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Convergence Study of a Self-Consistent Orthogonalized-Plane-Wave Band Calculation for Hexagonal CdS

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The electronic band structure of hexagonal CdS is calculated by means of a self-consistent orthogonalized-plane-wave model, using Slater's approximation for the exchange term. In order to determine the number of plane waves to be used in the Fourier expansion of the valence states, a convergence study is discussed for the starting model and for the final self-consistent model. It is concluded that the starting model is unsatisfactory from a convergence standpoint, while the self-consistent model has sufficiently well converged for 245 plane waves. The resulting band structure is presented for the high-symmetry points of the Brillouin zone. The spin-orbit splitting of the top valence band and the effective mass along the c axis of the zone are calculated from this band structure. The results are then compared with experiment.

I. INTRODUCTION

Relatively few calculations from first principles of the band structure of wurtzite (commonly called hexagonal) II–VI compounds have been performed, in comparison with the large amount of work which has been reported on the cubic group IV or III–V semiconductors. The II–VI compound which has received some attention is ZnS. The first calculation of wurtzite ZnS using the orthogonalized-plane-wave (OPW) method of Herring[1] was that of Herman and Skillman.[2] They used a potential which was constructed from a superposition of atomic potentials and a wave function composed of a linear combination of approximately 50 plane waves. Other preliminary calculations of wurtzite ZnS band structure have been carried out by the augmented-plane-wave[3] and pseudopotential[4] methods. For CdS, some of the present authors have reported earlier[5] the energy band structure of this compound using the OPW method with 147 plane waves. While the results of this earlier calculation were self-consistent, the number of plane waves used was insufficient to produce a true convergence, and the results were adjusted empirically to fit the experimentally determined value of the band gap.

The purpose of this paper is to present the results of a fully convergent and self-consistent OPW band calculation of wurtzite CdS, to discuss the convergence with respect to the number of plane waves of the starting model and of the self-consistent model, and to compare the resulting self-consistent band structure with experiment.

In Sec. II, general information as to the lattice parameters used, notation, and calculating procedure is given. Then in Sec. III a convergence study of the CdS energy bands derived from a simple superposition of atomic potentials (labeled "starting model") is presented and compared with the convergence of the energy bands of a hypothetical wurtzite structure Ge crystal calculated using the same type of potential. The results of the starting model are then taken as the zeroth iteration results for the self-consistent model. The self-consistent convergence study is presented in Sec. IV, and the band picture is given and compared with experiment in Sec. V.

II. GENERAL INFORMATION

The wurtzite CdS lattice parameters used in the calculation were obtained from the work of Balkanski and des Cloizeaux[6] and are listed in Table I. We have followed Slater[7] in our choice of coordinate system for defining the unit cell of the lattice and the position of the four atoms within the cell. That work was also followed in the application of group-theoretical techniques to the problem with one exception. The labeling of the Γ_5 and Γ_6 irreducible representations used in this paper is reversed from Slater's notation to conform with the notation commonly used by most experimentalists.[8] The Brillouin zone with the symmetry points labeled is shown in Fig. 1.

Following the usual OPW formalism, the atomic states of Cd and S are divided into tightly bound core

Table I. CdS lattice parameters used in this calculation.

A[a]	C[b]	U[c]
4.137 Å	6.719 Å	0.37506

[a] Length of lattice vector perpendicular to the c axis.
[b] Length of lattice vector parallel to the c axis.
[c] The Cd lattice and S lattice are separated by a distance in the c direction of cu.

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

[2] F. Herman and S. Skillman, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961), p. 20.

[3] U. Rossler and M. Lietz, Phys. Status Solidi **17**, 597 (1966).

[4] J. C. Phillips [J. Phys. Soc. Japan Suppl. **21**, 3 (1966)] comments on work of T. K. Bergstresser and M. L. Cohen (to be published).

[5] T. C. Collins, R. N. Euwema, and J. S. DeWitt, J. Phys. Soc. Japan Suppl. **21**, 15 (1966).

[6] M. Balkanski and J. des Cloizeaux, J. Phys. Radium **21**, 825 (1960).

[7] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1965), Vol. II.

[8] D. C. Reynolds, C. W. Litton, T. C. Collins, Phys. Status Solidi **9**, 645; **12**, 3 (1965).

TABLE II. Valence states (atomic states simulated by OPW's).

S	Cd
$3s^2$ $3p^4$	$5s^2$

states (which are assumed to see a spherically symmetric potential) and loosely bound valence states (which are Fourier analyzed into OPW's). The choice of valence states is shown in Table II. Although in the free atoms the $4d$ core-state energy of Cd is higher than the $3s$ valence-state energy of S, the Cd $4d$ state must be considered a core state. Attempts to include this state among the valence states failed; the additional valence-band energies attributable to the $4d$ state of Cd appear high up in the conduction band. It is concluded from this that any reasonable number of plane waves completely fails to simulate the complicated d-state structure. The $3s$ state of S must then be considered a valence state because of its large overlap with the Cd $4d$ state.

Because the core electrons are assumed to see a spherically symmetric potential, their wave functions have the form

$$\Phi_{n,l,m}(\mathbf{r})=Y_{l,m}(\theta,\phi)P_{nl}(r)/r, \tag{1}$$

where $Y_{l,m}$ is a spherical harmonic. The valence wave functions are Fourier expansions of plane waves orthogonalized to the core states and are of the form

$$\Psi_\nu(\mathbf{r})=\sum_{\mathbf{k}} B_{\mathbf{k}}\Big[e^{i\mathbf{k}\cdot\mathbf{r}}-\sum_{\text{atoms}}\sum_{n,l} e^{i\mathbf{k}\cdot\mathbf{R}_a}A_{n,l;\mathbf{k}}\Phi_{n,l;\mathbf{k}} \times(\mathbf{r}-\mathbf{R}_a)\Big], \tag{2}$$

where the $A_{n,l;\mathbf{k}}$ are chosen so that Ψ_ν is orthogonal to all core wave functions. (For a detailed outline of the OPW method the reader is referred to Woodruff.[9]) The presence of the core function in Ψ_ν leads by the variational procedure to the matrix eigenvalue problem

$$\mathbf{HB}=\lambda\mathbf{UB}, \tag{3}$$

where $\mathbf{H}$ and $\mathbf{U}$ are Hermitian matrices and $\mathbf{U}$ is also positive definite.

A convenient method of solving this problem on a computer is to decompose $\mathbf{U}$ into the product

$$\mathbf{U}=\mathbf{LL}^\dagger, \tag{4}$$

where $\mathbf{L}$ is a lower triangular matrix ($L_{ij}=0$ for $i<j$).[10]

TABLE III. Core-shift energies used in the zeroth iteration.

S	Cd
−1.5575 Ry	−1.4130 Ry

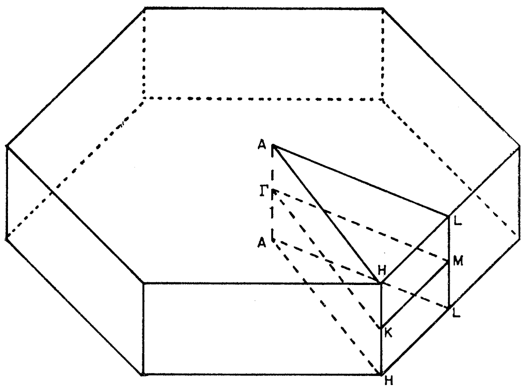

FIG. 1. Brillouin zone of CdS.

Using this decomposition, Eq. (3) then reduces to the equivalent problem

$$\mathbf{L}^{-1}\mathbf{H}(\mathbf{L}^{-1})^\dagger\mathbf{L}^\dagger\mathbf{B}=\lambda\mathbf{L}^\dagger\mathbf{B}. \tag{5}$$

The matrix $\mathbf{L}^{-1}\mathbf{H}(\mathbf{L}^{-1})^\dagger$ can then be diagonalized by a Jacobi method[11] or, better, can be decomposed into tridiagonal form and a technique of Householder used to determine only the desired number of eigenvectors and eigenvalues.[12,13] The virtue of using Eq. (5) to solve the eigenvalue problem is that only one diagonalization must be performed rather than the customary two. The calculation of $\mathbf{L}$ and $\mathbf{L}^\dagger$ can be quickly performed using almost no scratch storage. By means of this technique, we were able to handle 75 by 75 complex matrices on an IBM 7094 with a $32K$ core storage capacity.

III. STARTING MODEL

As the starting model for the self-consistent study we form our potential for CdS in exactly the same way that Herman and Skillman[2,14] did for ZnS. The free atomic Cd and S wave functions are found using Slater's free-electron exchange approximation[15]; that is, the exchange potential is assumed proportional to the cube root of the electron density. The potential is calculated for the free atoms packed into the wurtzite lattice. Core-shift energies are obtained by summing the near-neighbor potentials at a S and a Cd site. The calculated core shifts are displayed in Table III. Using the free atomic core states and the resulting potential and core shifts, the valence-band structure was calculated at the center of the Brillouin zone (Γ point) for varying numbers of plane waves. As can be seen from Fig. 2 the convergence of this model is so poor for the number of

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[9] T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. V, p. 367.

[10] B. Wendroff, *Theoretical Numerical Analysis* (Academic Press Inc., New York).

[11] J. Greenstadt, *Mathematical Methods for Digital Computer*, edited by A. Ralston and H. S. Silf (John Wiley & Sons, Inc., New York, 1960), p. 84.

[12] J. H. Wilkinson, Computer J. **3**, 23 (1960).

[13] J. H. Wilkinson, Computer J. **1**, 90 (1958).

[14] The authors are indebted to Dr. Frank Herman and his group for cooperating in a detailed comparison of their starting model energy-band programs.

[15] J. C. Slater, Phys. Rev. **81**, 385 (1951).

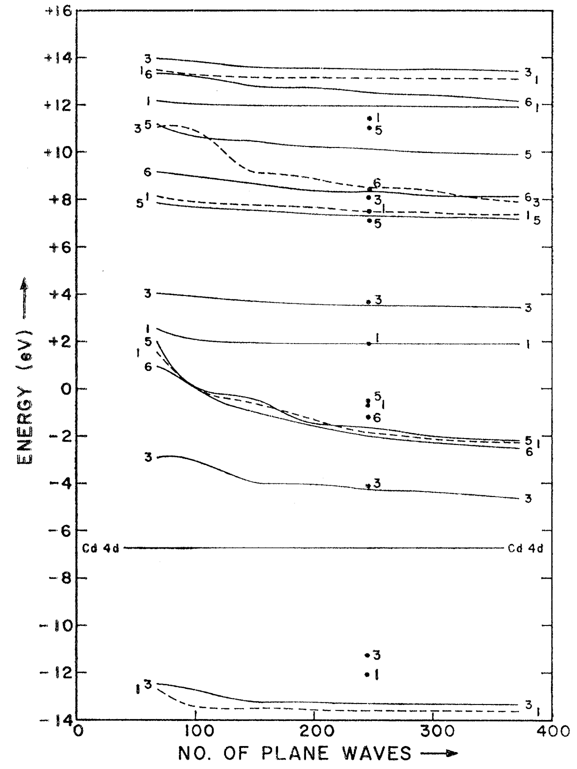

FIG. 2. The lowest energy eigenvalues versus the number of plane waves at the Γ point of wurtzite CdS using the "Starting Model." The numbers labelling each line refer to the irreducible representations of the Γ point except for the Cd 4*d* level, which is the core energy of the 4*d* state of Cd. The points above 245 plane waves are the self-consistent results with the energy of the conduction bands of the two models put equal. The zero energy value of the vertical axis is arbitrary.

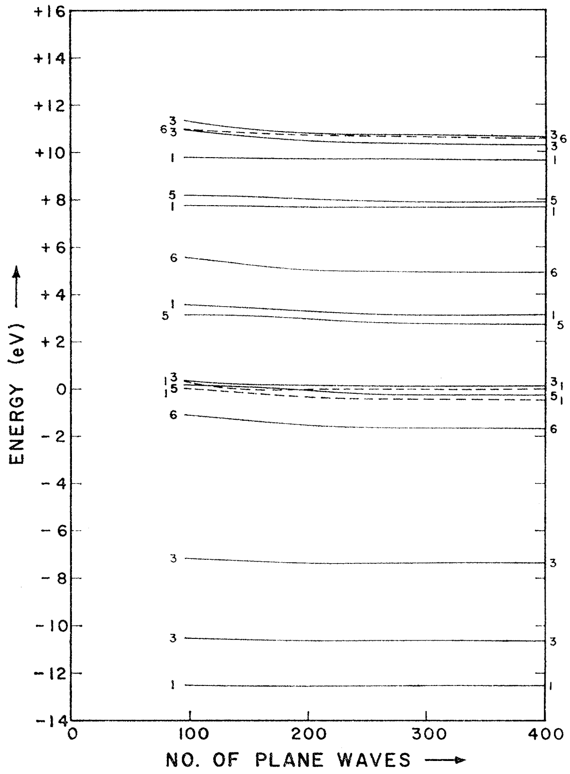

FIG. 3. The lowest energy eigenvalues versus the number of plane waves at the Γ point of wurtzite Ge using the "Starting Model." The numbers labeling each line refer to the irreducible representations of the Γ point. The zero energy value of the vertical axis is arbitrary.

plane waves tested that the band structure depends critically upon the number used. The expeirmental band gap[16] of 2.58 eV representing the difference in energies between the first Γ_5 state and the third Γ_1 state is soon exceeded.[17]

In order to determine whether similar convergence difficulties exist for Ge, a study was made of (nonexistent) wurtzite Ge.[18] That is, the potential was formed in the manner prescribed above with Ge atoms at each S and Cd lattice site. An ideal wurtzite lattice was assumed with the nearest-neighbor distance taken to be the same as the actual nearest-neighbor distance in Ge. As can be seen from Fig. 3, the convergence of the results for wurtzite Ge is much less critically dependent upon the number of plane waves than the calculations for CdS. This difference in convergence is thought to be caused by the Cd 4*d* state, which is considered a core state but has properties intermediate between core and valence states. This state mixes strongly with the valence states via the orthogonalization terms. Thus, the change to the Hamiltonian due to overlap of the atomic functions becomes much more significant for the Cd 4*d* state than for any of the other more deeply lying core states.

IV. SELF-CONSISTENT MODEL

In the iterated band model, the valence electron density should properly be obtained by integration over all states of the Brillouin zone. We have approximated this integral, however, by calculating the valence-electron density at the six high-symmetry points indi-

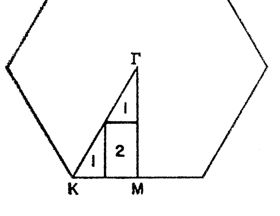

FIG. 4. A plane in the Brillouin zone which includes the Γ, *K*, and *M* point which shows the area in the twelfth of the zone which is closest to each of the points.

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[16] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[17] Dr. F. Herman has suggested that this lack of convergence might be due in part to the fact that our starting model (unlike his) ignores atomic overlap when calculating core wave functions and energies. Consequently, our core and valence electrons have different Hamiltonians, and so the valence electron energies might be expected to "worm down into the core."

[18] Our program at present will only handle wurtzite symmetry.

cated in Fig. 1, and selectively weighting the separate contributions. The weighting used is indicated in Fig. 4, which depicts a hexagonal section of the Brillouin zone divided into regions closest to Γ, K, and M. The M and L points were weighted twice as heavily as the other four points since twice as many electron states occur near these points in the zone.

Our iteration procedure closely follows the work of Herman.[19] The valence wave functions have the form of Eq. (2). The resulting valence-electron density contains plane-wave terms labeled $\rho_{\text{pw}}{}^v$ and terms involving core states which are labeled $\rho_c{}^v$. The $\rho_c{}^v$ expression is always treated in its spherically symmetrized form—$(\rho_c{}^v)_{\text{s.s.}}$—about the Cd and S sites. A program validity check which keeps track of the number of electrons in the unit cell,

$$\int_{\Omega_0} \rho_{\text{pw}}{}^v d\tau + \int_{\Omega_0} (\rho_c{}^v)_{\text{s.s.}} d\tau + \int_{\Omega_0} \rho^c d\tau = 2(Z_{\text{Cd}} + Z_{\text{S}}), \quad (6)$$

agrees to within 10^{-5} of an electron. Here Ω_0 is the unit cell volume, $Z_{\text{Cd}} = 48$, $Z_{\text{S}} = 16$, and ρ^c is the core density.

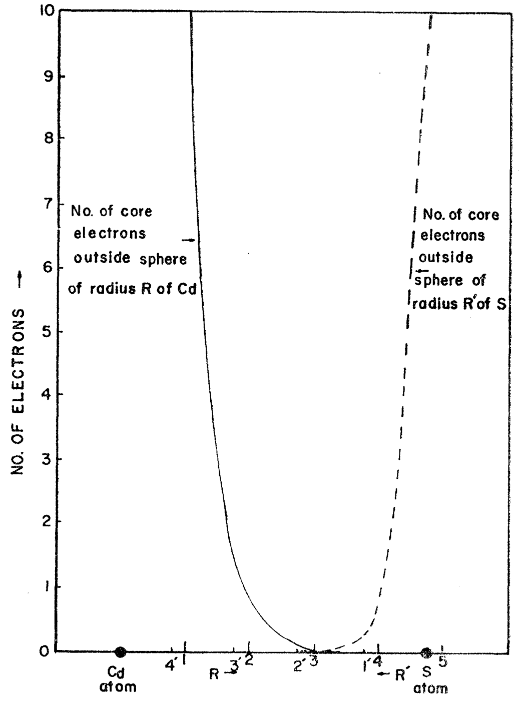

FIG. 5. A plot of the electron density outside the spherical core of both Cd and S. The unprimed numbers along the horizontal axis refer to the distance from the Cd atom (atomic units) and the primed number to the distance from the S atom (atomic units).

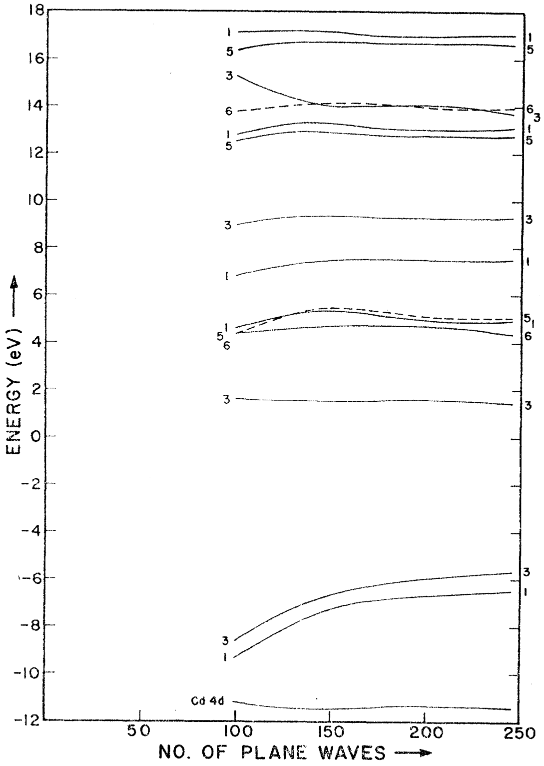

FIG. 6. The lowest-energy eigenvalues versus the number of plane waves at the Γ point of wurtzite CdS using the "Self-Consistent Model." The numbers labeling each line refer to the irreducible representations of the Γ point except for the Cd 4d which represents the core energy of the 4d state of Cd. The zero energy value of the vertical axis is arbitrary.

The calculation of the contribution to the potential seen by the core due to the zero Fourier component of $\rho_{\text{pw}}{}^v$ and the unbalanced nuclear charge

$$Q_a = Z_a - \int_a \rho_c d\tau - \int_a (\rho_c{}^v)_{\text{s.s.}} d\tau \quad (7)$$

is treated by writing the potential in the form

$$V(r) = V_M + (4\pi/3\Omega_0) Q_t r^2, \quad (8)$$

where V_m is determined by a Madelung calculation.[20] The constant charge background contributes the parabolic term in which $Q_t = 2(Q_{\text{S}} + Q_{\text{Cd}})$. This potential is cut off at a radius where the nearest-neighbor charge distribution becomes significant, as shown in Fig. 5. The cutoff is required because of the increasing complexity due to the overlapping wave functions. Changing the cutoff by a reasonable amount changes the resulting core energies by several eV; even the deepest core levels shift by this amount because of the rearrangement of the outer charge distribution.

In order to determine the Fourier components of the exchange potential, $\rho^{1/3}$ is separated into a smooth part

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[19] F. Herman, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 3.

[20] G. Liebfried, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1955), Vol. 7, Part 1, p. 132.

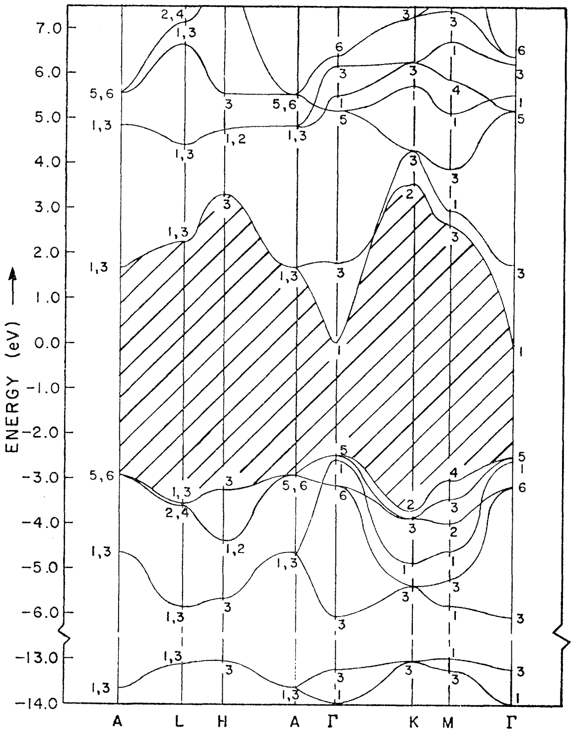

FIG. 7. The E-versus-K curves of the self-consistent calculation of wurtzite CdS using 245 plane waves. The numbers along the lines above the symmetry points represent the irreducible representation of the particular point group. The line between the Γ and A symmetry points was calculated, but the other lines were drawn by eye. The energy of the Cd $4d$ state with zero energy for the conduction band at the Γ point is -18.98 eV.

TABLE IV. The lowest energy eigenvalues at the six symmetry points and the irreducible representations to which they belong for a maximum K^2 value of 7.64 Ry or approximately 245 plane waves. The zero value has been taken as the lowest point in the conduction band.

Irr. rep.	Energy (eV)	Irr. rep.	Energy (eV)	Irr. rep.	Energy (eV)
				M_3	7.40
				M_1	6.77
				M_4	5.87
Γ_6	6.41			M_1	5.13
Γ_3	6.20			M_3	3.86
Γ_1	5.51	K_3	7.28	M_1	2.94
Γ_5	5.20	K_3	6.26	M_3	2.62
Γ_3	1.77	K_1	5.73	M_4	-3.02
Γ_1	0.00	K_3	4.30	M_3	-3.46
Γ_5	-2.50	K_2	3.55	M_2	-3.98
Γ_1	-2.59	K_2	-3.72	M_1	-4.63
Γ_6	-3.18	K_3	-3.86	M_3	-5.27
Γ_3	-6.09	K_1	-4.88	M_1	-5.81
Γ_3	-13.21	K_3	-5.39	M_1	-13.00
Γ_1	-13.99	K_3	-13.05	M_3	-13.25
A_5, A_6	5.58	H_3	5.55	L_2, L_4	7.18
A_1, A_3	4.85	H_1, H_2	4.75	L_1, L_3	6.67
A_1, A_3	1.69	H_3	3.32	L_1, L_3	4.41
A_5, A_6	-2.91	H_3	-3.25	L_1, L_3	2.28
A_1, A_3	-4.64	H_1, H_2	-4.40	L_1, L_3	-3.52
A_1, A_3	-13.66	H_3	-5.68	L_1, L_3	-3.60
		H_3	-13.06	L_2, L_4	-5.85
				L_1, L_3	-13.14

and a strongly core-dependent part.

$$\rho^{1/3}=\{\rho^{1/3}-[(\rho_c^v)_{\text{s.s.}}+\rho^c]^{1/3}\}+[(\rho_c^v)_{\text{s.s.}}+\rho^c]^{1/3}. \quad (9)$$

The first term is evaluated over a crystal mesh of 729 inequivalent points and the second spherically symmetric term is evaluated by radial integrals over the S and Cd lattice sites, combined with structure factors in the usual way.[9]

Self-consistent runs utilizing the above procedure were made for 99, 147, 209, and 245 plane waves. Iteration of core and valence distributions continued until successive valence energies differed by less than 0.05 eV. The resulting valence energy band structure at the Γ point, together with the core $4d$ energy of Cd, is shown in Fig. 6. The over-all structure of the bands is well established at 147 plane waves, despite the fact that the band gap was only 2.05 eV as compared with the experimental value of 2.58 eV. By 245 plane waves, convergence appears to be sufficiently well established although the lowest Γ_1 and Γ_3 states are still rising slightly. The upper valence band and lower conduction bands are varying very little and perhaps randomly. The band gap at the Γ point has risen to 2.50 eV and the structure of the bands at all six symmetry points is well defined. It is thus concluded that adequate convergence has been obtained.

The convergence behavior of the starting model and the self-consistent model are strikingly different. About the only similarity is the behavior of the fourth Γ_3 band which dips sharply down between 100 and 147 plane waves. The self-consistent model is much more convergent. One reason is the neglect of atom overlap when calculating core states in the starting model (see Ref. 17 in Sec. III). Another reason is that the valence-electron distribution is much smoother when described by plane waves than when described by a complicated superposition of spherically symmetric atomic functions. We have no explanation for the systematic rise of the bottom Γ_1 and Γ_3 bands in the self-consistent model.

V. CdS ENERGY-BAND STRUCTURE

The band structure resulting from the self-consistent calculation using 245 plane waves is shown in Fig. 7 and the term values at the six symmetry points are tabulated in Table IV. The band gap of 2.50 eV was surprisingly close to the experimental value of 2.58 eV. This accidental agreement does not imply an over-all accuracy of this amount, but because of the lack of direct experimental information, no empirical adjustments were made. To estimate the uncertainty in the final band structure, the self-consistent 147 plane-wave results were adjusted by raising the zero Fourier coefficient of the potential by 0.34 Ry to match the 245 plane-wave band gap. The resulting top valence and

TABLE V. Effective mass parallel to the c axis at the Γ point of the top valence and bottom conduction bands. The results are in units of the free-electron mass.

Band	Theoretical	Experimental
Top valence band	3.6	5[a]
Bottom conduction band	0.22	0.17[b]

[a] See Ref. 16.
[b] See Ref. 22.

lower conduction band energies differed by less than 0.2 eV, with the ordering of the bands unchanged. It is thus concluded that the uncertainty in the final band energies for this model is less than 0.2 eV.

It can also be noted that the energy of the Cd $4d$ state changes considerably from the starting model (see Fig. 2) to that of the self-consistent calculation (see Fig. 6). The starting model energy is about that assigned experimentally by Cardona and Harbeke.[21] We suggest that perhaps the experimentally observed transitions are due to states other than the Cd $4d$ states; however, no estimation of how well the self-consistent model gives relative core and valence energies can yet be made.

The effective masses (neglecting spin-orbit effects) of the top valence and bottom conduction bands at the Γ point in the direction of the c axis were obtained from the curvature of the bands (Table V). The result for the conduction band is quite close to the experimental value.[22] The result for the valence hole mass is also excellent considering that the spin-orbit splitting of the valence band was not included.

The spin-orbit splitting of the valence band was also calculated at the Γ point using first-order perturbation theory (Table VI). The uncertainty in the theoretical numbers reflects the uncertainty of the crystal-field splitting of the Γ_5-Γ_1 energies of the top valence band. Despite the uncertainties, these values are close to the experimental values.

TABLE VI. Splitting of the top valence bands at Γ, with spin-orbit effects included as a perturbation. Units are eV.

Bands	Theoretical	Experimental
$\Gamma_9-\Gamma_7$	0.02–0.03	0.016
$\Gamma_7-\Gamma_7$	0.04–0.07	0.057

A rough fit of the OPW energy-band results by a pseudopotential model[23] has been made. From this simplified model, a calculation of the imaginary part of the dielectric constant, $\epsilon_2(\omega)$, in the optical and near-ultraviolet regions, assuming direct transitions only, was made.[24] The preliminary results show the characteristic A peak (which arises from the large density of states found in regions that include the Γ-M axis) and the characteristic B peak (which arises from the large density of states found in regions that include the L point) which have been observed by Cardona and Harbeke[21]; however, the peaks are a few tenths of an eV higher in energy than the experimentally observed values. A much more detailed study is presently being performed and will be reported later.[25]

VI. CONCLUSIONS

Many approximations have been made in the present model: The exchange potential is approximated by Slater's $\rho^{1/3}$ simplification; electron correlation is neglected; relativistic and spin-orbit effects are ignored during the iteration; the integral over the Brillouin zone is approximated by a weighted sum over high-symmetry points; core states are assumed nonoverlapping, and are assumed to see a spherically symmetrical potential; and ρ_c^v is spherically symmetrized. It is satisfying that the resulting band gap, effective masses, spin-orbit splittings, and imaginary part of the dielectric constant agree as closely with experiment as they do. The convergence of the upper valence states and lower conduction states seems adequate for 245 plane waves. The relevant band energies seem well determined for this model to within 0.2 eV.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Frank Herman for several very valuable conversations and communications. They also wish to thank Captain Louis Zaytoun and Andrew O'Hare for excellent programming assistance.

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[21] M. Cardona and G. Harbeke, Phys. Rev. **137**, A1467 (1965).
[22] W. S. Baer and R. N. Dexter, Phys. Rev. **135**, A1388 (1964).
[23] J. C. Phillips, Phys. Rev. **112**, 685 (1958).
[24] T. C. Collins, R. N. Euwema, and J. S. DeWitt, Bull. Am. Phys. Soc. **12**, 321 (1967).
[25] T. C. Collins, J. S. DeWitt, and R. N. Euwema (to be published).