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Energy-Band Structure of Aluminum Arsenide

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A first-principles self-consistent orthogonalized-plane-wave energy-band calculation has been performed for cubic AlAs 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 AlAs. The imaginary part of the dielectric constant, spin-orbit splittings, effective masses, and the x-ray form factors (Fourier transforms of the electron charge density) have been calculated. The theoretical results are compared with the available experimental data.

I. INTRODUCTION

ONE of the few cubic III-V compounds about which there is very little published information is AlAs. This is in large part due to difficulties in its preparation. Single crystals of a given purity of the indirect-gap III-V compounds such as AlAs, AlP, and AlSb are generally more difficult than the direct-gap compounds to grow. This is due to the fact that these indirect band gap compounds have much higher melting point temperatures (~1740° for AlAs[1]) and hence, have considerably more chemical reaction with the surroundings. These compounds are unstable as crystals when left exposed to moist atmosphere.[2] Despite the difficulties in fabrication, there is a great deal of interest in the indirect-gap III-V compounds from a device standpoint. Their large band gaps, and consequently, their ability to operate at higher ambient temperatures, is one reason for this interest.[3]

The purpose of this paper is to report for AlAs a theoretical calculation of the band structure, the imaginary part of the dielectric constant (ϵ_2) derived from the theoretical bands, spin-orbit splittings, effective masses, 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,[4] ZnS and ZnSe,[5] GaAs,[6] and Si.[7] For ZnS, GaAs, and Si, where relativity is not important, the unadjusted band energies fit all known experimental facts when Slater's exchange approximation[8] is made for the Hartree-Fock exchange term. Kohn and Sham's exchange approximation[9] always gives bands which are too compressed, while Liberman's exchange approximation[10] results in bands which are too widely spread out. Although Slater's eigenvalues do give bands which seem to fit experiment for our self-consistent OPW model (this is the relevant fact for this paper), no solid theoretical discussion as yet exists explaining why this is so. Nor has this fact been confirmed for other energy-band models. These exchange approximations are discussed at length in another paper.[11]

II. SELF-CONSISTENT OPW CALCULATIONS

The orthogonalized-plane-wave method of Herring[12] is used to calculate the electron energies. In the SCOPW model,[4,5] 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,

$$\psi_{k_0}(r)=\sum B_u\left[\frac{1}{\Omega_0}e^{ik_u\cdot \mathrm{r}}-\sum_a e^{ik_u\cdot R_a}\sum A_{cu}{}^a\psi_c(r-R_a)\right],$$

where $k_\mu=k_0+K_\mu$, k_0 locates the electron within the first Brillouin zone, K_μ 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 that $\psi(r)$ 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

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[3] R. J. Stirn (private communication); in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press, Inc., New York, to be published).

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expansion with a reasonable number of OPW's determines the division of the electron states into core and valence states. For Al, the $3s$ and $3p$ states (for As the $4s$ and $4p$ states) are taken as the valence states. Very good convergence is obtained when 229 OPW's 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 of $\rho(r)^{1/3}$ 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 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.[5]

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.[13] In our experience, this procedure gives the ϵ_2 peaks at the correct energies. However, the relative peak heights do not match experiment because of their dependence upon the poor pseudopotential wave functions, and because of complicated electron-hole and electron-phonon interactions which are ignored in our model.

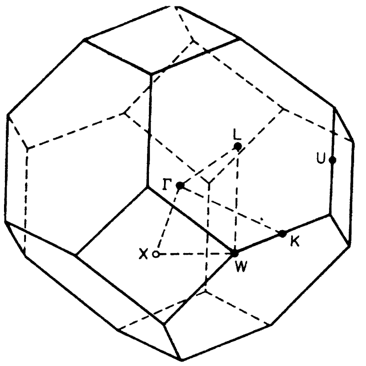

FIG. 1. The zinc-blende Brillouin zone with high-symmetry points labeled.

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 splitting is

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

where $V(r)$ is the potential, $\hat{\sigma}$ is the Pauli spin operator, and q is the fine-structure constant. The Γ_{15v} SCOPW valence wave 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 5.66 Å.[2,14,15] This lattice constant appears to be well established even though others are often quoted (for example 5.61 Å,[16] 5.62 Å,[17] and 5.63 Å[18]) in the literature. Self-consistent calculations were also made with a lattice constant of 5.63 Å to check the effects of pressure.

The energy bands based on Slater's exchange and a lattice constant of 5.66 Å are shown in Fig. 2. The energy eigenvalues resulting from the self-consistent calculation using Slater's (with lattice constant = 5.63 and 5.66 Å) and Kohn and Sham's (with lattice constant = 5.66 Å) exchange are given in Table I. The Kohn and Sham results are shown only because they give one an idea of the effect of varying the exchange constant. The results obtained using Slater's exchange and a lattice constant of 5.66 Å are the significant results for comparisons with experiment. The results obtained using a lattice constant of 5.63 Å show the effects of pressure on the band structure. 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 Kohn and Sham's exchange. The opposite

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conclusion could hold if a non-self-consistent atomic potential had been used.[5–7,11,19]

The valence-band structure is very similar to that of the other III-V compounds. It is very similar to that of AlP.[19] Unfortunately, no experimental evidence (other than the value of the direct and indirect gaps) of the band structure is currently available. The accuracy of the reported direct and indirect gap is questionable since in all cases the material measured has been impure and is composed of small crystallites.[2]

The calculated indirect band gap ($X_{1c}-\Gamma_{15v}$) is 2.38 eV. The room-temperature band gap obtained from absorption data is 2.16 eV.[20] From emission data Kischio[1] obtained a band gap of 2.13 eV at room temperature and 2.25 eV at absolute zero. Mead and Spitzer[21] have studied the photovoltaic response of surface barrier contacts on AlAs. They obtained 2.1 eV for the indirect transition and a higher transition at 2.9 eV which they identified as the direct transition.

TABLE I. Self-consistent energy eigenvalues for cubic AlAs based on Slater's (with lattice constant of 5.63 and 5.66 Å) and Kohn-Sham's (with lattice constant of 5.66 Å) 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's exchange $LC=5.63$ Å	Slater's exchange $LC=5.66$ Å	Kohn-Sham's exchange $LC=5.66$ Å
Γ_{15c}	4.62	4.57	3.96
Γ_{1c}	2.71	2.50	2.50
Γ_{15v}	0.0	0.0	0.0
Γ_{1v}	−11.53	−11.48	−11.58
X_{3c}	2.88	2.86	2.00
X_{1c}	2.37	2.38	1.22
X_{5v}	−2.04	−2.01	−2.31
X_{3v}	−5.24	−5.20	−5.59
X_{1v}	−9.60	−9.61	−9.35
$X_{3c}-X_{5v}$	4.92	4.87	4.31
$X_{1c}-X_{5v}$	4.41	4.39	3.53
L_{1c}	8.79	8.74	7.44
L_{3c}	5.28	5.25	4.42
L_{1c}	2.67	2.57	2.15
L_{3v}	−0.81	−0.80	−0.90
L_{1v}	−5.27	−5.22	−5.75
L_{1v}	−10.15	−10.14	−9.99
$L_{3c}-L_{3v}$	6.09	6.05	7.44
$L_{1c}-L_{3v}$	3.48	3.37	4.42
W_{1c}	5.93	5.83	5.60
W_{4c}	5.10	5.09	4.19
W_{4v}	−2.55	−2.51	−3.02
W_{2v}	−2.89	−2.83	−3.37
W_{1v}	−4.96	−4.93	−5.23
W_{3v}	−9.57	−9.58	−9.31
$W_{4c}-W_{4v}$	7.65	7.60	7.21

Additional evidence of the indirect nature of the minimum energy gap has been reported on the basis of optical absorption studies on the AlAs-GaAs system by Black and Ku.[14] An abrupt change of slope between the two linear regions of the energy-gap-versus-composition curve occurred at 2.0 eV and 50 mole% AlAs. Extrapolation toward the Al-rich end of the composition range gave a band-gap value in good agreement with that obtained from the photoresponse and optical-absorption data. However, Black and Ku concluded that the energy gap in this system does not follow a linear interpolation between the direct transition minima of the terminal compounds.

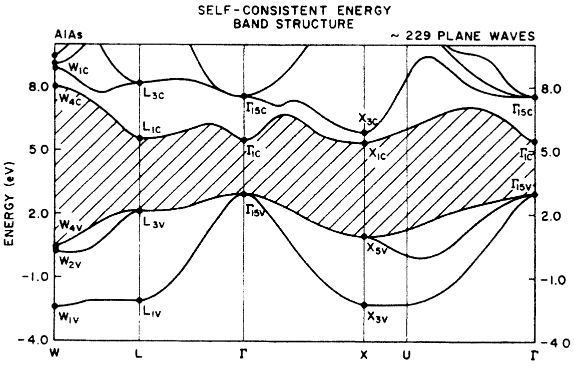

FIG. 2. SCOPW energy-band structure of AlAs. The solid dots denote SCOPW energy levels. The solid lines were obtained by fitting a pseudopotential type interpolation scheme to the SCOPW energy levels.

The imaginary part of the dielectric constant (ϵ_2) is given in Fig. 3. The location of some of the major transitions are also indicated. Since no experimentally determined ϵ_2 exists it is not possible to make a comparison. It should be remembered that the detailed ϵ_2 shape is unreliable, while the peak positions are much more reliable. The ϵ_2 curve of AlAs is very similar to that of AlP.[19]

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

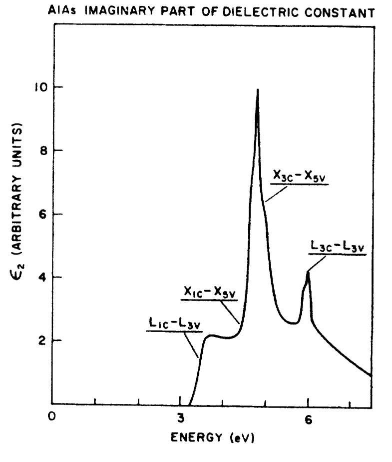

FIG. 3. Theoretical ϵ_2 curve for AlAs with the location of the high-symmetry-point transitions shown.

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TABLE II. Theoretical AlAs form factors determined using various exchange potentials. The calculations were made with a lattice constant of 5.66 Å.

hkl	RHF	Slater	Kohn-Sham
111	119.59	121.88	120.37
200	70.52	71.56	70.62
220	131.43	132.24	130.49
311	97.15	97.17	95.96
222	58.91	59.04	58.37
400	113.46	114.11	112.44
331	85.25	86.48	85.05
420	52.19	52.42	51.81
224	100.84	102.30	100.33
115	76.36	77.35	75.90
333	76.36	77.23	75.79

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. From Table II it can be seen that for the higher reflections the RHF results agree with the results obtained using Kohn and Sham's exchange potential. This good agreement illustrates the well-known general result that the Kohn and Sham wave functions are very good for free-atom calculations. For the low reflections the RHF results are generally too small in semiconductors. The opposite result applies in metals where the valence change spreads out. The Slater results generally give slightly better agreement with experiment for lower reflections.[22]

The spin-orbit splitting at $k=0$ of the top Γ_{15v} 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 0.36 eV. Braunstein and Kane[23] have estimated the spin-orbit splitting to be 0.29 eV based on atomic considerations.

Effective masses have been calculated for the top valence band at the Γ point and for the bottom conduction band at the Γ and X points. For the Γ_{15} valence band (where spin-orbit splitting has been neglected) $m_\Gamma^*=1.06$ for the [111] direction and 0.49 for the [100] direction. For the conduction band $m_\Gamma^*=0.15$ for both the [111] direction and the [100] direction. Braunstein and Kane gave 0.11 as an estimate of the conduction-band electron effective mass at the $k=0$ minima. The effective mass at the X point (where the lowest minimum in the conduction band occurs) was calculated to be $m_X^*=2.0$ in the [100] direction. From an analysis of carrier concentration data, Whitaker has calculated an electron effective mass of 0.5.[15]

IV. CONCLUSIONS

The validity of these calculations cannot be fully judged because of the absence of comprehensive experimental results. It should be remembered that these results are based completely on first principle with no adjustment to fit experiment. The only experimental data used is the lattice constant. In the final analysis the validity of these results depends upon the applicability of Slater's exchange approximation and the validity of the SCOPW model. Past experience on many compounds gives us considerable faith in the validity of these results.

Note added in proof. We are indebted to Lorenz for observing that the spin-orbit splitting raises the theoretical value of the top Γ point valence band by about 0.12 eV, making the resulting theoretical indirect band gap of 2.26 eV agree more closely with experiment.

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