Semiempirical tight-binding band structure of II_3V_2 semiconductors: Cd_3P_2, Zn_3P_2, Cd_3As_2, and Zn_3As_2

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Semiempirical tight-binding electronic-energy-band structures of the following II_3V_2 semiconductors are presented: Cd_3P_2, Zn_3P_2, Cd_3As_2, and Zn_3As_2. The zinc-blende approximation of the real crystal structure was used. The calculations were carried out within the nearest- and second-nearest-neighbor approximation and the single s and p atomic-orbital basis set. The tight-binding parameters were obtained empirically by fitting calculated density of valence states and reflectivity spectra to the empirical spectrum. The presented parametrization of the band structures provides an accurate representation of the valence bands and an adequate description of the lowest and most important conduction bands of II_3V_2 semiconductors.

I. INTRODUCTION

Cd_3P_2, Zn_3P_2, Cd_3As_2, and Zn_3As_2, members of II_3V_2 group compound semiconductors have recently been intensively investigated.[1-34] The photovoltaic properties of Zn_3P_2 (Ref. 1) and unusual transport properties of Cd_3As_2 have attracted some interest for future potential applications. Recently, a method to produce superlattices containing Zn_3P_2 and Zn_3As_2 layers has been reported.[2] Cadmium phosphide Cd_3P_2 has been found to show light emission at low temperatures in the near-infrared region.[3] Cadmium arsenide Cd_3As_2 is a degenerate semiconductor with an exceptionally large mobility, low effective mass, and a small energy gap.[4]

To understand many of the optical and electrical properties of devices, it is necessary to know the structure of the energy bands. The semiempirical–tight-binding (SETB) method[35] seems to be the simplest method available for obtaining a quantitatively useful semiconductor band structure. In this method, band energies are obtained by diagonalization of a Hamiltonian matrix that describes interaction between atomiclike orbitals localized on neighboring atoms. Many studies of the bulk and surface electronic structure of the tetrahedrally coordinated semiconductors have been successfully carried out within the nearest-neighbor approximation and the single s and p atomiclike orbital basis set.

The major difficulty in a theoretical work originates from the exceptionally complicated crystal structures of II_3V_2 compounds and a large unit cell.

The crystal structure of phosphide-type compounds (Cd_3P_2, Zn_3P_2) is a primitive tetragonal lattice with a unit cell containing 16 P atoms and 24 anion atoms. The space group belongs to D_{4h}^{15}.[36]

The crystal structure of Zn_3P_2 and Cd_3P_2 is presented in Fig. 1. As shown in Fig. 1, the cation atoms (Zn, Cd) in a unit cell are located on four equally spaced planes perpendicular to the c axis, whereas the phosphorus atoms lie on parallel planes midway between two adjacent cation planes. Each cation atom is tetrahedrally coordi-

nated with phosphorus atoms as their nearest neighbors, while a phosphorus atom is surrounded by cation atoms located at six of the eight corners of a cube, the two "vacant" sites being at diagonally opposite corners of a cubic face. An examination of Fig. 1 shows that there are two kinds of phosphorus layers and four of cation. The cation layers differ in the positions of cation "vacancies."

The arsenic-type compounds (Cd_3As_2, Zn_3As_2) crystallize in a body-centered-tetragonal structure with 64 As
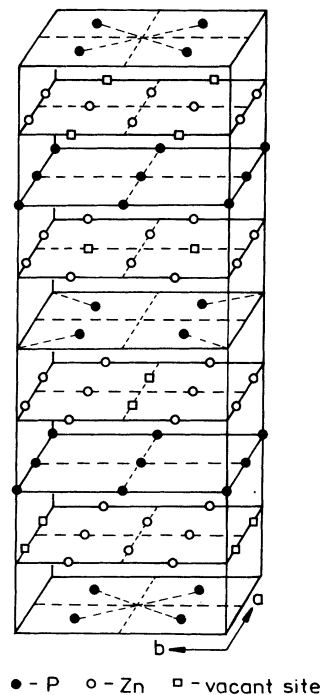

FIG. 1. The atoms system in the unit cell of phosphoric compounds. In the picture, the system of atoms for α-Zn_3P_2 according to Ref. 36 is presented (the c axis is prolonged twice). To obtain the structure of Cd_3P_2, Zn atoms for Cd ones should be changed.

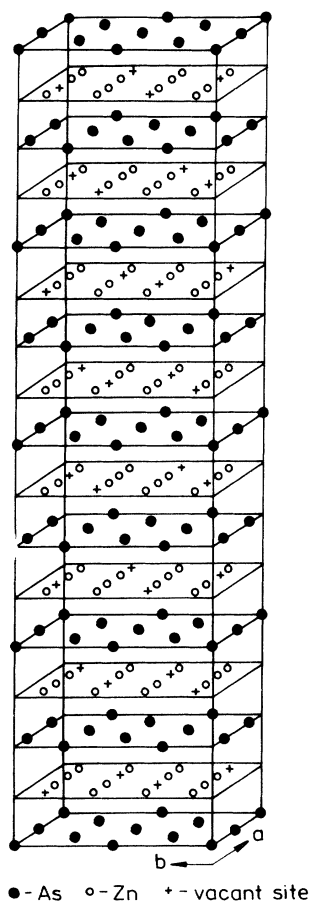<u>50</u> 7331

● - As   ○ - Zn   + - vacant site

FIG. 2. The atoms system in the unit cell of arsenic compounds. In the picture, the system of atoms for αZnAs according to Ref. 37 is presented (the c axis is prolonged twice). To obtain the structure of Cd_3As_2, Zn atoms for Cd ones should be changed.

atoms and 96 cation atoms (Zn, Cd) per unit cell. Its space group belongs to C_{4v}^{12}.[37] Such a large unit cell contains a large number of valence electrons (512 valence electrons per unit cell). (See Fig. 2.)

For arsenides, the unit cell can be divided into eight equal spaces with metal atoms on each plane and arsenic atoms at $z = \frac{1}{16}c$ below the planes. Similar to the case of phosphides, each metal atom is tetrahedrally coordinated with arsenic atoms as nearest neighbor, while the As atom is surrounded by metal atoms located at six of the eight corners of a cube, the two "vacant" sites being at diagonally opposite corners of a cubic face. Therefore, the arsenides crystal structure differs from the phosphides only in the metal-vacancy site arrangement (see Fig. 1).

The tight-binding-structure calculations for II_3V_2 semiconducting compounds including the real crystal structures requires diagonalization of the matrix Hamiltonian of large dimension. Including only one s and three p states for each atom, one obtains the matrix Hamiltonian of 160×160 for phosphorus and 640×640 for arsenic compounds. Therefore, some approximation leading to the reduction of Hamiltonian dimensions is needed. This

means that some simplifications of the crystal structure should be made.

Lin-Chung[5] has performed pseudopotential calculations for the energy-band structures of Cd_3As_2, Zn_3As_2, Cd_3P_2, and Zn_3P_2. The crystal structure has been simplified by filling all the vacancy sites. This approximation consists of viewing the II_3V_2 crystal as an antifluorite structure with metal ion "vacancies" distributed periodically throughout the crystal. Calculated in this way, band structures resemble closely that of III-V and II-VI compounds. The results of these calculations give the overestimated energy gap and very narrow three upper valence bands as compared to the experimental UV and x-ray photoemission data.[6-8]

In our earlier papers,[9,10] we have shown that an accurate parametrization of the valence bands of II_3V_2 compounds can be achieved within a SETB model by use of the zinc-blende approximation of real crystal structure. In Ref. 9, following Harisson's idea of an universal SETB model, we constructed an sp^3 universal model for II_3V_2 compounds. Next, to improve the description of valence bands of Zn_3P_2 and Zn_3As_2 individually we selected tight-binding matrix elements including second-nearest-neighbor interactions.[10] Our approximation was based on the close resemblance of the experimentally obtained spectral responses in photoemission[7] and reflectivity studies[11-16] of II_3V_2 compounds to those of the III-V zinc-blende one.

In Ref. 10, we presented the structure of Zn_3P_2 using a zinc blende and anitifluorite approximation of the real crystal structure. Both approximations differ from the real structure in opposite ways. The antifluorite structure contains more metal atoms, whereas the zinc-blende structure contains less metal atoms than the real one. However, the number of valence electrons in the unit cell must be the same in both cases. In both approaches, there is one anion atom in the unit cell, which supplies five electrons. The remaining three electrons are supplied by fictitious metal atoms, which replace the real metal atoms.

The antifluorite unit cell was formed by simply filling the metal vacant sites by fictitious atoms. It gives two metal atoms per unit cell, which supplies three valence electrons. The valence bands of resulting band structure have bonding character and are formed from anion and cation states. The lower conduction bands are formed mainly from the atomic states of the one of cation in the antifluorite unit cell. They have rather nonbinding character. Curvature of the lower conduction band is determined mainly by interactions with the second-nearest neighbors.[10]

The zinc-blende approximation was formed by replacing three atoms of Cd (or Zn) with two equivalent fictitious atoms having three valence electrons each but the same atomic energies of s and p states as removed metal atoms. As a consequence, the real structure was replaced by the zinc-blende one with one metal atom in the unit cell. The resulting band structures are similar to those for III-V semiconducting compounds, but having a greater degree of metalicity.

In this paper, we concentrate on obtaining the set of

tight-binding parameters properly describing not only the valence bands, but the lowest conduction band as well. The aim of our parametrization is to acquire the tight-binding energy-bands structure properly reproducing the experimentally obtained density of valence states (DOVS) and reflectivity spectra, simultaneously. The simultaneous proper description of conduction and valence bands is very important in calculation of the values of deep-level energy. In our calculations, we use the zinc-blende approximation of a real crystal structure.

II. PARAMETERS

The matrix elements of the Hamiltonian were obtained empirically by use of the Lin-Chung pseudopotential band-structure calculation and other available (experimental) data[5,7,12,14−16,27] by the method described below. In selecting a method for the matrix elements determination, we concentrated on producing energy bands which density of states properly reproduced experimentally obtained[7] density of valence states and calculated reflectance spectra are in accordance with experimental ones. The band structures were fitted at the Γ, X, and L points, where the Hamiltonian was block diagonal. The energies of the upper valence bands at the X and L points have been extracted from the experimental UV and x-ray photoemission data given in Ref. 7. Unfortunately, it was impossible to obtain unambiguous experimental data for the lower s-like valence band at the X and Γ points because their signal overlapped with strong Zn $3d$ corelike levels for Zn_3P_2 and Zn_3P_2 and Zn_3As_2 and Cd $4d$ corelike levels for Cd_3P_2 and Cd_3As_2, lying in the same spectral range.[7,20] So we took the energies of X_1^v and Γ_1^v states, as well as the energy of Γ_{15}^c, from Lin-Chung's pseudopotential calculations.[5] The energy of Γ_1^c was assumed to be of the value of the direct energy gap at room temperature. Additionally, following Vogl, Hjalmarson, and Dow,[38] we took the difference between the anion and cation s and p on-site matrix elements of the Hamiltonian to be proportional to the difference in neutral free-atom Hartree-Fock orbital energies.

During the fitting procedure, the pseudopotential data of energy of conduction bands at X and L points were taken as an input data. They were, next, adjusted by a suitable choice of parameters in such a way so as to reproduce properly the main feature of experimental reflectivity spectra.

The band-structure energy at high-symmetry points are listed in Table I. We set the top of the valence bands $E(\Gamma_{15}^v)$ to be zero, as is commonly done.

The tight-binding parameters determined by the scheme described above are listed in Table II. The notations in the table are those of Talwar and Ting,[39] and Slater and Koster.[40] Only nine first- and nine second-nearest-neighbor parameters were enough to describe properly the experimental DOVS and reflectivity spectra. The zinc-blende approximation was used, which resulted in the 8×8 Hamiltonian matrix.

It is interesting to compare our parameters for II_3V_2 semiconductors with parameters obtained for III-V compounds with the same anion atoms and II-V compounds

involving Zn or Cd atoms. By comparing our parameters to parameters for III-V compounds (presented in Refs. 39, 41, and 42) we can see that the general trends are conserved. Equivalent II_3V_2 parameters have the same signs and similar absolute values. However, there are greater differences between diagonal matrix elements $E_{xx}(0,0,0)1$ and $E_{ss}(0,0,0)1$, which determine metalicity of semiconductor. As a consequence, an adequate energy difference between Γ_1^c and Γ_{15}^v is less for the II_3V_2 semiconductors. The values of $E_{xx}(0,1,1)$ parameters are positive and $E_{xx}(1,1,0)$ negative, so they have the same physical meaning as for tethrahedrally bonded semiconductors.

TABLE I. Tight-binding parameters (in eV) obtained in the present work for zinc-blende models of Zn_3P_2, Cd_3P_2, Zn_3As_2, and Cd_3As_2. The notation is that of Refs. 39 and 40.

Interaction integrals	Zn_3P_2	Cd_3P_2	Zn_3As_2	Cd_3As_2
$E_{ss}(0,0,0)0$	−8.123	−8.403	−8.710	−9.019
$E_{ss}(0,0,0)1$	−0.767	−0.537	−1.541	−1.341
$E_{xx}(0,0,0)0$	0.913	1.05	0.372	0.086
$E_{xx}(0,0,0)1$	3.737	4.116	3.000	2.910
$4E_{ss}(0.5,0.5,0.5)$	−4.683	−3.087	−5.090	−3.683
$4E_{sx}(0.5,0.5,0.5)01$	3.149	1.905	3.461	2.119
$4E_{sx}(0.5,0.5,0.5)10$	4.031	3.980	3.938	3.631
$4E_{xx}(0.5,0.5,0.5)$	1.413	1.462	2.260	1.859
$4E_{xy}(0.5,0.5,0.5)$	5.764	6.289	4.891	4.300
$4E_{xx}(0,1,1)0$	−2.240	−2.450	−1.200	−1.200
$4E_{xx}(0,1,1)1$	−0.710	−1.073	−1.280	0.855
$4E_{xy}(1,1,0)0$	0.538	1.311	0.941	1.266
$4E_{xy}(1,1,0)1$	0.362	−0.878	0.886	0.110
$4E_{xx}(1,1,0)0$	0.864	0.927	1.191	1.107
$4E_{xx}(1,1,0)1$	0.978	0.820	0.782	0.543
$4E_{sx}(1,1,0)0$	0.000	0.000	−0.100	−1.000
$4E_{sx}(1,1,0)1$	−1.260	−1.300	0.000	0.000
$4E_{sx}(0,1,1)1$	−0.100	−0.500	−0.400	−0.350

TABLE II. Energy levels of Zn_3P_2, Cd_3P_2, Zn_3As_2, and Cd_3As_2 (in eV) at Γ, X, and L critical points using the parameters of Table I. The zero of energy is considered at the top of the valence band.

Level	Zn_3P_2	Cd_3P_2	Zn_3As_2	Cd_3As_2
Γ_1^v	−10.40	−9.47	−11.35	−10.5
Γ_{15}^v	0.00	0.00	0.00	0.00
Γ_1^c	1.55	0.53	1.00	0.10
Γ_{15}^c	5.40	5.14	4.48	4.24
X_1^v	−9.10	−8.76	−9.9	−9.45
X_3^v	−6.10	−6.10	−6.4	−6.10
X_5^v	−2.00	−2.00	−2.15	−1.95
X_1^c	2.03	1.76	1.35	1.40
X_3^c	2.28	2.31	1.65	1.43
L_1^v	−9.38	−8.91	−10.35	−9.74
L_2^v	−5.55	−5.92	−5.70	−5.66
L_3^v	−1.05	−1.10	−1.20	−1.05
L_1^c	1.41	0.69	0.53	0.28
L_3^c	6.60	6.7	6.40	5.30

On the other hand, the $E_{xy}(1,10)$ parameters, which determine the position of L_3^v energy, should be positive and greater than the $E_{xx}(1,1,0)$ ones. As can be seen, it is not true in all cases. That fact, however, may be interpreted as neglecting the contribution of the three center integrals.[41,42]

Since there are so many parameters involved, but so few reliable experimental data exist, we are not able to give a consistent method to obtain all the first- and second-nearest-neighbor tight-binding parameters as in[41,42] for III-V and II-VI semiconductors. Nevertheless, the general trends for first- and second-nearest-neighbor parameters are conserved.

III. RESULTS AND DISCUSSION

Figure 3 shows the II-V tight-binding structures obtained by using our parameters in comparison with Lin-Chung's pseudopotential band structures.[5] The shapes of the valence and lower conduction bands are generally similar to those calculated by Lin-Chung. However, the upper three valence bands obtained from our calculations are considerably broader than those predicted by Lin-

Chung. This is in accordance with experiment.[7]

In Fig. 4, theoretically calculated reflectance spectra, as compared to experimental results obtained by several authors,[12,14−16,27] are presented. The fit is good for all compounds especially for the energies up to 5.0–6.0 eV.

The calculated DOVS are shown in Fig. 5. In order to compare with experimental x-ray photoemission spectra (XPS) we convoluted our "raw" density of states by a Gaussian of width $\gamma = 0.2$ eV.

As can be seen, the three-peak structure of the valence bands for all compounds are well reproduced and the peaks' positions in the calculated DOVS match perfectly well those in the observed XPS spectra.

It should be emphasized that there are some differences in experimentally obtained density of valence band states between II-V phosphides and II-V arsenides. The second peak on the experimental DOVS curve of Cd_3P_2 and Zn_3P_2 is very well shaped and moved to higher energy contrary to Zn_3As_2 and Cd_3As_2, where it is weakly visible in the background of the lowest energy peak. To reproduce properly this feature in the calculated DOVS curve, the high value of $4E(1,1,0)1$ parameter was needed. This parameter determines the position of the second
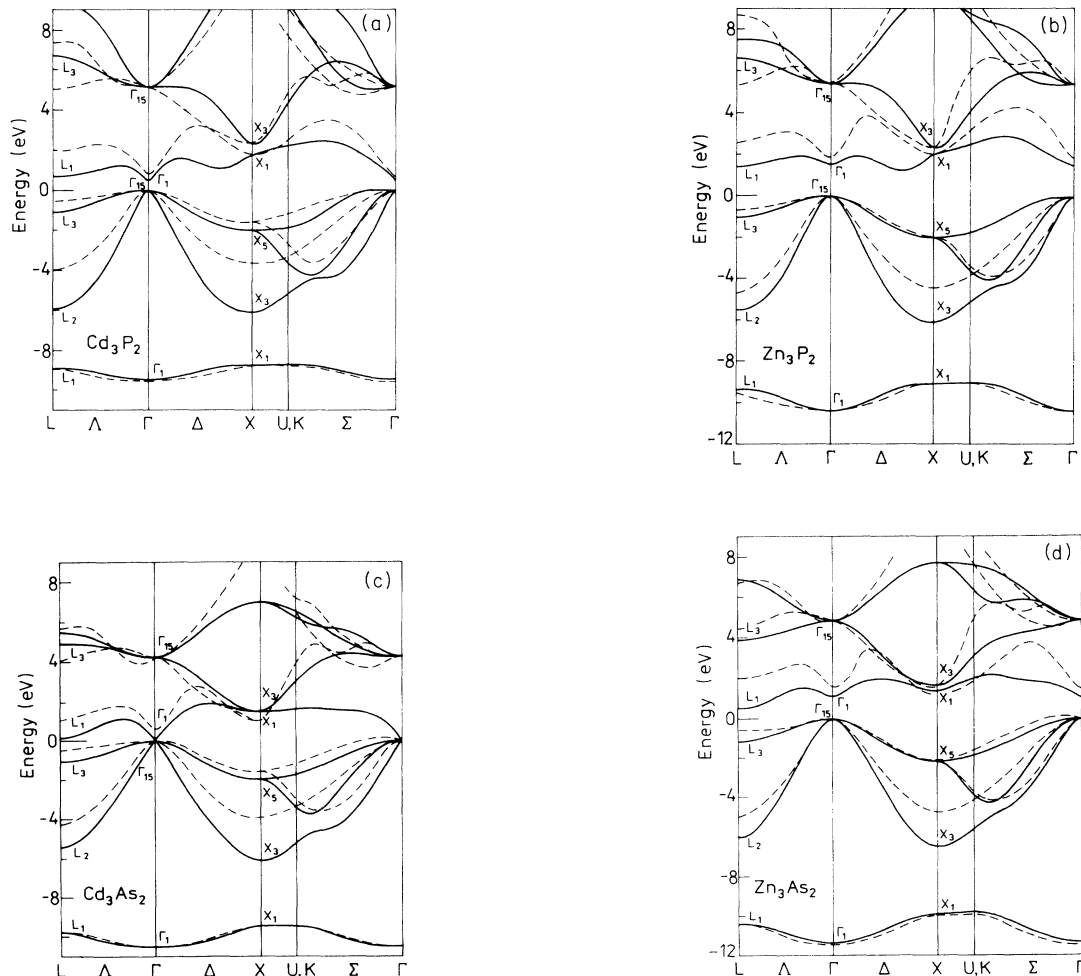

FIG. 3. The tight-binding sp^3 band structures of the II_2V_3 compounds based on the zinc-blende structure model (solid line), the Lin-Chung pseudopotential band structure of II_3V_2 (Ref. 5) (dashed line).
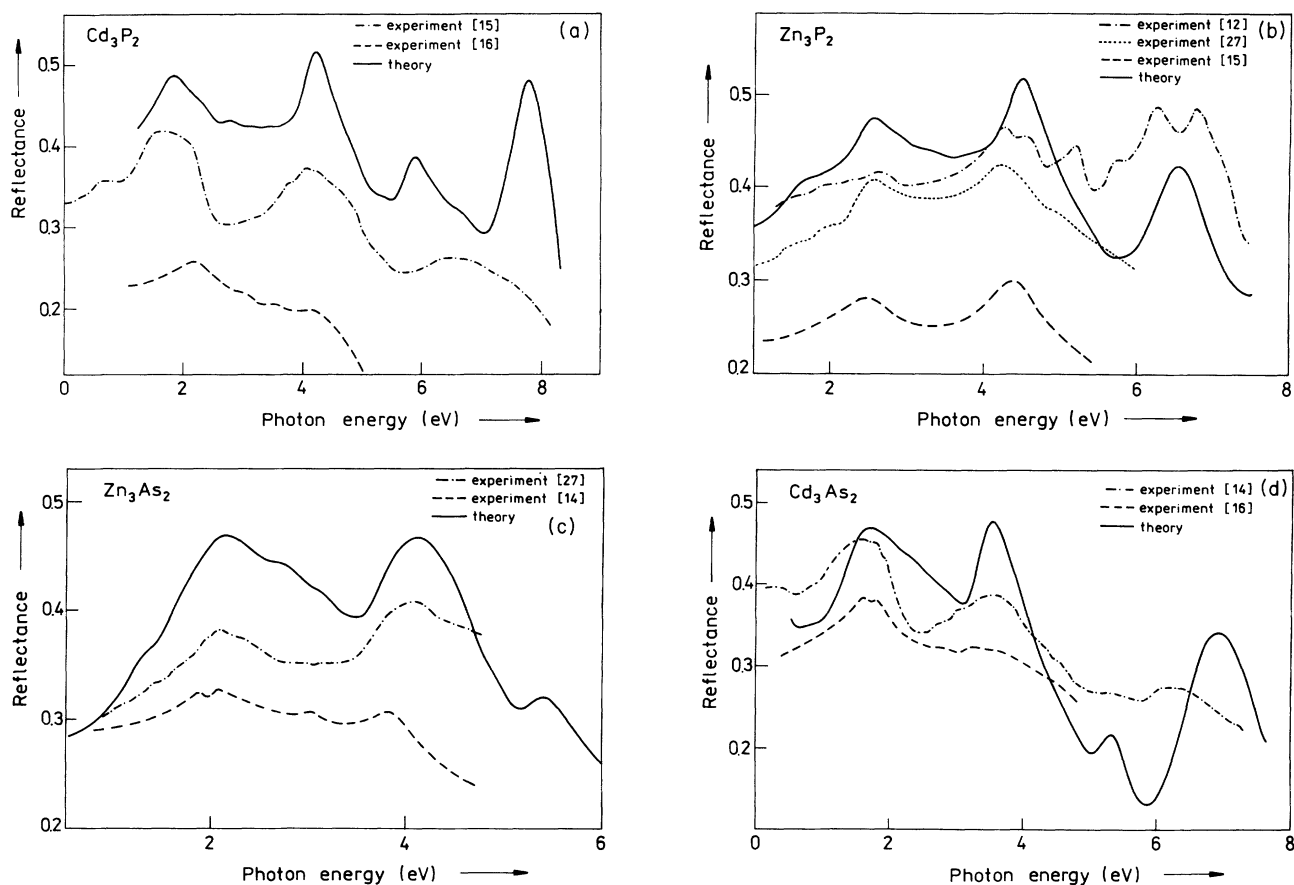
FIG. 4. The reflectance spectra of the II_3V_2 compounds calculated from the model (solid lines), as compared to the experimental ones (Refs. 12,14–16,27) (dashed lines).
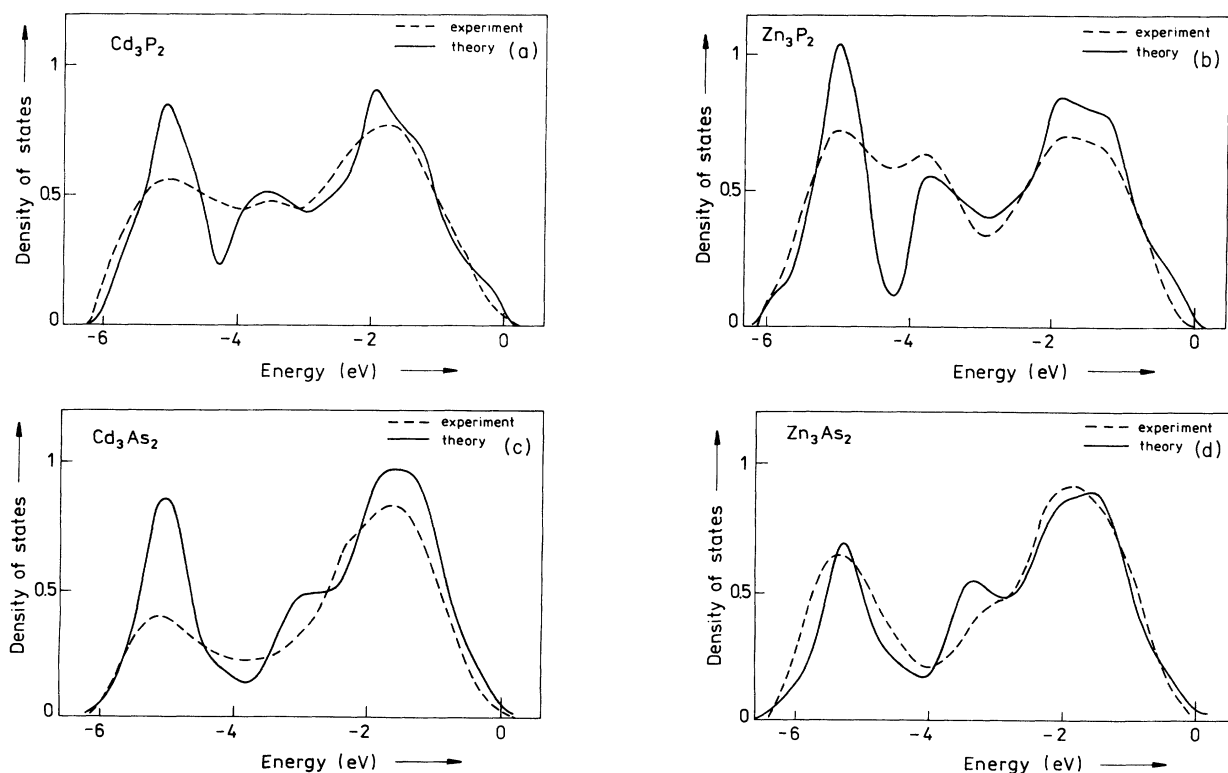

FIG. 5. Densities of valence states of the II_3V_2 compounds calculated from the model (solid lines), the experimental DOVS (Ref. 7) (dashed lines).

DOVS peak. It led to the creation of an additional minimum on Δ line for the lowest conduction band (see Fig. 3).

For Cd_3P_2, this second minimum has higher energy than that at the Γ point, so Cd_3P_2 remains the semiconductor with a direct energy gap. It is in agreement with the Lin-Chung calculation and experimental results. It was clearly proved both by optical[26] and Shubnikow–de Haas experiment[32] that Cd_3P_2 has a direct energy gap at Γ point equal to 0.53 eV at room temperature.

In the case of Zn_3P_2, the situation is different. The minimum created on Δ line is an absolute minimum. It was impossible to remove this minimum without destroying the second DOVS peak. As a consequence, the absolute minimum of the Zn_3P_2 conduction band lies on the Δ line, not at the Γ point. In contrast to the Lin-Chung calculation, our model predicts for Zn_3P_2 the indirect energy band equal to 1.2 eV. It is in contradiction with the commonly accepted direct type of energy gap in Zn_3P_2 located within 1.55–1.6 eV at room temperature.[11,13,17] However, among the papers devoted to this problem there are a few that claim indirect energy gap equal at room temperature to 1.26,[18] 1.315,[19] and 1.4 eV.[20] Unfortunately, until now there has been no strict experimental evidence of the phonon-assisted indirect transitions in Zn_3P_2.

Another explanation of the weak singularities observed on optical spectra within 1.2–1.45-eV energy range are based on their correlation with defect-related transition.[17,21−23] This problem needs further careful investigation.

There is also another discrepancy between the band structure calculated using our set of parameters and Lin-Chung's band structures. For Zn_3As_2, our model predicts an indirect energy gap at L point, whereas the experiments performed up to now indicate only direct transition at 0.99 eV at room temperature.[24,25] This discrepancy results from the lower of 0.62-eV value of $E(L_3^v)$ energy extracted from XPS data than energy obtained by Lin-Chung. For the proper description of the location of the E_1 peak on reflectivity spectra, the lower value of the conduction band at L_1^c point was needed. As

a result, the absolute minimum of the conduction band of Zn_3As_2 was moved to the L point. This discrepancy between theory and experiment stimulates further investigations in this field.

The energy gap obtained for Cd_3As_2 from our set of tight-binding parameters is in good accordance with the value equal to 0.1 eV commonly accepted as the optical band gap, despite the suggested inverted band structure at Γ point (see Ref. 26 and papers cited therein).

It should be mentioned that in our tight-binding model the spin-orbit interaction and tetragonal distortion have been ignored. Including those effects would probably give the reflectance spectra more rich details.[14,15]

IV. CONCLUSIONS

Semiempirical tight-binding electronic-energy-band structures of the following II_3V_2 semiconductors are presented: Cd_3P_2, Zn_3P_2, Cd_3As_2, and Zn_3As_2. The zinc-blende approximation of the real crystal structure was used. The calculations were carried out within the nearest- and second-nearest-neighbor approximation and the single s and p atomic-orbital basis set. The tight-binding parameters were obtained empirically by fitting calculated density of valence states and reflectivity spectra to the empirical one. The presented parametrization of the band structure provide an accurate representation of the valence bands and an adequate description of the lowest and most important conduction bands of II_3V_2 semiconductors.

We should emphasize that the model based on the zinc-blende hypothetical structure is very advantageous because it is simple, and model parameters reflect some chemical trends (it is possible to compare the model parameters of the II_3V_2 compounds with those of III-V and II-VI semiconducting compounds.)[9]

ACKNOWLEDGMENT

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