PHYSICAL REVIEW B VOLUME 52, NUMBER 3 15 JULY 1995-I

Ab initio pseudopotential calculations of the band lineups at strained ZnS/ZnSe interfaces: Including the 3*d* electrons of Zn as valence states

A. Qteish
Center for Theoretical and Applied Physics, Yarmouk University, Irbid, Jordan

R. Said and N. Meskini
Departement de Physique, Faculté des Science de Tunis, Campus Universitaire, Belvedere, Tunis, Tunisia

A. Nazzal
Department of Physics, Yarmouk University, Irbid, Jordan

(Received 23 August 1994)

A first-principles pseudopotential approach has been used to calculate the valence-band offset (Λ_v) at strained ZnS/ZnSe (001) interfaces, and the structural and electronic structure properties of ZnS and ZnSe. In these calculations the semicore 3*d* electrons of Zn are included as relaxed valence states. Three strain configurations, corresponding to growth on ZnS_xSe_{1-x} (001) (with $x=0$, 0.5, and 1) substrates were considered. We found that Λ_v varies almost linearly between 0.43 and 0.78 eV in the above strain range, with the state at the top of the valence band in ZnSe being higher in energy. The averages of Λ_v and the conduction-band offset are found to be independent of the strain state and with values of 0.50 and 0.23 eV, respectively. These results and that of the other studied properties are found to be in excellent agreement with experiment and all-electron calculations. The charge density associated with the *d* bands shows some deviations from being spherically symmetric around the Zn ions and has appreciable magnitude in the anions regions, which suggests that the *dp* hybridization is quite strong.

I. INTRODUCTION

ZnS and ZnSe are wide band-gap semiconductors with direct energy gaps of 3.80 and 2.80 eV, respectively, and a lattice mismatch of about 4.5% between them. Strained superlattices and quantum wells consisting of ZnS and ZnSe have received a lot of interest recently because of (a) their potential applications in optoelectronic devices operating in the visible-light range,[1,2] (b) the possibility of having a vanishingly small conduction-band offset (Λ_c),[3] and (c) they show a transition from type I to type II behavior under hydrostatic pressure.[4,5] The band lineups are the key quantities in the analysis of optical and electrical properties of semiconductor superlattices. Despite extensive experimental and theoretical investigations, the value of the valence-band offset (Λ_v) at the ZnS/ZnSe interfaces is still controversial. The main aim of this work is to contribute to a more accurate and reliable determination of Λ_v at ZnS/ZnSe interfaces. Moreover, strained ZnS/ZnSe interfaces can be considered as a prototype of lattice-mismatched interfaces between II-VI compounds.

The experimental determination of Λ_v has been carried out using different techniques. The confined exciton luminescence in the above strained superlattices has been extensively studied in the past few years.[6] The remarkable feature of these investigations is the poor agreement among their results. Recently, Trager-Cowan *et al.*[7] have carried out calculations of the confinement energies in the experimentally studied ZnS/ZnSe superlattices, using an effective-mass theory approach, in which Λ_v is used as an adjustable parameter. They found that a best fit to these experimental results can be obtained by assuming that the 1-eV difference in the energy band gaps is accommodated as Λ_v (so that $\Lambda_c=0$). Such a conclusion is not supported by the most reliable direct measurements of Λ_v, using x-ray photoelectron emission spectra (XPS), which give a value of 0.57 eV, in the free standing strain configuration;[8] and values of 0.73 and 0.25 eV for Λ_v and Λ_c, respectively, between bulk *unstrained* ZnS and ZnSe.[9]

It is now well established that self-consistent calculations based on the local-density approximation (LDA) for the exchange-correlation potential,[10] provide accurate results for Λ_v at semiconductor-semiconductor interfaces.[11] Theoretical investigations of Λ_v at ZnS/ZnSe interfaces have been performed, using linear-muffin-tin-orbital (LMTO),[12] full potential (FP)-LMTO,[13] self-consistent pseudopotential,[14] and model solid theory (MST) (Refs. 8 and 15) approaches. The LMTO calculations gave an averaged Λ_v ($\Lambda_{u,\text{av}}$) [neglecting the effects of the splitting of the top of the valence-band states, due to both the spin-orbit interaction and uniaxial strain] of about 0.5 eV, which strongly supports the lower experimental values. However, the other theoretical calculations gave larger values of Λ_v (see Table V), in good agreement with the experimental indications of a vanishingly small Λ_c. The disagreement between the results of the LMTO and the other calculations has been attributed to the treatment of the semicore *d* electrons of Zn, as frozen-core states in the latter.

The bonding in group-IV elemental and III-V, and II-

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TABLE I. Calculated and experimental values of the lattice parameter (d), bulk modulus (B_0), and its pressure derivative (B_0') for ZnS and ZnSe.

Compound	Structural parameters	Present work	Ref. 34 PP-PW	Ref. 34 LAPW	FLAPW Ref. 35	FP-LMTO Ref. 13	Experiment Ref. 33
ZnS	d (Å)	5.352	5.349	5.353		5.320	5.404
	B_0 (GPa)	83	82	87			76.9
	B'	4.43	4.60	4.9			4.91
ZnSe	d (Å)	5.627			5.636	5.630	5.667
	B_0 (GPa)	69			66.7		62.5
	B'	4.63					

VI compound semiconductors are primarily of sp^3 character. However, in some of these materials, the highest occupied d states are rather shallow in energy and, in these cases, they play a significant role in both the electronic structure and the structural properties. For example, in II-VI compounds, the d bands lie within the valence band, between 7 to 11 eV below the valence-band maximum,[16] which clearly show that they should be included as valence bands in very accurate theoretical calculations. However, it has been recently shown[17] that Λ_v can be accurately obtained by treating the semicore d electrons as part of the core, *provided* that nonlinear core exchange-correlation corrections[18] (hereafter referred to as nonlinear core corrections), which take into account the overlap between the valence and core charge densities, are included.

The application of the pseudopotential plane-wave (PP-PW) technique to systems containing transition metals and first row elements was, until very recently, quite impossible, because of the very large number of PW's required to expand the sharply peaked wave functions of these atoms. New ideas and schemes have been introduced to generate highly optimized pseudopotentials,[19–22] which reduce drastically the numbers of PW's required. These developments together with very efficient total-energy minimization techniques,[23,24] have made it possible to extend the range of applications of the above method to cover almost all the atoms of the periodic table.

In the present work, we used highly optimized Zn pseudopotentials,[22] the conjugate gradient minimization method[24] and the LDA, to calculate Λ_v at strained ZnS/ZnSe (001) interfaces, including the semicore $3d$ electrons of Zn as valence states. Three strain configurations have been considered, corresponding to growth on $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ substrates with $x=0$, 0.5, and 1 (hereafter referred to as A, B, and C strain configurations). Moreover, the structural and electronic structure properties of ZnS and ZnSe have been similarly calculated. The results so obtained are discussed in comparison with the available experimental and other theoretical data. To the best of our knowledge, this is the first *ab initio* pseudopotential study of Λ_v in which the semicore d electrons have been relaxed.

The rest of the paper is organized as follows. In Sec. II, we describe the effects of biaxial strain on the electronic structure of cubic semiconductors. In Sec. III, we very briefly describe our computational method and the details of the calculations. In Sec. IV, we report and discuss our results for the structural properties and charge density (Sec. IV A), band structure and deformation potentials of bulk ZnS and ZnSe (Sec. IV B), and band lineups (Sec. IV C). Finally, Sec. V contains a summary of our main results and conclusions.

II. EFFECTS OF STRAIN ON BAND EDGES

Since we are mainly interest in Λ_v at strained ZnS/ZnSe interfaces, and both ZnS and ZnSe are direct band-gap semiconductors, we will consider here only the effects of biaxial strain on the states at the top of the valence band and on the average band gap. Moreover, we limit our discussion to the coherent biaxial strain appropriate for epitaxial growth along the [100] direction. This effect can be described by the tensor

$$e_{ij}=\begin{bmatrix}\epsilon_{xx} & 0 & 0\\ 0 & \epsilon_{xx} & 0\\ 0 & 0 & \epsilon_{zz}\end{bmatrix}, \qquad (1)$$

where $\epsilon_{xx}=(d_{\parallel}-d)/d$ and $\epsilon_{zz}=(d_{\perp}-d)/d$. Here, d is the equilibrium lattice parameter, and $d_{\parallel}$ and $d_{\perp}$ are, respectively, the lattice parameters parallel and normal to the interface. Details of the determination of $d_{\perp}$ are given in Sec. III.

The effects of the above strain on the band edges of cubic semiconductors is normally divided into isotropic and uniaxial contributions. The band gaps at the Γ point, which we write as $E_c-E_{v_i}$, where i denotes the three states at the top of the valence band, are given by

$$E_c-E_{v_i}=E_{g,\mathrm{av}}-\Delta E_{v_i}\ , \qquad (2)$$

where

$$E_{g,\mathrm{av}}=E_g-\delta E_H\ . \qquad (3)$$

In these expressions δE_H is the shift in the average band gap $E_{g,\mathrm{av}}$, due to the isotropic component of the strain ($\epsilon_{\mathrm{is}}=\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}$, which is equal to the fractional volume change), and E_g is the band gap at zero strain and in the absence of spin-orbit splitting. The splittings, ΔE_{v_i}, of the states at the top of the valence band with respect to the average value are given by

$$
\begin{aligned}
\Delta E_{v_2} &= \tfrac{1}{3}\Delta_0 - \tfrac{1}{2}\delta E_{001} , \\
\Delta E_{v_1} &= -\tfrac{1}{6}\Delta_0 + \tfrac{1}{4}\delta E_{001} \\
&\quad + \tfrac{1}{2}[\Delta_0^2 + \Delta_0 \delta E_{001} + \tfrac{9}{4}(\delta E_{001})^2]^{1/2} , \\
\Delta E_{v_3} &= -\tfrac{1}{6}\Delta_0 + \tfrac{1}{4}\delta E_{001} \\
&\quad - \tfrac{1}{2}[\Delta_0^2 + \Delta_0 \delta E_{001} + \tfrac{9}{4}(\delta E_{001})^2]^{1/2} ,
\end{aligned}
\tag{4}
$$

where Δ_0 is the spin-orbit splitting parameter and δE_{001} is the linear splitting of the multiplets, due to the uniaxial component of the strain ($\epsilon_{\text{ax}} = \epsilon_{zz} - \epsilon_{xx}$). The band v_2 corresponds to the $|\frac{3}{2},\frac{3}{2}\rangle$ (heavy-hole) state, whereas v_1 and v_3 are mixtures of the $|\frac{3}{2},\frac{1}{2}\rangle$ (light-hole) and $|\frac{1}{2},\frac{1}{2}\rangle$ (spin-orbit split-off) states. Within the linear deformation-potential theory, δE_H and δE_{001} are related to the strain by

$$\delta E_H = a\epsilon_{\text{is}} , \tag{5}$$

and

$$\delta E_{001} = 2b\epsilon_{\text{ax}} , \tag{6}$$

where a and b are the usual linear deformation potentials. Nonlinear effects[25] are found to be unimportant in the strain range considered and have not been discussed in this work.

III. METHOD AND COMPUTATIONAL DETAILS

As described in Ref. 25, Λ_v can be calculated from the relation

$$\Lambda_v = [E_{\text{VBM}}(L) - E_{\text{VBM}}(R)] + [\bar{V}_{\text{tot}}(L) - \bar{V}_{\text{tot}}(R)] , \tag{7}$$

where E_{VBM} and $\bar{V}_{\text{tot}}$ are, respectively, the energy of the valence-band maximum (VBM), and the averaged total potential (defined as the sum of the averaged Hartree, exchange correlation and the local part of the ionic potential). The first term in Eq. (7) is obtained from self-consistent band-structure calculations for strained ZnS and ZnSe without including spin-orbit coupling. E_{VBM} is then determined with the help of Eq. (4): the self-consistently calculated values of δE_{001} and the experimental values of Δ_0 (we used values for Δ_0 of 0.07 and 0.43 eV for ZnS and ZnSe, respectively) are used to calculate ΔE_{v_i}, as described in Sec. II. The second term in Eq. (7) (the so-called potential lineup) is extracted from similar calculations for supercells containing thick slabs of the two materials. The macroscopic averaging used to calculate $\bar{V}_{\text{tot}}$ was performed using the moving-slab averaging technique of Baldereschi, Baroni, and Resta.[26]

In our present work, ideal interfaces have been assumed. Interface relaxation, which is found to have only very small effects[13] on Λ_v, has been neglected. Under these assumptions, the supercells used in the potential lineup calculations can be described by three structural parameters: $d_\parallel$ which is equal to that of the assumed substrate, and two values of $d_\perp$, one for each of the two compounds. The values of $d_\perp$ for each strain configuration are usually obtained by minimizing the elastic energy, which gives

$$d_\perp = d_i[1 - D_i(d_\parallel / d_i - 1)] , \tag{8}$$

where d_i is the equilibrium lattice parameter of material i and D_i is a constant which depends on the elastic constants c_{11}, c_{12}, and c_{44} of material i and on the direction of biaxial strain. In the case of the (001) oriented interfaces, D^{001} is given by

$$D^{001} = 2c_{12}/c_{11} . \tag{9}$$

The values of c_{11} and c_{12} used in this work are 1.067 and 0.666 Mbar for ZnS; 0.826, and 0.498 Mbar for ZnSe (which are the same values used by Shahzad, Olego, and Van de Walle[8]). In the band lineup and band-structure calculations, we used the values 5.40 and 5.65 Å for d of bulk ZnS and ZnSe, respectively, and their arithmetic mean for $d_\parallel$ in the B strain configuration.

The calculations were performed using a first-principles pseudopotential approach and the Ceperley-Alder form[27] of the LDA as parametrized by Perdew and Zunger.[28] The Kohn-Sham equations were solved by expanding the wave functions in terms of a plane-wave basis and using the Teter, Payne, and Allan conjugate gradient total-energy minimization technique.[24] In Ref. 24, no recipe for the band-structure calculations has been given. However, a similar technique for such calculations has been developed, based on updating the wave functions via minimizing individually the eigenvalues, under the constraint of the orthogonality condition of the eigenfunctions. More details about this technique will be given elsewhere.[29] For the supercell calculations, PW's up to 30 Ry in energy were included. Increasing the cutoff energy to 35 Ry changed the potential lineup by only few meV. In the band structure and structural properties calculations of strained ZnS and ZnSe (two atoms unit cell), we have used a 55-Ry energy cutoff, which gives very good convergence for the total energy, see below. The Brillouin-zone integrations were performed by sampling on regular $4\times4\times4$ and $4\times4\times2$ Monkhorst-Pack[30] meshes for strained zinc-blende and supercell structures, respectively.

The pseudopotentials for Zn, S, and Se were generated using the Kerker scheme[31] in Klienman-Bylander form.[32] The Se and S pseudopotentials are rather smooth and do not pose any convergence problems, with respect to the number of PW's, and the cutoff energy is determined by the deep d pseudopotential of Zn. For Zn, we used highly optimized pseudopotentials generated following very closely the steps of Lin *et al.*,[22] for which very good convergence can be achieved using a 55-Ry energy cutoff (see Table III of Ref. 22).

IV. RESULTS AND DISCUSSION

A. Structural properties and charge density of bulk ZnS and ZnSe

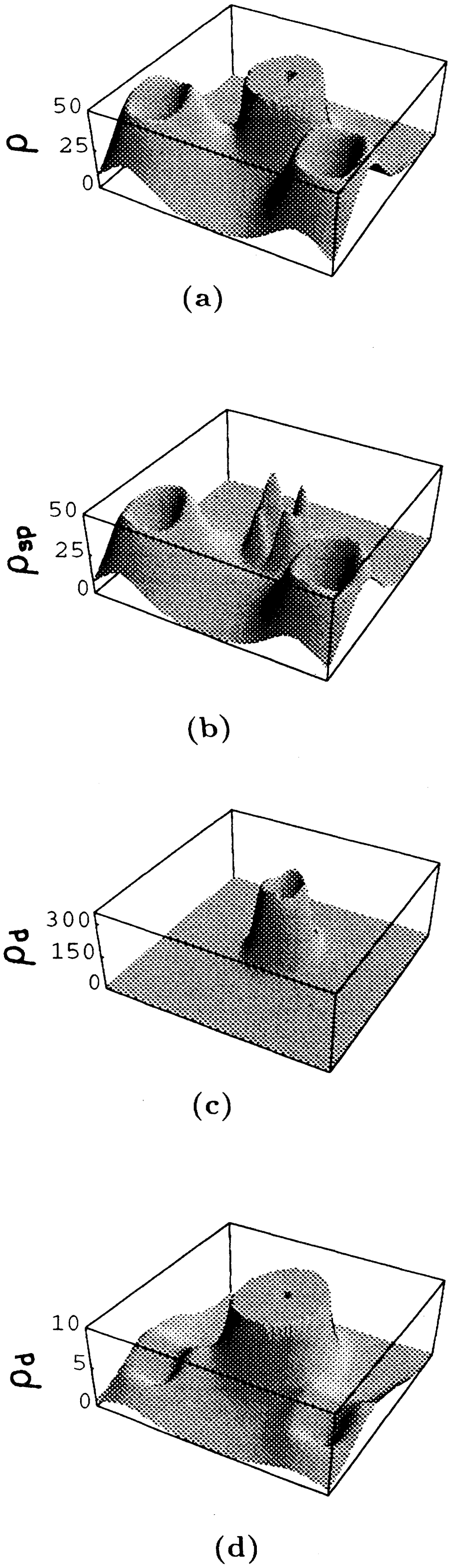
The structural properties of bulk ZnS and ZnSe are determined by calculating the total energy at several different volumes. About 10% variation of the volume on both sides of the equilibrium volume has been allowed. In Table I we show our calculated results for d, bulk modulus (B_0), and the pressure derivative of B_0 for both compounds, obtained by fitting the calculated total energies to Murnaghan's equation of state. The experimental data[33] and other similarly calculated values[34,35] (i.e., treating the semicore d electrons as valence states) are also shown. It is evident from Table I that the agreement between our results and the other theoretical ones is extremely good, and both are in excellent agreement with experiment. The calculated values of d and B_0 for the two compounds are within 1% and 10% of the corresponding experimental values, respectively. Such errors are of the same order as those in the corresponding LDA results, for III-V and group-IV materials.

Engel and Needs[36] have shown that the structural properties of ZnS can be significantly improved by including the nonlinear core corrections. The errors in their calculated d and B_0 were, respectively, about 4% and 37%, compared with 13% and 88% when the above corrections were not included. Our results shows that there is a clear further improvement over the results of Ref. 36, due to the relaxation of the semicore d electrons, which, in turn, indicates the important role of the latter on the calculated structural properties and bonding in II-VI compounds.

In Fig. 1, we show three-dimensional plots of the valence charge density, ρ, of ZnS in the plane of the bonds chain, and its decomposition into ρ_{sp} (calculated from the wave functions of the lowest and the three uppermost valence bands), and ρ_d (calculated from the wave functions of the occupied d bands) contributions. Both ρ_{sp} and ρ_d are properly symmetrized. The remarkable features to note are (i) the ρ_d is not spherically symmetric around the positions of the Zn ions, and that there is a

TABLE II. Energy levels (eV) at high-symmetry **k** points for ZnS, compared with the results of Martins, Troullier, and Wei (Ref. 34), calculated using a pseudopotential plane-wave (PP-PW) and linearized augmented plane-wave (LAPW) methods, and with the available experimental data.

Eigen-values	Present work	Ref. 34 PP-PW	Ref. 34 LAPW	Experiment Ref. 33
Γ_{1v}	−13.21	−13.07	−13.11	−13.50
$\Gamma_{15v}(d)$	−6.65	−6.63	−6.55	∼ −10.00
$\Gamma_{12v}(d)$	−6.17	−6.16	−6.09	∼ −10.00
Γ_{15v}	0.00	0.00	0.00	0.00
Γ_{1c}	1.79	1.84	1.81	3.80
Γ_{15c}	6.21	6.15	6.19	8.35
X_1	−11.92	−11.77	−11.84	−12.00
X_{3v}	−4.77	−4.74	−4.70	−5.50
X_{5v}	−2.32	−2.29	−2.25	−2.50
X_{1c}	3.19	2.19	3.18	
X_{3c}	3.90	3.87	3.87	4.90
L_1	−12.24	−12.10	−12.16	−12.40
L_{1v}	−5.47	−5.43	−5.38	−5.50
L_{3v}	−0.92	−0.90	−0.88	−1.40
L_{1c}	3.30	3.05	3.05	
L_{3c}	6.78	6.75	6.76	



(a)

(b)

(c)

(d)

FIG. 1. Three-dimensional plots of the total charge density, ρ, of ZnS (a) and its decomposition into sp, ρ_{sp} (b) and d, ρ_d (c) and (d) contributions. All plotted functions are in units of electron/unit cell. Note the change in scale.

depletion of charge along the bonds [see Fig. 1(c)]. (ii) From Figs. 1(a) and 1(d) one can easily see that a rather significant ρ_d exists around the anion positions. The ρ of ZnSe, which is not shown here, is found to have a very similar behavior. Features (i) and (ii) can be understood as the result of the symmetry allowed *dp* hybridization in II-VI compounds, which seems to be quite strong. This demonstrates further that the semicore *d* electrons contribute quite appreciably to the bonding of these materials, and explains the significant effects of these electrons on the structural and electronic structure properties of II-VI compounds, see above and the following subsection.

B. Band structure and deformation potentials of ZnS and ZnSe

The band structures of cubic ZnS and ZnSe compounds are calculated using the method described very briefly in Sec. III. In Figs. 2 and 3, we show the band structures of ZnS and ZnSe, respectively, along the high-symmetry directions. The calculated energy eigenvalues at the high-symmetry points are reported and compared with other calculations and experiment in Tables II and III, respectively. Figures 2 and 3 show that the topology of the band structures compares very well with other calculations.[34,35] Whereas, excellent quantitative agreement between our calculated results and those of the all-electron calculations can be inferred from Tables II and III. When using LDA in band-structure calculations for II-VI compounds, two main shortcomings have been observed: (i) the band gaps, E_g, are usually underestimated (known as the band-gap problem) and (ii) the position of the occupied *d* bands is about 2–3 eV higher in energy compared to experiment. Our results also have these deficiencies: when compared with the corresponding experimental data, the calculated band gaps are underestimated by 53% and 61%, and the *d* bands are higher in energy by about 3.4 and 2.3 eV, respectively, for ZnS and ZnSe.

The band gaps calculated for several II-VI compounds using different levels of approximation for the semicore *d* electrons are summarized in Table VI of Ref. 15. In Ref. 15, it was shown that the calculated band gaps, using the nonlinear core corrections are about 0.3 to 0.4 eV larger than the corresponding values obtained from all-electron calculations. The excellent agreement between our present results and the all-electron results indicates that above discrepancies are mainly due to the relaxation of the semicore *d* electrons, as expected.

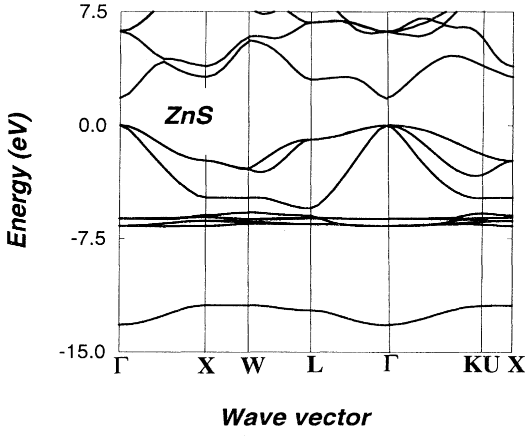


FIG. 2. Calculated band structure of ZnS.

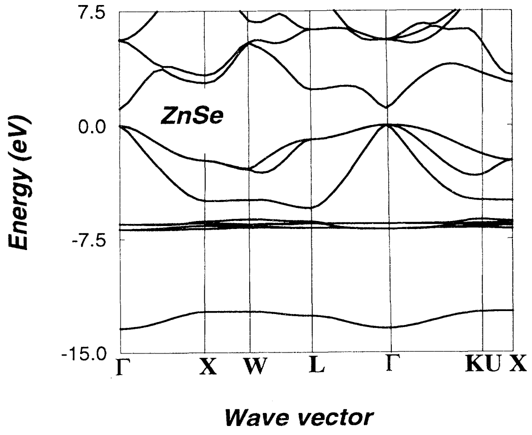


FIG. 3. Calculated band structure of ZnSe.

In Table IV, we show the calculated deformation potentials *a* and *b* (see Sec. II) for ZnS and ZnSe, compared with other theoretical and experimental results. We found that the nonlinear strain effects on the averaged band gap and the splitting of the valence-band states are rather small, and therefore we have neglected them. The

TABLE III. Energy levels (eV) at high-symmetry **k** points for ZnSe, compared with results of Continenza, Massidda, and Freeman (Ref. 35), calculated using the full-potential LAPW method with Hedin-Lundqvist (HL) and Ceperly-Alder (CA) forms of LDA, and with the available experimental data listed in Ref. 35.

Eigenvalues	Present work	Ref. 35 HL	Ref. 35 CA	Experiment
Γ_{1v}	−13.42	−13.43	−13.37	−15.2±0.6
$\Gamma_{15v}(d)$	−6.85	−6.79	−6.77	−9.2±0.15 −8.9±0.4
$\Gamma_{12v}(d)$	−6.48	−6.42	−6.41	−8.6
Γ_{15v}	0.00	0.00	0.00	0.0
Γ_{1c}	1.10	1.10	1.08	2.80
Γ_{15c}	5.59	5.69	5.70	
X_1	−12.32	−12.33	−12.30	−12.5±0.4
X_{3v}	−4.96	−4.92	−4.89	−5.3±0.3
X_{5v}	−2.30	−2.27	−2.24	−2.1±0.3
X_{1c}	2.77	2.79	2.82	
X_{3c}	3.28	3.33	3.34	
L_1	−12.60	−12.61	−12.57	−13.1±0.3
L_{1v}	−5.43	−5.41	−5.35	−1.3±0.3 0.7±0.2
L_{3v}	−0.92	−0.91	−0.91	
L_{1c}	2.34	2.38	2.37	
L_{3c}	6.26	6.32	6.33	

TABLE IV. Calculated and experimental values of the deformation potentials *a* and *b* for ZnS and ZnSe.

		a (eV)	*b* (eV)
ZnS	This work	−3.88	−1.16
	Shahzad, Olego, and Van de Walle (Ref. 8)	−6.40	−1.25
	Qteish and Needs (Ref. 15)		−1.39
	Ves *et al.* (Ref. 38)	−4.53	
	Bernard and Zunger (Ref. 37)	−4.00	
	Experiment (Ref. 33)	−4.00	−0.75
ZnSe	This work	−3.69	−1.29
	Shahzad, Olego, and Van de Walle (Ref. 8)	−5.82	−1.20
	Qteish and Needs (Ref. 15)		−1.36
	Bernard and Zunger (Ref. 37)	−4.20	
	Cardona and Christensen (Ref. 39)	−4.64	
	Experiment (Ref. 33)	−5.40, −4.80	−1.20

reported results were obtained at small values of strain (about 1% lattice mismatch). As is clear from this table, our calculated results for *b* and *a* compare very well with the experimentally determined values and with those of other theoretical calculations. Another feature to note from Table IV is that *a* seems to be more sensitive than *b* to the computational method. This can be understood, since experience has shown that the minimum conduction-band energy is much more sensitive to the energy cutoff used than the valence-band maximum.

C. Band lineups

The valence-band offsets are calculated as described in Sec. III. In Fig. 4, we show the averaged total potential $\bar{V}_{\text{tot}}$, and the averaged ρ, $\bar{\rho}$, for $(\text{ZnS})_2/(\text{ZnSe})_2$ (001) superlattice with the three considered strain configurations. The important feature to note here is the short-ranged effects of the interfaces, which, fortunately, allowed us to extract the potential lineups using the above ultrathin superlattices. This is not surprising, since such a feature has already been noticed before,[25] in the case of highly strained GaAs/GaSb superlattices.

The calculated values of Λ_v are compared with those of other self-consistent calculations and MST in Table V. It is evident from this table that our results are in perfect agreement with the FP-LMTO results of Methfessel, Agrawal, and Scheffler;[13] while the LMTO results of Gorczyca and Christensen[12] are generally lower in energy, especially for the *A* strain configuration. Table V also shows that there is quite a large disagreement between our results and those of the pseudopotential calculations of Ref. 14 and MST calculations,[8,15] most notably with the former for the *A* strain configuration, where the difference is about 0.4 eV. The disagreement can be understood as a result of improper treatment of the semicore *d* electrons in the calculations of Ref. 14, and the approximations inherent in the MST, which does not take into consideration any interface effects.

Recently, Qteish and Needs[17] have shown that Λ_v can be accurately obtained with the semicore *d* electrons treated as frozen core, *provided* that nonlinear core corrections are included. The results obtained using such an approach for several interfaces involving II-VI compounds compare very well with experiment and all-electron calculations. Now, since both the present results and those of Ref. 17 agree very well with the results of the all-electron calculations, we believe that the conclusions of Ref. 17 are correct (that the relaxation of semicore *d* electrons is unimportant in the Λ_v calculations),

TABLE V. Calculated valence-band offsets (Λ_v) and averaged valence-band offsets ($\Lambda_{v,\text{av}}$) at ZnS/ZnSe (001) interfaces with three strain configurations. The model solid theory (MST) values of $\Lambda_{v,\text{av}}$ are for unstrained bulk ZnS and ZnSe. The *A*, *B*, and *C* strain configurations correspond to coherent growth on ZnSe, $\text{ZnSe}_{0.5}\text{S}_{0.5}$, and ZnS substrates, respectively. All tabulated results are in units of eV.

Strain configuration	Band offset	Present work	Model solid theory Ref. 15	Model solid theory Ref. 8	LMTO Ref. 12	FP-LMTO Ref. 13	PP-PW Ref. 14
A	$\Lambda_{v,\text{av}}$	0.49	0.74	0.78	0.24	0.52	
	Λ_v	0.43	0.52	0.58	0.24	0.43	0.84
B	$\Lambda_{v,\text{av}}$	0.50	0.74	0.78	0.41	0.53	
	Λ_v	0.57	0.72	0.79	0.54	0.61	
C	$\Lambda_{v,\text{av}}$	0.51	0.74	0.78	0.41	0.50	
	Λ_v	0.78	0.90	0.98	0.65	0.82	0.95

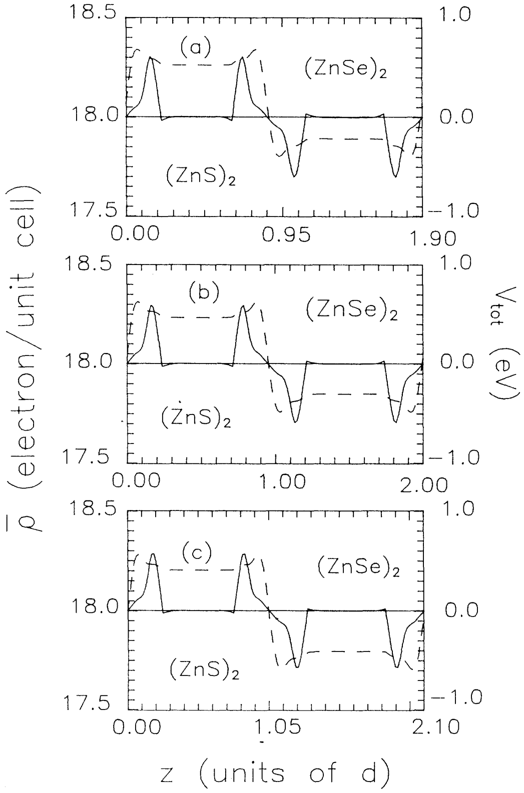


FIG. 4. Averaged charge density, $\bar{\rho}$ (solid lines) and averaged total potential, $\bar{V}_{\text{tot}}$ (dashed lines) for $(\text{ZnS})_2/(\text{ZnSe})_2$ (001) superlattice, with *A* (a), *B* (b), and *C* (c) strain configurations. *d* is the lattice parameter of the corresponding substrate, see text.

in spite of important role of the relaxation of the semicore *d* electrons on the structural properties and the band structure. More calculations are needed to clarify this point, and such calculations are presently underway.

We now compare our results with experiment. Very recently, Trager-Cowan *et al.*[7] have found that a best fit to the scattered exciton energies obtained by several groups using different ZnS/ZnSe superlattices can be obtained by assuming a vanishing Λ_c—all the difference in the energy band gaps (about 1 eV) is accommodated as Λ_v, in apparent contradiction with our results, especially in the case of a strain state close to the *A* configuration. However, indirect experimental determination of Λ_v from exciton luminescence measurements requires the knowledge of the layer thickness, composition, interface sharpness, and strain profile of the samples, which are not always known to a good accuracy, in addition to the theoretical uncertainties, due to the use of the effective-mass approximation. It would be of interest to repeat the calculations of Ref. 7 using the presently calculated band lineups to see how they compare with experiment. On the other hand, direct experimental determination of Λ_v using XPS for eight $\text{ZnS}_x\text{Se}_{1-x}/\text{ZnSe}$ superlattices has been carried out by Shahzad, Olego, and Van de Walle.[8] Unfortunately, only one of these results can be compared safely with the theoretical results. This is the one measured for the free-standing strain configuration with $x=0.19$ (sample *e* in Table III of Ref. 8). Linearly extrapolating the measured Λ_v for this sample to $x=1$ gives 0.57 eV, which is, incidently, in excellent agreement with our present results and those of all-electron calculations, as has been previously noted.[12,13] More recent XPS measurements of Taguchi *et al.*[9] have given values of 0.73 and 0.25 eV for Λ_v and Λ_c, respectively, between bulk *unstrained* ZnSe and ZnS. The determination of Λ_v between bulk *unstrained* semiconducting material is the basic idea of the MST, from which Λ_v, for any strain configuration, can be calculated with the help of the deformation-potential theory. Comparing the XPS results of Ref. 9 for Λ_v with those of MST (see Table V), one can see that it is smaller, for example, by only 0.11 eV than the results of Qteish and Needs.[15] Thus, a very good estimate of Λ_v at ZnS/ZnSe (001) interface with *A*, *B*, and *C* strain configurations can be obtained by simply subtracting 0.11 eV from the MST results of Ref. 15, giving 0.41, 0.61, and 0.79 eV, respectively, which are also in excellent agreement with our results (0.43, 0.57, and 0.78 eV) and those of FP-LMTO calculations[13] (0.43, 0.62, and 0.82 eV).

The conduction-band offset, Λ_c, at the above interface for each of the three strain configurations considered are calculated according to the relation

$$\Lambda_c = E_{g,\text{av}}(\text{ZnS}) - E_{g,\text{av}}(\text{ZnSe}) - \Lambda_{v,\text{av}} \,. \tag{10}$$

The $E_{g,\text{av}}$ are calculated using Eq. (3), where for E_g, we used the corresponding experimental values, averaged over the spin-orbit splitting at zero strain; for δE_H, we used the self-consistently calculated values (for the *A*, *B*, and *C* strain configurations, respectively, these values are 0.00, 0.07, and 0.14 eV for ZnSe: −0.15, −0.09, and 0.00 eV for ZnS). This gives values of Λ_c of 0.24, 0.22, and 0.23 eV for *A*, *B*, and *C* strain configurations, respectively. It is interesting to note that Λ_c is almost independent on the strain state and is very close to the experimental value of 0.25 eV.[9]

To conclude this subsection, we say that the excellent agreement between the XPS measurements of Λ_v and our calculated results and those of the FP-LMTO calculations[13] enhances the credibility of all these results. Therefore, one could argue that it is now well established that $\Lambda_{v,\text{av}}$ is independent of the interface strain state and is about 0.50 eV. Assuming that $\Lambda_{v,\text{av}}$ varies linearly with composition and using Eq. (4) to calculate the splitting of the top of the valence-band states, a very good estimate of Λ_v at $\text{ZnS}_x\text{Se}_{1-x}/\text{ZnS}_y\text{Se}_{1-y}$ interfaces as functions of strain can be easily obtained. This would be very useful for device design, as well as for the characterization of ZnS/ZnSe superlattices and heterostructures. Here, only the (001) interface orientation has been considered. However, the orientation dependence of $\Lambda_{v,\text{av}}$ at ZnS/ZnSe interfaces for two strain configurations has been studied by Gorczyca and Christensen.[12] It has been found that it has a very weak orientation dependence. Therefore, the above arguments can also be applied to other interface orientations.

V. CONCLUSIONS

We have used highly optimized pseudopotentials and the local density approximation method to study the band lineups at strained ZnS/ZnSe (001) interfaces, considering the semicore 3*d* electrons of Zn as relaxed valence states. This has been done at three strain configurations, corresponding to growth on the ZnS, $ZnS_{0.5}Se_{0.5}$, and ZnSe substrates. The structural properties and band structures of bulk ZnS and ZnSe have also been similarly investigated. In the following, we draw our main conclusions.

(1) The heavy-hole valence-band offset varies almost linearly with strain between 0.43 and 0.78 eV (with the state at the top of the valence band in ZnSe being higher in energy), in the range of strain considered. The averaged valence-band offsets and the conduction-band offsets are independent of strain and are about 0.50 and 0.23 eV, respectively.

(2) Our calculated band lineups are found to be in very good agreement with the direct experimental measurements and the full potential LMTO calculations, which demonstrates the reliability of all these results.

(3) Although the conduction-band offset is rather small, it is not vanishingly small, as has previously been suggested.

(4) The semicore *d* charge density is found to have appreciable values around the anion positions, suggesting a rather strong *pd* hybridization and a significant role of these electrons in bonding and other properties of II-VI compounds.

(5) The perfect agreement between our results and those of all-electron calculations, for all the presently studied properties, highlights the recent developments in the pseudopotential plane-wave technique, and demonstrates that it is both possible and practical to use this approach to explicitly treat the cation semicore *d* electrons in II-VI based complex systems.

ACKNOWLEDGMENTS

One of us (R.S.) would like to thank Dr. Sami Mahmood and the Center for Theoretical and Applied Physics at Yarmouk University for financial support and kind hospitality where the bulk of this work was done. Part of this work was done while (A.Q.) was visiting Cambridge University, and he would like to thank Professor Volker Heine and the other members of the Theory of Condensed Matter Group for their kind hospitality, and the Islamic Development Bank, Jeddah–Saudi Arabia, for financial support. The calculations were performed using CASTEP (Cambridge serial total energy package), and the authors are indebted to Dr. Mike C. Payne and the other colleagues, whose developments in CASTEP have been used. Many thanks go to Dr. Richard J. Needs for a critical reading of the manuscript.

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