectivity and transmission measurements.[12] Based on measurements of crystals of $Al_xGa_{1-x}P$ with x up to 0.3, Merz and Lynch have estimated the bandgap of pure AlP to be between 2.6 and 2.7 eV.[13]

Since AlP is isoelectronic with Si, whose band structure is better known, Herman[14] and Bassani and Yoshimine[15] and Poplavnoi[16] have attempted to relate

the band structure of AlP to that of Si. The most recent calculation of this type was that of Poplavnoi in which he found a bandgap of 2.4 eV. For comparison purposes the band structure of Si as calculated by our SCOPW model is shown in Fig. 3.[6] As one would expect, there is a great deal of similarity in the band structures.

The imaginary part of the dielectric constant ϵ_2 is given in Fig. 4. The locations of some of the major transitions are also indicated. Since no experimentally determined ϵ_2 exists, it is not possible to make a comparison. This ϵ_2 has the same shape as that of Si. It differs mainly in that all the structure is shifted about 1 eV to higher energies. It should be remembered that the detailed ϵ_2 shape is unreliable, while the peak positions are much more reliable.

In Table II theoretical Fourier components of the charge density (the x-ray form factors) are given. The Fourier components in the column headed RHF are obtained by the superposition of relativistic Hartree-Fock free atoms placed in the crystalline lattice. The columns are headed with the exchange potential used in the SCOPW model. It can be seen from Table II that for the higher reflections the RHF results agree with the Kohn-Sham results. This good agreement illustrates the well-known general result that the Kohn-Sham wave functions are very good for free-atom calculations. For the lower reflections, the RHF results are generally too small in semiconductors. This implies a concentration of valence charge in the crystal. The opposite result applies in metals where the valence charge spreads out. The Slater results generally give slightly better agreement with experiment for the lower reflections.[17]

The spin-orbit splitting at $k=0$ of the top Γ_{15} valence band into Γ_7 and Γ_8 bands has been found by the use of first-order perturbation theory on the self-consistent Slater Γ_{15v} wave functions to be 0.023 eV. Braunstein
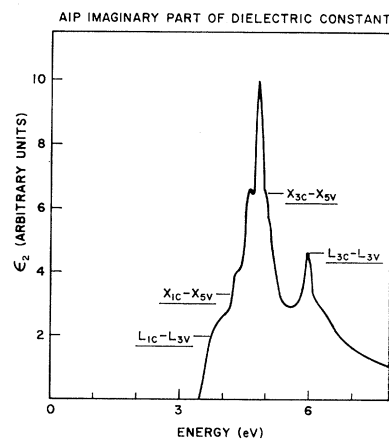
TABLE II. Theoretical AlP form factors determined by using various exchange potentials.

hkl	RHF	Slater	Kohn-Sham
111	60.15	62.07	60.94
200	5.15	5.97	5.51
220	69.94	70.49	69.32
311	46.23	46.04	45.39
222	2.83	2.84	2.82
400	59.78	60.07	59.15
331	40.43	41.26	40.49
420	3.22	2.88	3.16

[11] H. J. Hrostowski, Bell Lab. Record **34**, 246 (1956).
[12] H. G. Grimmeiss, W. Kischio, and A. Rabenau, J. Phys. Chem. Solids **16**, 302 (1960).
[13] J. L. Merz and R. T. Lynch, J. Appl. Phys. **39**, 1988 (1968).
[14] F. Herman, J. Electron. **1**, 103 (1955).
[15] F. Bassani and M. Yoshimine, Phys. Rev. **130**, 20 (1963).
[16] A. S. Poplavnoi, Fiz. Tverd. Tela **8**, 2238 (1966) [English transl.: Sov. Phys.—Solid State **8**, 1179 (1967)].

FIG. 4. Theoretical ϵ_2 curve for cubic AlP with the location of the high-symmetry point transitions shown.

[17] P. M. Raccah, R. N. Euwema, D. J. Stukel, and T. C. Collins, Phys. Rev. (to be published).

and Kane have estimated the spin-orbit splitting to be 0.05 eV based on atomic considerations.[18]

Effective masses have been calculated at $k=0$ for the top valence and bottom conduction bands. For the Γ_{15} valence band (where spin-orbit splitting has been neglected) $m^*=1.5$ for the [111] direction and 0.63 for the [100] direction. For the conduction band, $m^*=0.23$ for both the [111] and [100] directions. Braunstein and Kane[18] give 0.13 as an estimate of the electron effective mass at the $k=0$ minima.

IV. CONCLUSIONS

The validity of these reported calculations cannot be judged because of the absence of experimental results.

[18] R. Braunstein and E. O. Kane, J. Phys. Chem. Solids 23, 1423 (1962).

They are based on no assumptions other than a lattice constant of 5.42 Å (which should be accurate to about ±0.03 Å), the applicability of Slater's exchange approximation (which has been demonstrated to work for similar compounds), and the validity of the SCOPW model and programs (which have given good results on many compounds). It is hoped that this work serves to stimulate interest in this compound which has considerable potential for applications.

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Theory of Donor-Acceptor Dipairs in Semiconductors*

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From an analysis of the distribution of donors and acceptors we determine the existence and concentration of dipairs in heavily doped compensated semiconductors. The electronic energy levels of symmetrical planar dipairs are determined by perturbation theory. States corresponding both to a single bound exciton and to two bound excitons are considered. Anti-Stokes and double excitation mechanisms of luminescence are predicted for dipairs.

SINCE donor-acceptor pairs (DA) were proposed as luminescent centers in compound semiconductors over a dozen years ago,[1] an extensive literature[2] has evolved on pairs, particularly as sites for the radiative recombination of electrons and positive holes. These investigations include both unassociated pairs characterized by large DA distances, and associated pairs characterized by small DA distances.

In our recent investigations of II–VI compound semiconductors with quite high concentrations of compensated dopants, for example, $ZnS:3\times10^{-2}CuInS_2$, we have become concerned with the existence and identity of higher associates, with their electronic states, and with any unique contributions they make to optical and electrical properties. The purpose of this paper is to report preliminary analyses of the statistical mechanics of higher associates, particularly of dipairs $(DA)_2$, the quantum mechanics of their electronic states, and finally predicted contributions of dipairs to luminescent properties.

In considering the statistical mechanical problem of

[1] J. S. Prener and F. E. Williams, Phys. Rev. 101, 1427 (1956).
[2] For a review, see F. Williams, Phys. Status Solidi 25, 493 (1968).

the distribution function for pairs, dipairs, and other associates, we shall consider the zinc-blende lattice with equal concentrations of donors D^+ and acceptors A^-, both constrained to occupy the same type of substitutional lattice site, for example, cation sites. Because there are different isomers of higher associates, that is, geometrically distinguishable associates, we shall usually be concerned with the energetically most favorable isomers, for example, in the case of symmetrical nearest-neighbor dipairs, with the planar isomer. If we assume that the D^+ and A^- interact Coulombically and express the energy of formation from point defects E_d in terms of the energy of formation of the corresponding pair E_p, we find that $E_d=2.586E_p$, $2.333E_p$, and $2.000E_p$ for the planar, linear and tetrahedral dipairs, respectively. The last corresponds to zero energy of formation from pairs. The binding energy of the two pairs to form the planar dipair is $0.586\,E_p$.

The relative importance of three-body associates $(DAD)^+$ and $(ADA)^-$ and of dipairs can be estimated by considering their respective energies of formation and the following equilibrium:

$$2(DAD)^+ + 2(ADA)^- \overset{\Delta E}{\rightleftarrows} 3(DA)_2, \qquad (1)$$
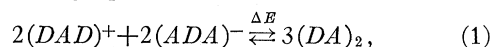
where $\Delta E = 1.76E_p$, favoring symmetrical planar di-