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Role of *d* electrons in the zinc-blende semiconductors ZnS, ZnSe, and ZnTe

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We perform *ab initio* pseudopotential total-energy calculations for ZnS, ZnSe, and ZnTe. Unlike in most previous calculations, we include Zn 3*d* orbitals (and, in case of ZnTe, Te 4*d* orbitals as well) as part of the valence states in order to study the behavior of the *d* electrons and their influence on energy levels. The results for the structural and electronic properties are in better agreement with experimental data than in the case where *d* electrons are considered as part of the core states. The role of the *d* electrons in determining the bonding strength of the material and the character of the states near the band gap is analyzed and discussed.

The wide band gap II-VI semiconductors have been regarded as promising materials for the fabrication of visible-light-emitting devices[1,2] for decades. ZnS, ZnSe, and ZnTe are the prototype II-VI semiconductors and their cubic phase, which occurs naturally as a mineral, has been called the zinc-blende structure. In recent years, ZnSe has received particular attention as a blue-lasing material and tremendous experimental efforts have been made to fabricate a sustainable ZnSe blue laser. On the theoretical side, many authors have studied these semiconductors to explore their electronic properties, using various computational methods.[3-5] Some calculations[6] have ignored the Zn 3*d* orbitals, assuming them to be part of the chemically inert atomic cores. Though a dramatic reduction in computer time has been achieved, the ignorance of the contribution of the Zn 3*d* electrons to chemical bonding in semiconductors may cause problems in depicting physical properties of the material. Photoemission spectra[7,8] show evidence of cation *d* bands and some recent calculations[9,10] treating the cation *d* electrons as valence electrons have indicated that the cation *d* electrons may play a significant role in II-VI and III-V semiconductors.

In the present study, we consider the Zn 3*d* orbitals as part of the valence states and carry out total-energy calculations using the *ab initio* pseudopotential method. Our calculations are performed in the framework of the density-functional theory within the local density approximation (LDA). Soft norm-conserving pseudopotentials by Troullier and Martins[11] are employed and they are recast into the fully nonlocal separable form as suggested by Kleinman and Bylander.[12] We choose the *s* pseudopotential as the local component to avoid the ghost states.[13] Transferability of the pseudopotentials is checked by calculating and comparing the logarithmic derivatives of the all-electron and pseudo wave functions. The exchange-correlation potential in the Ceperly-Alder form[14] as parametrized by Perdew and Zunger[15] is used. For diagonalization of the matrix equation, we adopt the block-Davidson iterative method[16] with some modifications for optimal performance. The total energy of the system is determined by means of the momentum-space (i.e., the plane-wave basis set) formalism.[17] This method involves the integration over the Brillouin zone, which is carried out with the use of 28 special *k* points within the irreducible wedge of the Brillouin zone. Our calculations include the plane waves with kinetic energy up to 81 Ry, corresponding to a basis set size of $\sim$ 3000, which has been tested to be sufficient for the convergence.

In Table I, we present the structural properties of these materials derived from the Murnaghan's equation-of-state[18] fit to the calculated data points. The results obtained by taking the Zn 3*d* orbitals as part of the valence states are compared with those obtained by two other methods as follows. If we consider the Zn 3*d* orbitals as part of the core states, the calculated equilibrium lattice constants are smaller than experiment by 15.1%, 13.3%, and 10.2%, the calculated bulk moduli are larger by 123%, 110%, and 73%, and the calculated cohesive energies are also larger by 110%, 163%, and 94% for ZnS, ZnSe, and ZnTe, respectively. On the other hand, if we add the partial core correction (PCC) (Ref. 19) to it, the calculated lattice constants are smaller than experiment by 8.8%, 8.3%, and 6.7%, the bulk moduli are larger by 57%, 58%, and 38%, and the cohesive energies are larger by 58.5%, 108%, and 62.9% for ZnS, ZnSe, and ZnTe, respectively. When the Zn 3*d* orbitals are considered as part of the valence states, the results improve dramatically. The calculated lattice constants in this case are smaller than experiment by 0.6%, 1.3%, and 2.3% and the bulk moduli are larger by 9.9%, 12.2%, and 3.9% and the cohesive energies are larger by 13.7%, 56.4%, and 30.0% for ZnS, ZnSe, and ZnTe, respectively. The increase of the lattice constants to nearly the experimental values originates from the correct consideration of the *p*-*d* antibonding. When the Zn 3*d* electrons are treated as core states, the effect of *p*-*d* antibonding is neglected, which results in too short a lattice constant. The system of a shorter lattice constant is stiffer to external pressure and the corresponding bulk modulus will be larger than in the case where the Zn 3*d* electrons are taken as valence states. The relative error in the bulk moduli in the state-of-the-art calculation is typically ~10% and the above results (3.9~12.2%) with Zn 3*d* electrons included in the valence band are quite acceptable. Treating the Zn 3*d* electrons as valence states tends to weaken the co-

TABLE I. Structural parameters of ZnS, ZnSe, and ZnTe (lattice constants a_0, cohesive energy E_c, and bulk modulus B_0) obtained by pseudopotential calculations without valence Zn 3*d* electrons, with the partial core correction (PCC), and with valence Zn 3*d* electrons. For ZnSe and ZnTe, calculations including anion *d* electrons are also listed. Experimental results are given for comparison.

	ZnS				ZnSe					ZnTe				
	without Zn-3*d*	PCC	Zn-3*d*	Expt.[a]	without Zn-3*d*	PCC	Zn-3*d*	Zn-3*d*, Se-3*d*	Expt.[a]	without Zn-3*d*	PCC	Zn-3*d*	Zn-3*d*, Te-4*d*	Expt.[a]
a_0 (Å)	4.5906	4.9286	5.3710	5.4041	4.9163	5.1982	5.5923	5.6383	5.6676	5.4789	5.6948	5.9655	6.1026	6.1037
E_c (eV)	13.30	10.04	7.26	6.33	11.53	9.13	6.85	6.34	4.38	9.35	7.85	6.27	5.76	4.82
B_0 (GPa)	171.6	120.8	84.5	76.9	131.7	98.9	70.1	65.2	62.5	88.0	70.5	52.9	52.9	50.9

[a] See Ref. 21.

valent bond and reduce the cohesive energy. If we repeat the calculation treating the Te 4*d* and the Se 3*d* electrons as valence electrons as well as the Zn 3*d* electrons, the results improve even further. Especially, we obtain $a_0 = 6.1026$ Å for the lattice constant for ZnTe, in excellent agreement with the experimental value of 6.1037 Å. Other results also improve appreciably as explicitly given in the table. But the cohesive energy is still higher than the experimental value, which is a well-known problem of the LDA. In the atomic calculation, the charge density of the states in the outermost atomic shells is distributed highly inhomogeneously around the core region. The LDA usually underestimates the absolute magnitude of the exchange-correlation energy (which is a negative quantity) contributed from these states, hence overestimates the cohesive energy.

We then calculate the energy band structure of ZnS, ZnSe, and ZnTe. If we were to present the band structure at the theoretically obtained equilibrium lattice constant with *d* electrons omitted from the valence band (i.e., included in the core), the results would be too poor to be compared with experimental data or with other computational results treating *d* electrons as valence states. For instance, ZnS, ZnSe, and ZnTe would all be indirect band gap materials with conduction band minima at X. We, therefore, calculate the band structure at the experimental equilibrium lattice constant in case the Zn 3*d* electrons are omitted or the PCC is used. On the other hand, if the Zn 3*d* electrons are retained in the valence band, the calculation of the band structure at the theoretically obtained equilibrium lattice constant does not pose such a problem. The results are given in Table II. It is clear that the calculations that include Zn 3*d* electrons ("Zn 3*d*") are in better agreement with experiment than those "without Zn 3*d*" or those with the "PCC" in the valence band (below the gap). In the conduction band (above the gap), it looks as though the results get worse as we elaborate our calculational scheme step by step from the poorest method of "without Zn 3*d*" to the "PCC" to with "Zn 3*d*." This apparent trend, of course, is an artifact of the LDA that does not include the self-energy correction. If we take the self-energy correction term from the literature[20] (~1.6 eV for ZnS, ~1.4 eV for ZnSe, and ~1.1 eV for ZnTe near the band gap) and add it to the present results, the trend reverses. Furthermore, since the spin-orbit splittings[20] for ZnS, ZnSe, and ZnTe are about 0.07 eV, 0.4 eV, and 1.0 eV, respectively, we must subtract the correction term (one third of the spin-orbit splitting) from our calculated band gap, which does not include the spin-orbit splitting. Last, it turns out essential to treat the Te 4*d* electrons as valence states to get the correct band structure (denoted by "Zn *d*, Te *d*" in the table); otherwise, ZnTe would be an indirect band gap semiconductor with the conduction band minimum at X. (It is surprising that Te 4*d* states lying far below all other valence states have any effects on states near the gap. We will come back to this point later.) Considering all these effects, the calculated minimum band gaps

TABLE II. Energy levels of ZnS, ZnSe, and ZnTe at some symmetry points. These levels are calculated at experimental lattice constants in case Zn 3*d* is omitted or the partial core correction (PCC) is used, whereas they are calculated at calculated equilibrium lattice constants in case Zn 3*d* is retained. For ZnTe, the calculation including Te 4*d* electrons is also listed.

	ZnS				ZnSe				ZnTe				
	without Zn-3*d*	PCC	Zn-3*d*	Expt.[a]	without Zn-3*d*	PCC	Zn-3*d*	Expt.[a]	without Zn-3*d*	PCC	Zn-3*d*	Zn-3*d*, Te-4*d*	Expt.[a]
a_0 (Å)	5.4041	5.4041	5.3710	5.4041	5.6676	5.6676	5.5923	5.6676	6.1037	6.1037	5.9655	6.1026	6.1037
Γ_{1v}	−12.00	−12.03	−13.16	−13.50	−12.03	−12.06	−13.17	−15.23	−10.37	−10.40	−11.52	−11.06	−13.0
$\Gamma_{15v}(d)$			−6.95	−10.0			−7.22	−9.21			−7.71	−7.41	−9.84
$\Gamma_{12v}(d)$			−6.49	−9.03			−6.85	−8.9			−7.47	−7.20	−9.1
Γ_{15v}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Γ_{1c}	3.16	2.99	2.10	3.80	2.70	2.29	1.58	2.69	2.73	2.62	2.37	1.95	2.27
Γ_{15c}	7.29	7.21	6.21	8.35	6.30	6.23	5.35		4.13	4.09	3.31	4.48	4.82
X_{1v}	−10.53	−10.56	−11.85	−12.0	−10.73	−10.76	−11.94	−12.5	−8.75	−8.78	−10.01	−9.72	−11.6
X_{3v}	−4.07	−4.12	−4.76	−5.5	−4.24	−4.28	−5.02	−5.3	−4.52	−4.55	−5.43	−5.03	−5.5
X_{5v}	−1.48	−1.49	−2.35	−2.5	−1.56	−1.57	−2.39	−2.1	−1.69	−1.70	−2.48	−2.24	−2.4
X_{1c}	3.69	3.57	3.17		3.18	3.07	2.63		1.97	1.90	1.49	2.35	3.05
X_{3c}	4.60	4.49	4.05	4.9	3.72	3.62	3.23		2.21	2.13	1.73	2.59	
L_{1v}	−10.91	−10.94	−12.18	−12.4	−11.07	−11.10	−12.25	−13.1	−9.21	−9.24	−10.41	−10.07	−12.0
L_{1v}	−4.30	−4.35	−5.47	−5.5	−4.39	−4.44	−5.53		−4.52	−4.55	−5.63	−5.20	−5.5
L_{3v}	−0.51	−0.51	−0.92	−1.4	−0.56	−0.56	−0.96	−1.3	−0.65	−0.65	−1.05	−0.93	−1.1
L_{1c}	4.21	4.08	3.29		3.31	3.20	2.53		2.23	2.16	1.74	2.12	2.38

[a] See Ref. 21.

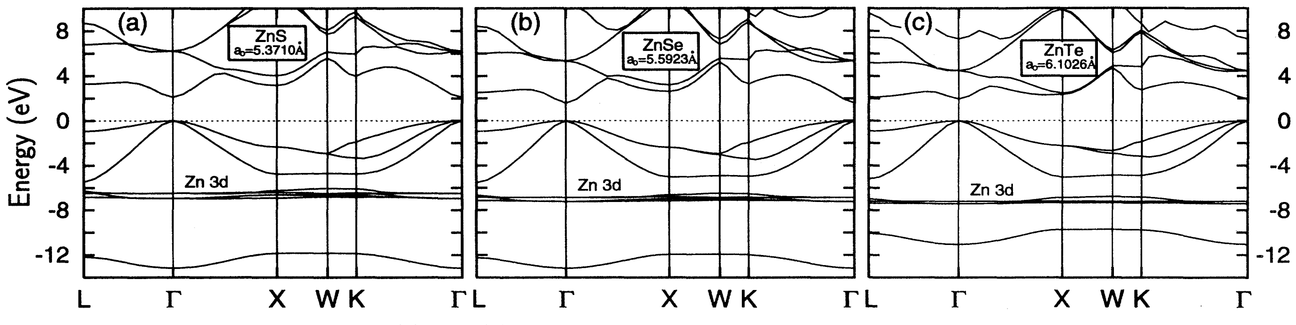

FIG. 1. Calculated band structures of (a) ZnS, (b) ZnSe, and (c) ZnTe at their calculated equilibrium lattice constants. Zn $3d$ electrons are considered as valence electrons. For ZnTe, Te $4d$ electrons are considered as valence electrons as well.

(at Γ) are 3.72, 2.85, and 2.72 eV compared with experimental values of 3.80, 2.69, and 2.27 eV, respectively. The experimental values may go up a little bit in the low temperature limit where all the theoretical calculations are done.

Figure 1 shows the calculated band structure of these materials with the valence Zn $3d$ electrons at their calculated equilibrium lattice constant. At the bottom, there is an anion s band exhibiting a weak dispersion. A group of bands above it is composed of five Zn $3d$ bands. There are Zn $3d$ bands centered around -6.9 eV for ZnS, -7.0 eV for ZnSe, and -7.6 eV for ZnTe. The d bands are very narrow and show very little dispersion. The finite bandwidth results from the p-d hybridization with the anion p bands. The bandwidth (i.e., splitting) of Zn $3d$ levels at Γ is 0.46 eV for ZnS, 0.37 eV for ZnSe, and 0.21 eV for ZnTe (Table II), and this trend is obvious in Fig. 1 as well. The p-d hybridization repels the energy level of the Γ_{15v} states (having t_2 symmetry) downwards by $V_{pd}^2/(\varepsilon_d^{Zn} - \varepsilon_p^a)$, where V_{pd} is the p-d interaction matrix element, ε_d^{Zn} the Zn $3d$ level, and ε_p^a the anion p level.[9] The energy level of the Γ_{12v} states (having e symmetry) does not change. According to our calculation, the atomic orbital energy of Zn $3d$ electrons is -10.85 eV and the atomic orbital energies of S $3p$, Se $4p$, and Te $5p$ electrons are -7.12 eV, -6.69 eV, and -6.17 eV, respectively. Therefore, the bandwidth of d levels gets smaller as we go from ZnS to ZnSe to ZnTe. The Zn $3d$ bands lie 2–3 eV higher in energy than observed experimentally. This is believed to be a shortcoming of the LDA in which the exchange-correlation effect of the highly localized states is not fully included. A more complete inclusion of the exchange-correlation effect would lower the d levels. The calculated band gap is reduced when we treat the Zn d electrons as valence electrons, because the hybridization of the Zn d state with the p-like upper valence band results in the upward movement of the valence band maximum (VBM). Not shown in the figure are the five Te $4d$ bands at around -38 eV. It is rather hard to imagine that Te $4d$ electrons have any influence on the band gap states nearly 40 eV above them. We, therefore, analyze the character of states near the band gap. The symmetry-decomposed partial charges for the conduction and the valence band edges of ZnTe at k points of high symmetry are listed in Table III, with and without the Te $4d$ electrons in the valence shell. The partial charges clearly indicate Zn d-Te p hybridization for Γ_{15v} states in both cases, and that the Zn s character increases in L_{1c} and X_{1c} when the Te $4d$ electrons are treated as valence electrons. We plot the partial density of states in two cases in Fig. 2, which exhibits Zn d-Te p hybridization around -7.5 eV, as well as close to the VBM. Near the bottom of the conduction band, we find again a larger Zn s character, when we consider the Te $4d$ electrons, as valence electrons, than the other case in accordance with

TABLE III. Symmetry-decomposed partial charges [in unit of electrons/(a_B^3×state) × 100] for the conduction and valence band edge states of ZnTe at k points of high symmetry. Calculations with and without Te $4d$ in the valence states are compared. The muffin-tin radii $R_{\mathrm{MT}}(\mathrm{Zn})=1.40a_B$ and $R_{\mathrm{MT}}(\mathrm{Te})=1.50a_B$.

		Zn			Te		
		s	p	d	s	p	d
Zn 3*d*, without Te 4*d*	Γ_{15v}	0	2	18	0	32	0
	Γ_{1c}	70	0	0	119	0	0
	L_{3v}	0	4	12	0	27	0
	L_{1c}	53	1	5	47	2	2
	X_{5v}	0	4	6	0	22	0
	X_{1c}	37	0	0	0	5	3
Zn 3*d*, with Te 4*d*	Γ_{15v}	0	2	18	0	32	0
	Γ_{1c}	71	0	0	115	0	0
	L_{3v}	0	3	9	0	26	0
	L_{1c}	59	1	3	49	2	2
	X_{5v}	0	4	4	0	21	0
	X_{1c}	47	0	0	0	5	3

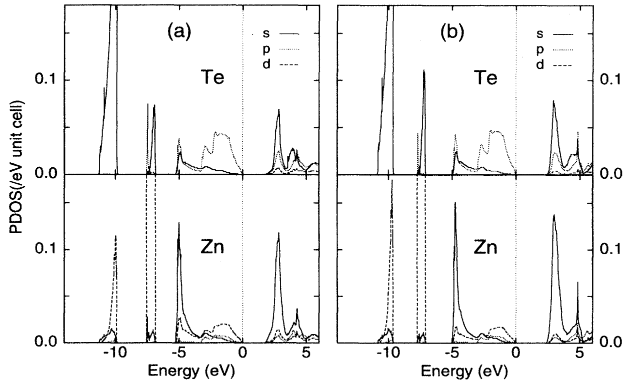

FIG. 2. The partial density of states of ZnTe at calculated equilibrium lattice constants (a) with Zn $3d$ electrons as valence electrons and (b) with both Zn $3d$ and Te $4d$ electrons as valence electrons.

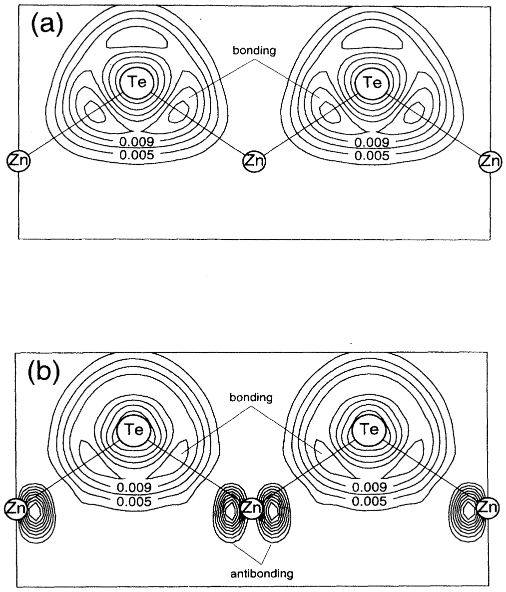

FIG. 3. Electronic charge density plot in the (110) plane of ZnTe for the valence band maximum state at Γ. The numbers are in electrons/a_B^3 and the contours are spaced by 0.002. (a) Without Zn 3d electrons in the valence band and (b) with Zn 3d and Te 4d electrons in the valence band.

the partial charge analysis in Table III. Such influence of Te 4d electrons, though indirect, eventually corrects the false ordering of the energy levels of states near the gap (we mentioned before that, without Te 4d electrons in the valence band, ZnTe would be an indirect band gap material with the conduction band minimum at X) and makes ZnTe a direct band gap material in agreement with experiment. We have also carried out the band structure calculation for ZnSe with Se 3d electrons included in the valence band. Unlike in ZnTe, the calculated band structure does not show appreciable changes by the inclusion of the Se d electrons and it is unnecessary to present the result separately in the table.

Figure 3 shows the charge density of the Γ_{15v} state at the valence band maximum in ZnTe. The bonding character of Zn p-Te p electrons around the Te site is demonstrated in both (a) and (b), namely, irrespective of the presence of the Zn 3d electrons in the valence band. On the other hand, the antibonding character around the Zn site is clearly exhibited only when the Zn 3d electrons are included in the valence band [Fig. 3(b)]. The p-d antibonding gives rise to charge transfer from the Zn-Te bond to the antibonding site around the Zn atom. Although we plot in Fig. 3(b) the charge density when both Zn 3d and Te 4d electrons are included in the valence band, we have checked that the presence of the Te 4d electrons does not influence the charge density of the Γ_{15v} state as long as the Zn 3d electrons are treated as valence states.

In conclusion, we have performed *ab initio* pseudopotential total-energy calculations for ZnS, ZnSe, and ZnTe. We have included Zn 3d orbitals (and, in case of ZnTe, Te 4d orbitals as well) as part of the valence states and compared the result with the case where those orbitals are included in the inert atomic cores. We find a significant improvement in the description of various structural and electronic properties as we elaborate our computational scheme stepwise from the one without Zn 3d electrons in the valence band to the one with the PCC to the one with Zn 3d electrons fully included in the valence band. For ZnTe, inclusion of Te 4d electrons in the valence band further improves the calculation and the final results are in excellent agreement with experiment.

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