PHYSICAL REVIEW B VOLUME 48, NUMBER 23 15 DECEMBER 1993-I

ZnS/ZnSe strained-layer superlattices under pressure

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(Received 30 July 1993)

First-principles density-functional calculations of the electronic properties of ZnS/ZnSe (001) strained-layer superlattices are used to investigate the influence of hydrostatic pressure on the valence-band offset (VBO). Three different strain modes corresponding to various values of the relative thicknesses of the two types of layers are considered. The pressure coefficients of the VBO's are found to be very sensitive to the strain mode. A I→II type conversion associated with the conduction-band crossover between the ZnSe well layers and ZnS barrier layers is found, in agreement with recent experimental data. The pressure behavior of the key quantities (VBO's, bulk moduli, energy gaps) is discussed for various strain modes.

I. INTRODUCTION

Recently, there has been much interest in the effects of the external modulations in semiconductor superlattices and quantum-well structures. In this respect strained-layer superlattices are especially interesting since they contain strains which can be influenced by choosing the alloy compositions, thicknesses of individual layers, or by applying the pressure or electric field. This allows the strain to be controlled, and in turn the superlattice electronic structure can be tuned.

Wide-gap ZnS/ZnS_xSe_{1-x} strained-layer superlattices (lattice mismatch of 4.5%) may be useful as tunable light emitters, either by variation of the constituent-layer thicknesses or the composition x, or by changing the external conditions such as hydrostatic pressure or electric field. To predict the electronic structure of the new artificial materials, it is necessary to know the bulk parameters, elastic constants, and pressure coefficients of the energy gaps as well as the heterojunction parameters such as the strains in the layers, and conduction- and valence-band offsets. A fit to the hydrostatic pressure dependence of the electronic levels can provide an excellent test of both the theory and parameter values.

In a previous paper[1] the electronic-structure calculations for ZnS/ZnSe (001) and (110) superlattices were carried out, and valence-band offsets (VBO's) in heterojunctions and "absolute" deformation potentials of the constituent compounds were derived. The present work uses the same method, i.e., self-consistent supercell calculations performed within the local-density approximation (LDA),[2] to calculate electronic properties of ZnS/ZnSe (001) superlattice as a function of hydrostatic pressure. As previously mentioned,[1] we apply here the relativistic linear-muffin-tin-orbital (LMTO) method. Three different strain modes are considered; pseudomorphic growth of ZnSe on a ZnS substrate, the reverse case, and "free-standing" case (equal thicknesses of both type of layers).

As already described,[1] the calculated VBO's are very sensitive to the atomic positions in the interface region. Therefore, it is necessary to replace macroscopically determined structure (from elastic constants of the constituents) by a fully relaxed structure. This relaxation is made by means of valence-force-field calculations in the Keating model.[3]

The pressure coefficients of VBO's are found to depend on the strain mode. Generally, the VBO increases with pressure, but whereas this dependence is pronounced in the case where ZnSe is pseudomorphically grown on a ZnS substrate, it is almost negligible for the reverse case. The more the VBO increases with pressure, the more the conduction-band offset (CBO) decreases with pressure. This effect leads to conversion from type I to type II associated with the conduction-band crossover between the ZnSe well layers and ZnS barrier layers. Unfortunately, the LDA causes considerable underestimation of energy gaps, and therefore, we have to adjust the gaps to experimental band gaps for bulk materials in order to estimate the CBO. This makes the estimated value of the crossover pressure somewhat ambiguous. Nevertheless, the calculation confirms the experimental finding of the type conversion under hydrostatic pressure.[4]

Other considered quantities such as bulk moduli, their pressure coefficients, and pressure coefficients of energy gaps are compared with the corresponding results for the bulk ZnS and ZnSe and discussed in the context of the various strain conditions.

The rest of this paper is organized as follows: in Sec. II the method of calculations is outlined including the determination of atomic positions in the interface region. Structural and electronic properties of the constituent materials (ZnS and ZnSe) under pressure are derived in Sec. III. The pressure dependence of the electronic structure of ZnS/ZnSe superlattice is discussed in Sec. IV. Finally, Sec. V contains a summary of our results.

II. METHOD OF CALCULATION

The LMTO method in the version that applies spherically symmetrized charge distributions and potentials in atomic spheres, i.e., space filling (and thus slightly overlapping) spheres, the atomic-sphere approximation (ASA),[5] is used to obtain the electronic structure of the considered superlattices. The self-consistent potentials

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are first calculated for the supercell geometry where the primitive cells (supercells) are chosen to have an odd number of compound layers on each side of the interface. In our calculations seven layers of each compound are taken into account. The ASA potential consists of individual atomic-sphere potentials, and therefore, we can extract the central-layer potentials, which are bulklike in shape if the cell is big enough. These potentials are then automatically adjusted on a common energy scale according to the polarizations caused by the interface formation, and the VBO's (defined as the difference between the valence-band maximum deeply inside the compound on the "right-hand side" and "left-hand side") are obtained by performing two single band-structure calculations, one with the right and one with the left central-cell potentials transferred to bulk crystal structures ("frozen-potential calculation").[6] From these band structures the valence-band maxima $E_v(R)$ and $E_v(L)$ are found and the VBO is determined as $\Delta E_v \equiv E_v(R) - E_v(L)$. It has to be pointed out that in the case of strained-layer superlattice, the bulklike structures used in the band calculations must be appropriately strained.

The self-consistent supercell potentials are generated by including all relativistic effects except the spin-orbit coupling. The final band calculations in the zinc-blende structure, from where the offsets are obtained, are Dirac relativistic. All calculations are performed within the local approximation to the density-functional theory. As usual, LMTO calculations for the semiconductors must include so-called "empty spheres" located in the interstitial positions, i.e., atomic spheres without "nuclear" charge (see Ref. 6 and references therein). Each layer contains two real atoms (cation and anion) and two empty spheres that in general are nonequivalent.

The calculations are performed in two energy panels: the lower panel contains the *s* states of anions while the rest of the states are included in the upper panel. The basis set includes the *s*, *p*, and *d* partial waves on all sites in the upper panel, the basis set in the lower panel is reduced by omission of the *d* partial waves on the sites of the anions and the empty spheres. The Zn 3*d* states are included as fully relaxed band states.

We consider three different strain modes corresponding to various values of the relative thicknesses of the two types of layers: (A) the lattice constant parallel to the interface is that of bulk ZnS, i.e., corresponding to a pseudomorphic growth of ZnSe on a ZnS substrate; (B) free-standing case: ZnS as well as ZnSe layers, both with the same thickness, assume lattice constants different from the bulk values;[1] and (C) pseudomorphic growth of ZnS on a ZnSe substrate.

The strained-layer lattice parameter $a_\perp$ perpendicular to the interface is allowed to relax to the value determined by the elastic properties of the material:

$$a_\perp = (1+\varepsilon_\perp)a \ ,$$

where

$$\varepsilon_\perp = D\left[1 - \frac{a_\parallel}{a}\right]$$

is the strain-tensor component for the deformation perpendicular to the interface, a is the bulk-lattice constant, $a_\parallel$ is the in-plane lattice constant, and D is a function of the elastic constants, depending on interface orientation (see, for example, Ref. 7).

The relations above determine the macroscopic strain state, but yield no information about the actual atomic positions in the interface region. We determine the actual atomic positions in the interface region by requiring that the force on each atom vanishes, forces being calculated within the Keating model[3] in the form which is generalized to heteropolar semiconductors.[8] The strain energy is expressed in terms of bond-stretching (α) and bond-bending (β) force constants. The atomic positions in the relaxed structures are obtained by minimizing the strain energy by allowing the atoms to move in the growth direction. Values of the force constants used here are obtained from the the corresponding elastic constants using the formula given by Martin[8] (with effective point-ion Coulombic forces added to the Keating model):

$$\alpha = a(c_{11} + 3c_{12} + 0.491 SC_0)/4$$

$$\beta = a(c_{11} - c_{12} - 0.053 SC_0)/4 \ ,$$

where $SC_0 = e_T^{*2}/\varepsilon_\infty r^4$, e_T is the dynamic effective charge, ε_∞ the dielectric constant, r the bond length, and a the lattice constant.

Results for the (001) ZnS/ZnSe superlattices at zero pressure were presented in a previous paper.[1] Here we focus our attention on the pressure effects. For the given value of hydrostatic pressure the force constants $\alpha(p)$ and $\beta(p)$ are expressed in terms of the lattice parameters and elastic constants: $a(p)$, $c_{11}(p)$, $c_{12}(p)$, and $SC_0(p)$, where

$$SC_0(p) = SC_0(0)\frac{a(0)^4 \varepsilon_\infty(0) e_T^{*2}(p)}{a(p)^4 \varepsilon_\infty(p) e_T^{*2}(0)} \ .$$

III. ZnS AND ZnSe UNDER PRESSURE

To perform the electronic band-structure calculations for the strained-layer superlattice, it is necessary to know the lattice and elastic constants of the constituent materials. For zero pressure the situation is rather simple, because we can take the values known from experiments.[8] The situation is much more complicated, when we want to get the pressure-volume relation for the superlattice. For each value of pressure, the values of lattice and elastic constants of constituent materials must correspond exactly to this value of pressure. There are some experimental data on the pressure dependence of the required parameters, but due to the scatter of the reported values[9] obtained by different methods and with different accuracy, it was necessary to perform consistent first-principles calculations of the total energy for bulk materials being

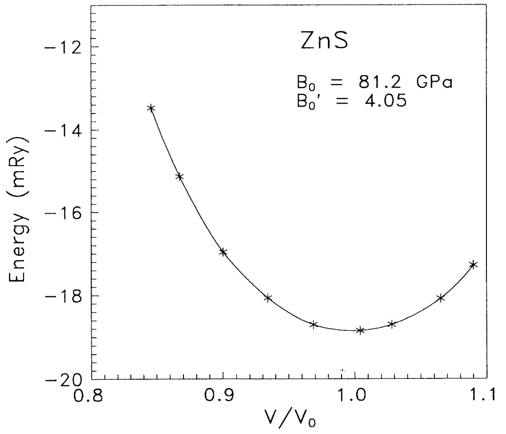

FIG. 1. Total energy per atom vs relative volume for ZnS.

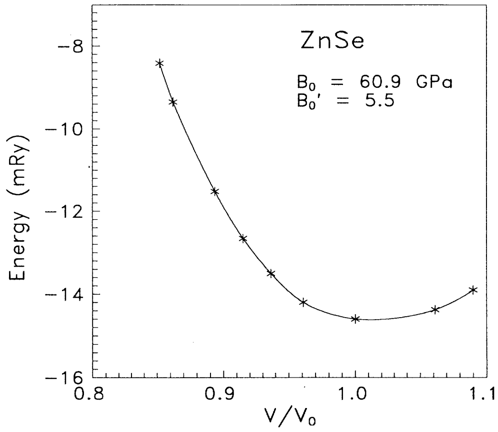

FIG. 2. Total energy per atom vs relative volume for ZnSe.

constituents of the superlattice in order to get the pressure-volume relations for both sides of heterojunction with similar accuracy and by the same method as later calculations for the superlattice. Also it is interesting to compare the pressure behavior of the electronic structure of superlattice with that of constituent materials.

The electronic-band-structure and total-energy calculations were performed for ZnS for 10 and for ZnSe for 13 volumes. The volume dependences of the total energies are shown on Figs. 1 and 2 for ZnS and ZnSe, respectively. From these calculations we have obtained the volume-pressure relations, the equilibrium lattice constants, the bulk moduli, and their pressure dependences. The results, together with the pressure coefficients of the main energy gaps, are summarized in Table I. Comparison with the experimental data is made, and we see that there is good agreement. The value of bulk modulus is smaller for ZnSe than for ZnS, but its pressure coefficient is larger. At a pressure of about 15 GPa the two bulk moduli become equal, and for higher pressures the bulk modulus of ZnSe is larger than that of ZnS. This is illustrated in Fig. 3. The lattice-constant–pressure relation for ZnS is compared with the experimental data[10] up to 10 GPa, and again, as one can see from Fig. 4, there is very good agreement between our calculations and experiment.

The obtained values of bulk moduli are starting points for the calculations of the electronic structure of superlattice for different values of pressure. Here we need the values of elastic constants $c_{11}(p)$ and $c_{12}(p)$ for both sides of the heterostructure. We are taking the values that correspond to our calculated bulk moduli $B_0(p)$, assuming experimental values[10,11] of the ratios c_{11}/c_{12} and experimental values[10,11] of the ratios $(dc_{11}/dp)/(dc_{12}/dp)$.

IV. ZnS/ZnSe SUPERLATTICE UNDER PRESSURE

In order to study the pressure dependence of the electronic structure of ZnS/ZnSe superlattice, the band-

TABLE I. Equilibrium lattice constants a, bulk moduli B_0, their pressure derivatives B_0', and pressure coefficients of the main energy gaps dE_g/dp, for ZnS and ZnSe.

	a (Å)		B_0 (GPa)		B_0'		dE_g/dp (meV/GPa)	
	Present calc.	Expt.	Present calc.	Expt.	Present calc.	Expt.	Present calc.	Expt.
ZnS	5.399	5.4093[a]	81.2	78.4[a] 77.1[c] 75.0[b]	4.05	4.0[b,c]	62	64[d] 63.5[b]
ZnSe	5.698	5.6676[a]	60.9	60.7[a] 62.4[e]	5.5	4.8[e]	63	71.7[e] 75[d] 60[f]

[a] Reference 9.
[b] Reference 12.
[c] Reference 10.
[e] Reference 13.
[d] Reference 14.
[f] Reference 15.

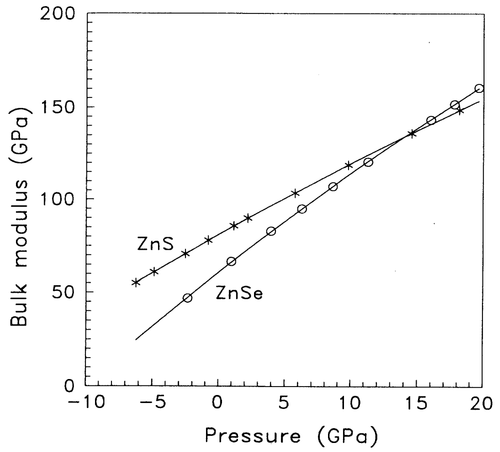

FIG. 3. Bulk moduli; dependences on pressure for ZnS and ZnSe.

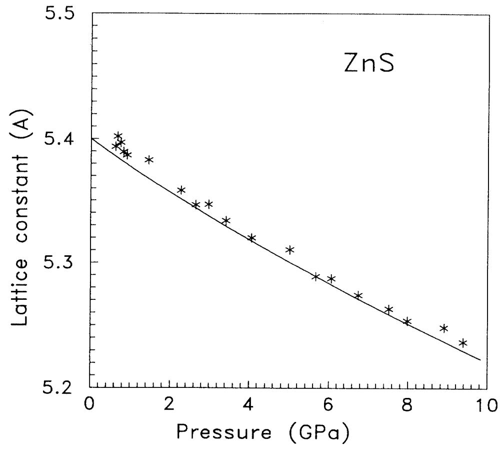

FIG. 4. Lattice constant of ZnS as a function of pressure in a comparison with the experimental data.

structure and total-energy calculations were performed for some values of hydrostatic pressure. The calculation of energy-volume and pressure-volume relations is much more complicated for the superlattices than for the bulk constituents where the volume alone is a free variable and the structure unchanged. For the superlattice we must treat the pressure as the variable and optimize the structure. Energy volume relations are presented in Figs. 5–7 for the strain modes *A*, *B*, and *C*, respectively. From the volume dependence of the total energy, we have obtained the volume-pressure relation, the equilibrium average lattice constants, the bulk moduli, and their pressure coefficients. The calculated band structures are used to derive the pressure coefficients of the energy gaps and the pressure dependence of the valence-band offset ΔE_v, defined as the difference between the energies of the highest occupied states in ZnSe and ZnS. All the results are summarized in Table II. In strain case *B*, the calculated bulk modulus and its pressure coefficients are "intermediate" in the sense that they are between the ZnS and ZnSe bulk values. For strain modes *A* and *B*, the calculated values of B_0 and B'_0 are clearly outside the range spanned by the bulk values.

It is interesting to compare the pressure dependence of the energy gaps derived for bulk ZnS and ZnSe crystals with those of ZnS and ZnSe being constituents of heterostructure. We consider central layers of both sides of heterostructure. The results are presented in Table II and in Figs. 8–10 for the three strain modes considered. Strain mode *A* corresponds to unstrained (bulklike) ZnS and strained ZnSe, so the pressure coefficient of E_g equal to 55 meV/GPa obtained for the ZnS side can be compared with the value 62 meV/GPa obtained for bulk ZnS. Similarly, for strain mode *C*, the ZnSe side corresponds to bulk ZnSe and the pressure coefficient of E_g, 61 meV/GPa, is very close to the bulk value, 63 meV/GPa. As we can see from Figs. 8–10, the pressure behavior of the energy gaps for superlattice is strongly nonlinear for all cases and sensitive to strain condition.

The calculated VBO's are even more sensitive to the strain conditions. As we can see from Table II and Fig. 11, the VBO increases rapidly with pressure for strain mode *A*, slightly less for *B*, and it is almost constant for mode *C*. As in the case of energy gaps, the pressure behavior of VBO's is strongly nonlinear and about 15 GPa (region of phase transitions in ZnS and ZnSe) they become almost pressure independent.

In agreement with the experiment,[4] we find that the conduction-band offset at zero pressure has the opposite sign of the VBO, i.e., the superlattice is of type I. According to the recent experimental data,[4] a conversion from type I to type II is observed at about 3 GPa. We

TABLE II. Bulk moduli B_0, pressure derivatives B'_0, valence-band offsets ΔE_v, their pressure derivatives $d\Delta E_v/dp$, and pressure coefficients dE_g/dp of the main energy gaps in the central layers of both sides of the ZnS/ZnSe heterostructure, for different strain modes: *A*, pseudomorphic growth of ZnSe on a ZnS substrate; *B*, "free-standing" case; *C*, pseudomorphic growth of ZnS on a ZnSe substrate.

Strain mode	B_0 (GPa)	B'_0	dE_g/dp (meV/GPa)		ΔE_v (eV)	$d\Delta E_v/dp$ (meV/GPa)
			ZnS	ZnSe		
A	102	1.8	55	41	0.66	54
B	74	4.9	63	52	0.56	29
C	50	8.6	70	61	0.22	10

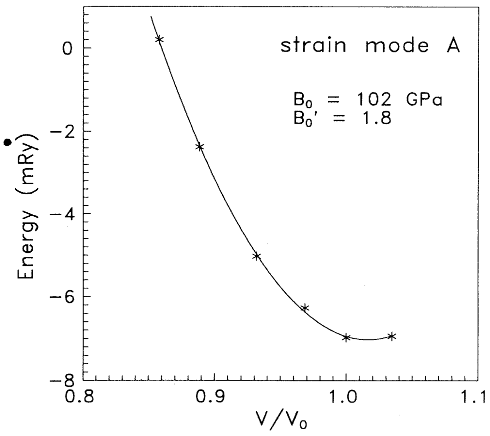

FIG. 5. Total energy per atom vs relative volume for ZnS/ZnSe superlattice strain mode *A*, i.e., pseudomorphic growth of ZnSe on a ZnS substrate.

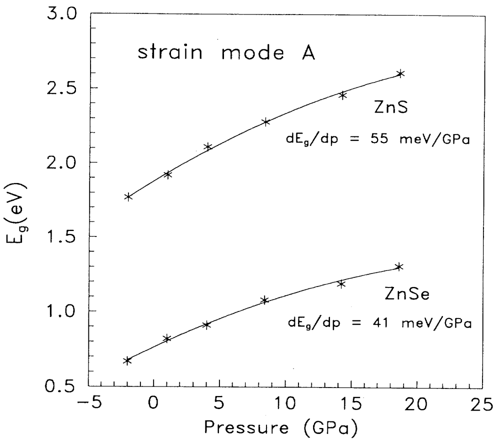

FIG. 8. Pressure dependence of the main energy gaps for both sides of ZnS/ZnSe heterostructure strain mode *A*, i.e., pseudomorphic growth of ZnSe on a ZnS substrate.

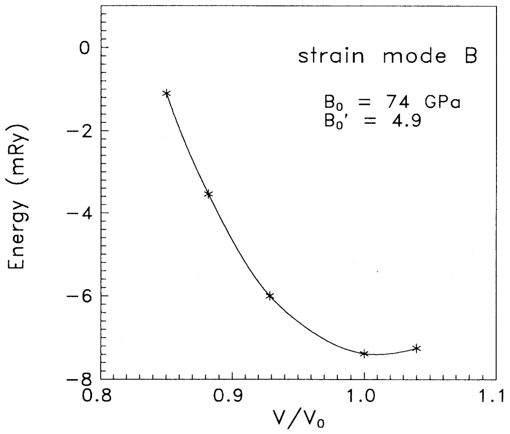

FIG. 6. Same as Fig. 5, but for strain mode *B*, i.e., "free-standing" case.

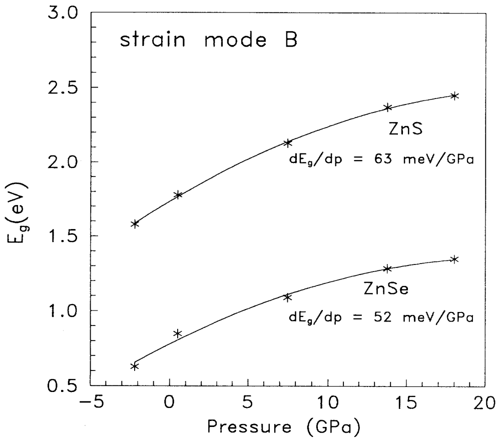

FIG. 9. Same as Fig. 8, but for strain mode *B*, i.e., "free-standing" case.

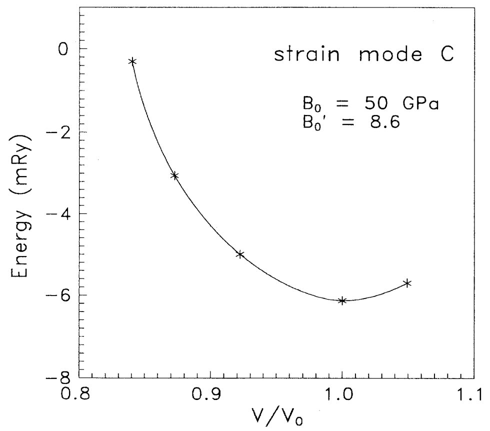

Fig. 7. Same as Fig. 5, but for strain mode *C*, i.e., pseudomorphic growth of ZnS on a ZnSe substrate.

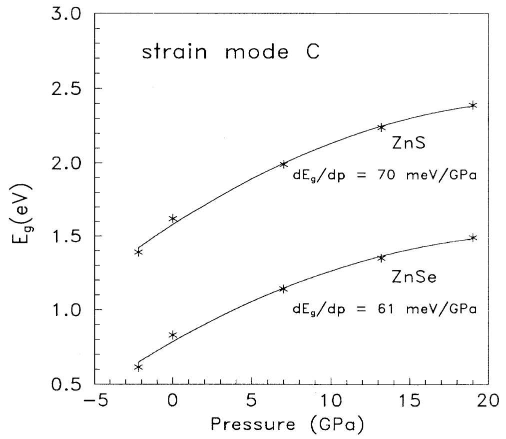

FIG. 10. Same as Fig. 8, but for strain mode *C*, i.e., pseudomorphic growth of ZnS on a ZnSe substrate.

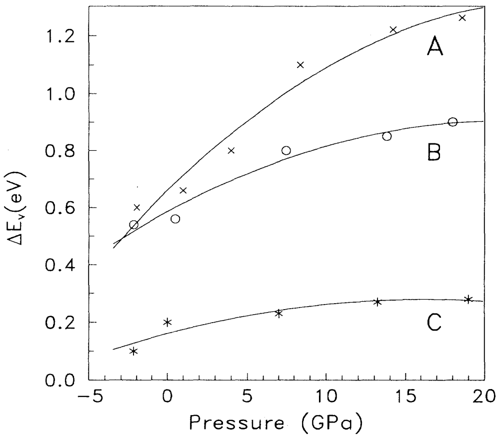

FIG. 11. Pressure dependence of the valence-band offset for ZnS/ZnSe superlattice.

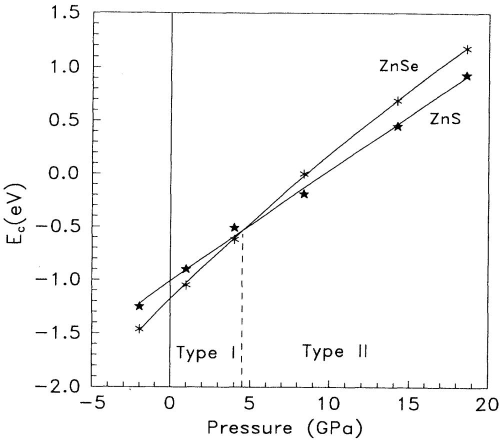

FIG. 13. Pressure dependence of the conduction-band edges for both ZnS and ZnSe layers for strain mode *A*, i.e., pseudomorphic growth of ZnSe on a ZnS substrate. The vertical dashed line indicates the crossover pressure.

also observe the Γ-Γ conduction-band crossover between the ZnSe well layers and ZnS barrier layers for *A* and *B* cases. The situation in case *A* is schematically presented in Fig. 12. To perform more detailed comparison with experiment[4] we have, at first, to adjust the obtained values of the energy gaps to their experimental values for zero pressure (LDA, as is well known, underestimates considerably values of energy gaps) taking into account strain effects caused by lattice nonmatching. To this purpose we use the deformation potentials of the energy gaps obtained for the bulk materials. Next, we determine the conduction-band offset ΔE_c at zero pressure as $\Delta E_c = E_g$ (ZnS)$-E_g$ (ZnSe)$-\Delta E_v$. The resulting pressure dependence of the conduction-band edges for the strain mode *A* is presented in Fig. 13. Our value of critical pressure P_c for conduction-band crossover is about 4.5 GPa, somewhat more than the experimental value 3 GPa, but we consider our value as a rough estimate due to the approximate method used to obtain the energy gaps at zero pressure (and due to the uncertainty in the experimental gap data). With the deformation potentials of the band gaps obtained for bulk materials (-4.5 and -3.7 eV for ZnS and ZnSe, respectively), and deformation potentials of the valence bands obtained previously[1] (-3.5 and -1.2 eV) we find the deformation potentials for the conduction bands: -8.0 eV for ZnS and 0.9 eV for ZnSe. Consequently, the pressure coefficient $d\Delta E_c/dp$ is equal: -18 meV/GPa neglecting the pressure dependence of VBO. Now taking into account the values $d\Delta E_v/dp$ for the strain modes considered, we get the following values of the pressure coefficients $d\Delta E_c/dp$: 35, 12, and -8 meV/GPa for *A*, *B*, and *C* cases, respectively. In case *A*, our estimated value of ΔE_c for zero pressure is 160 meV and again we get $P_c \simeq 4.5$ GPa. In case *B*, the estimated value of P_c is much higher. In case *C*, there is no type conversion at all. On the other hand, the experimental situation described in Ref. 4 is close to our case *A*, since the ZnS layers are twice as thick as the ZnSe layers.

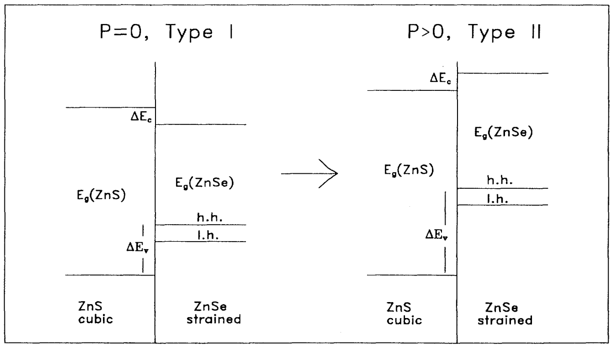

FIG. 12. Pressure-induced conversion from type I to type II of superlattice.

V. SUMMARY

In conclusion, the self-consistent supercell calculations show that the valence-band offset depends on hydrostatic pressure and in turn is strongly affected by the internal strain. For the three cases considered, thin layer of ZnSe on ZnS substrate (*A*), equal thickness (*B*), and thin layer of the ZnS on the ZnSe substrate (*C*), we find that ΔE_V increases with hydrostatic pressure. On the other hand, the conduction-band offset ΔE_c decreases for strain modes *A* and *B* (leading to the type conversion), and increases in case *C*. The estimated value of the crossover pressure ($P_c \simeq 4.5$ GPa) obtained for strain *A* is in reasonable agreement with the experiment ($P \simeq 3$ GPa). Thus, our calculation confirms the experimental observation of a pressure-induced type conversion in ZnS/ZnSe superlattice.

ACKNOWLEDGMENTS

One of us (I.G.) thanks the British Council (Academic link between Glasgow and Warsaw) for financial support. The work was further supported by Grant No.11-9001-3 from the Danish Natural Science Research Council.

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