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Ab initio calculations of the electronic structure of the wurtzite compounds CdS and CdSe

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We report *ab initio* calculations of the lattice constants and the electronic structure of the hexagonal wurtzite semiconductors CdS and CdSe. The calculations have been carried out self-consistently in the local-density approximation employing nonlocal, separable, and norm-conserving pseudopotentials. We use Cd^{12+} ionic pseudopotentials so that the Cd 4*d* electrons are explicitly taken into account as valence electrons. The calculated electronic structure is compared with photoemission data. Calculated and measured bands show good agreement in the energy region of the mostly anion-derived *s*-*p* valence bands. The calculated Cd 4*d* bands result for both compounds roughly 3 eV too high in energy as compared to the measured data. This rigid shift of the narrow 4*d* bands is related to correlation effects which are not fully taken into account in the local-density approximation.

I. INTRODUCTION

Tetrahedrally coordinated, ionic II-VI compound semiconductors and their surfaces have been the subject of angle-resolved photoemission investigations in recent years. The bulk compounds can crystallize in the cubic zinc-blende structure (e.g., ZnS, CdS, or CdSe), or in the hexagonal wurtzite structure (e.g., ZnS, ZnO, CdS, or CdSe). The cubic structure has two atoms (one anion and one cation), and the hexagonal structure has four atoms (two anions and two cations) in the bulk unit cell. The *d* electrons of the cations (3*d* for Zn and 4*d* for Cd) cannot be treated as core electrons when structural and electronic properties are to be calculated quantitatively. Taking the *d* electrons into account as valence electrons makes band-structure calculations fairly involved. This holds particularly for hexagonal crystals, which have twice as many atoms in the unit cell as cubic crystals. Due to the strong localization of the pseudopotentials and the respective wave functions, huge basis sets are needed if the hexagonal compounds are to be studied with plane-wave basis sets. Until very recently, no fully self-consistent *ab initio* band-structure calculations were available for hexagonal wurtzite-type II-VI compounds based on modern nonlocal, norm-conserving pseudopotentials.

In a recent paper[1] we reported a detailed study of the structural and electronic properties of hexagonal ZnS and ZnO. In that paper we scrutinized the influence of the closed Zn 3*d* electron shell on the calculated band structures and lattice constants. We showed that treating the Zn 3*d* electrons as valence electrons is a necessary step toward a quantitative description of the structure and electronic properties of those compounds. Using a Zn^{2+} ionic pseudopotential, we obtained lattice constants that were 13% (for ZnS) and 18% (for ZnO) too small, as compared to experiment, while our Zn^{12+} ionic pseudopotential yielded lattice constants for both ZnS and ZnO within 1% of the experimental data. The electronic structure calculated with the Zn^{12+} ionic pseudopotentials was found to agree much better with experiment than the one calculated with the Zn^{2+} ionic pseudopotential that treated the Zn 3*d* electrons as core electrons.

In this paper, we describe the results of an extension of our previous work on ZnS and ZnO to hexagonal 4*d* compounds CdS and CdSe. To our knowledge this study provides the first self-consistent calculations of the structural and electronic properties of wurtzite CdS and CdSe including Cd 4*d* electrons as valence electrons in the effective one-particle potential. It is necessary to treat the Cd 4*d* electrons as valence electrons since the 4*d* electron energies reside within the spectral range of the mainly anion-derived *s*-*p* valence bands. The local-density approximation (LDA)-term values of the relevant orbitals are −5.96 eV (Cd 5*s*), −11.9 eV (Cd 4*d*), −7.11 eV (S 3*p*), −17.28 eV (S 3*s*), −6.66 eV (Se 4*p*), and −17.48 eV (Se 4*s*). The self-consistent bulk band-structure calculations reported in this paper are a necessary prerequisite for state-of-the-art surface-band-structure calculations of wurtzite-structure CdSe and CdS.[2]

II. CALCULATIONAL DETAILS

Our calculations are performed in the framework of density-functional theory within the local-density approximation (LDA).[3] We have used nonlocal, norm-conserving pseudopotentials[4] in the separable form as suggested by Kleinman and Bylander.[5] The exchange and correlation potential is used in the Ceperley-Alder[6] form as parametrized by Perdew and Zunger.[7] An atom-centered Gaussian basis set of *s*, *p*, *d*, and s^* orbitals is employed for the expansion of the wave functions. For the Cd orbitals, five shells with decay constants of 0.2, 0.53, 1.41, 3.76, and 10.0 a.u. are used while for the S and Se orbitals it is three shells with decay constants of 0.2, 0.5, and 0.8 a.u. Brillouin-zone integrations have been carried out using six special **k** points[8] in the irreducible part of the zone. Spin-orbit coupling has not been taken into account explicitly in order to avoid doubling the size of all matrices. In CdS the spin-orbit effects on the *s*-*p* valence bands are less than 0.1 eV,[9] anyway. In CdSe the

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spin-orbit interactions lead to a band splitting of nearly 0.4 eV at the top of the valence bands. This has to be taken into consideration when we compare the results of our calculations, neglecting spin-orbit coupling with experimental data. Further computational details and the evaluation of the matrix elements of the nonlocal pseudopotentials are described in Ref. 1.

III. RESULTS AND DISCUSSION

We now turn to a brief presentation and discussion of the structural and electronic properties of hexagonal CdS and CdSe. Our calculations have shown that the inclusion of the Cd 4*d* electrons as valence electrons is mandatory for at least two reasons. First, only in this way can we arrive at an appropriate total energy which describes the structural properties correctly; and, second, there are appreciable *s*-*d* and *p*-*d* interactions which have to be taken into account for a reliable description of the dispersion of the bands.

From the total-energy curves we obtain the lattice constants. They are given in Table I in comparison with the experimental data. The agreement between theory and experiment is good, with deviations of roughly 2%. We observe a slight increase in the deviations between theory and experiment as compared to our results for hexagonal ZnS and ZnO[1] where our calculated lattice constants were within 1% of the measured values. This slight increase can be attributed to effects of the neglected spin-orbit coupling and to the stronger overlap between core and valence states in Cd as compared to Zn. Nevertheless, the agreement is very satisfactory, and it could only be obtained by using a Cd^{12+} ionic pseudopotential.

TABLE I. Calculated lattice constants (in Å) of CdS and CdSe in comparison with experimental data (Ref. 15).

		Theory	Expt.
CdS	*a*	4.03	4.13
	c	6.54	6.70
CdSe	*a*	4.21	4.30
	c	6.86	7.01

The band structures and densities of states (DOS) for hexagonal CdS and CdSe are compiled in Fig. 1. They have been calculated employing experimental lattice constants. In Fig. 1(a) we have included photoemission data at high-symmetry points for CdS as measured by Stoffel.[10] Considering the band structures and the densities of states for CdS and CdSe in direct comparison, we first note that they are very similar. The topology of the bands in each of the four groups of bands is basically the same. The lowest two bands are derived from anion *s* states. The following group of ten bands originates from the Cd 4*d* orbitals. Then there is a group of six mostly anion-derived *s*-*p* valence bands. The first two conduction bands are strongly dominated by cation *s* states. In both compounds, the *d* bands are clearly separated in en-

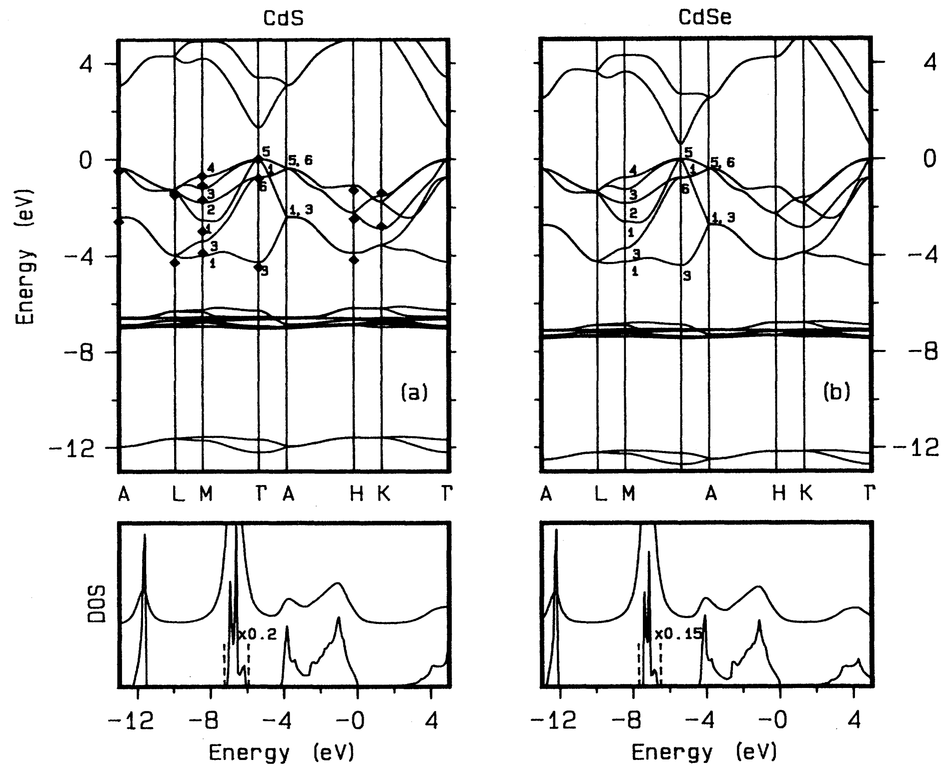

FIG. 1. Bulk band structure and density of states of hexagonal CdS (a) and CdSe (b) as calculated with a Cd^{12+} ionic pseudopotential. (a) includes data points from photoemission measurements by Stoffel (Ref. 10). The unbroadened DOS of the *d* bands is scaled down by constant factors of 0.2 (for CdS) and 0.15 (for CdSe) for the sake of clarity. In addition, broadened densities of states (Lorentzian broadening with 0.3 eV) are shown. Numbers refer to the conventional indices for symmetry-group representations.

ergy from the other two groups of valence bands. This is different from the case of ZnS and ZnO, where the Zn 3*d*-bands result very close to the anion-derived group of six mostly *p*-like valence bands (see Ref. 1), and from the case of GaN, where the Ga 3*d*-bands result close to the N *s*-like valence bands (see Ref. 11). Therefore, in CdS and CdSe the *d* orbitals show effects of the interaction with both the anion *s* and *p* orbitals, while in ZnO (Ref. 1) it is the *p*-*d* interaction, and in GaN (Ref. 11) the *s*-*d* interaction which dominates the coupling of the anions to the cationic *d* electrons. In Cd chalcogenides, *d* bands are characterized by three peaks in the unbroadened DOS since the *p*-*d* interaction shifts corresponding *d* bands to lower energies, and the *s*-*d* interaction shifts corresponding *d* bands to higher energies. Stoffel[10] attributed the occurrence of three peaks in his photoemission spectrum of the 4*d* bands of CdS to the influence of the *s*-*d* and *p*-*d* interactions. That notion is nicely confirmed by our results. In both compounds we find a *d*-band-width of less than 1 eV (CdS: 0.78 eV, CdSe: 0.62 eV). It is thus considerably smaller than the respective width in ZnO (see Ref. 1). The coupling of the *d* electrons with their neighboring anionic orbitals in CdS and CdSe can therefore be classified as intermediate when compared to ZnO and GaN.

We note in passing that the bulk band structure of wurtzite CdS was calculated self-consistently by Chang, Froyen, and Cohen[12] ten years ago. These authors treated the Cd 4*d* electrons as core electrons, which is not an entirely satisfying approximation according to our results. Those authors found a bandwidth of 4.1 eV for the upper six valence bands, and a total valence-band width of 11.7 eV. Our calculations yield a width of 4.3 and 12.3 eV for the respective band groups, in much closer agreement with the experimental values of 4.5 (Ref. 10) and 12.5 eV.[13]

The comparison of our calculated band structure for CdS with photoemission data[10] in Fig. 1(a) shows that the measured dispersion of the upper six valence bands is very nicely described by our results, except for a small underestimate of the related bandwidth by 0.2 eV. Furthermore, it should be noted that the two states M_{1v} and M_{3v} (the fourth and fifth bands) have not been resolved in experiment. Only one peak could be identified in the middle between M_{1v} and M_{3v}. It seems to result from a superposition of the two states clearly separated in our results. More detailed experimental information on this group of bands has been reported by Magnusson and Flodström.[14] These authors have taken photoelectron spectra for wave vectors along the Σ line of the bulk Brillouin zone of CdS and CdSe using polarized synchroton radiation. With light polarized parallel ($\mathbf{E}\|\mathbf{c}$) or perpendicular ($\mathbf{E}\perp\mathbf{c}$) to the mirror plane of the $(10\bar{1}0)$ surface, they were able to discern initial states with even or odd parities, respectively. The experimental data are compared with our results in Fig. 2. For both CdS and CdSe the ordering of the calculated bands of odd (M_2, M_4) and even (M_1, M_3) states is in agreement with the data. The dispersion of the bands is slightly underestimated in CdS, and more so in CdSe. Deviations amount to 0.26 (M_4, M_2) and 0.38 eV (M_1) for CdS, and up to 0.6 eV (M_1) for CdS. The agreement for the highest even states in CdS (M_3) is significantly better. To further improve the description of this group of valence bands, in particular in CdSe, spin-orbit coupling and quasiparticle corrections should be included in the calculations. From the comparisons in Fig. 2 we conclude that our calculations provide band structures which are, in particular for CdS, in reasonably good agreement with the photoemission data of Magnusson and Flodström.[14] The calculated bulk band structure for CdS may thus serve as a convenient starting point for surface-band-structure calculations.[2]

Finally we address two general shortcomings of our LDA results for CdS and CdSe. One is the energetic position of the *d* bands, and the other the magnitude of the fundamental band gap. The calculated *d* bands for both compounds result nearly 3 eV too high in energy compared to experiment, and the gap is underestimated by more than 50%. Both these deviations are in common with our previous results for ZnO and ZnS,[1] and are due to inherent shortcomings of the LDA. The reasons for these deviations, and possible means to overcome them in more elaborate calculations [self-interaction corrections (SIC) and quasiparticle band-structure calculations] have been addressed in general in Ref. 1. The theoretical and experimental values for the *d*-band positions and gap energies are given in Table II together with the results for ZnO and ZnS. The calculated position of the *d* bands in the bulk materials clearly follows the difference between the atomic LDA eigenvalues of the anion *p* and cation *d* levels. Due to a significant mixing of the *d* orbitals with the *p* wave functions at the top of the valence bands (Γ_{5v}), the wrong position of the *d* bands is to some extent transferred to the resulting wave functions in this energy region. As already discussed in Ref. 1, this mixing pushes the mainly *p*-derived upper valence bands toward the conduction bands, thus decreasing the gap width to a certain extent. In ZnO, where the Zn 3*d* contribution to the uppermost valence band at the Γ point amounts to

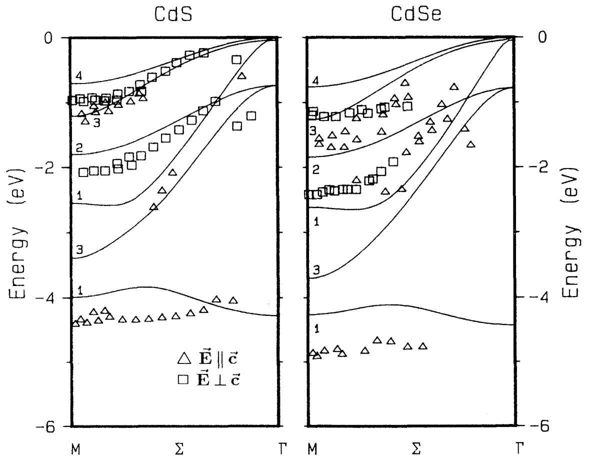

FIG. 2. Comparison of the calculated upper six valence bands with polarization- and angle-resolved photoemission data of Magnusson and Flodström (Ref. 14) along the Σ line of the bulk Brillouin zone. The experimental data refer to bands resulting from even (△) or odd (□) states.

TABLE II. Calculated and measured energy gaps (E_g) of II-VI compounds as well as calculated and measured d-band positions. For further comparison, the differences between atomic LDA eigenvalues Δ_{p-d} for anion p and cation d levels are given. All values are given in eV except for the percental contribution of the d-orbital admixture ($d(\Gamma_{5v})$) to the wave functions of the Γ_{5v} states at the top of the valence bands.

	ZnO	ZnS	CdS	CdSe
E_g^{th}	0.23	1.97	1.31	0.60
E_g^{expt}	3.44[a]	3.91[a]	2.58[a]	1.84[a]
E_d^{th}	-5.12	-5.80	-6.79	-7.18
E_d^{expt}	-7.80[b]	-9.03[c]	-9.64[c]	-10.04[c]
$\Delta_{p-d}^{\mathrm{atom}}$	1.22	3.31	4.79	5.29
$d(\Gamma_{5v})$	29.4	16.5	10.6	10.9

[a] Reference 15.
[b] Reference 16.
[c] Reference 17.

nearly 29%, the gap is even almost closed. This effect is less pronounced in CdS and CdSe since the d bands are lower in energy, and the mixing is thus smaller. In both compounds the d contribution to the Γ_{5v} valence-band state is nearly the same, namely about 11% (see Table II). The resulting upward shift of Γ_{5v} is thus similar in both compounds. Since the experimental gap in CdS is larger than in CdSe, the calculated gap for CdS is in better agreement with experiment than that for CdSe. Nevertheless, the calculated gap energies are only 50% (CdS) and 30% (CdSe) of the experimental values, respectively. These shortcomings are typical for LDA calculations, and they are somewhat enhanced by the inappropriate positioning of the d bands.

As a final point, we note from Table II that the deviation between calculated and measured d-band positions is roughly 3 eV for all four compounds ZnO, ZnS, CdS, and CdSe. This is revealing in view of the fact that the d bands are much closer to the p-like valence bands in ZnO and ZnS than in CdS and CdSe. This result, therefore, seems to hint at the fact that the wrong d-band position is largely due to an inappropriate description of correlation effects in the cations themselves rather than being a solid-state effect. This notion is confirmed by a SIC calculation for the S and Cd atoms by Chang, Froyen, and Cohen[12] which yields an increase of the level spacing between the S $3p$ and Cd $4d$ energy levels by about 2 eV as compared to the LDA term values.

In summary, we have obtained calculated lattice constants for CdS and CdSe in good agreement with experiment. Furthermore, the calculated band structure of CdS shows very good agreement with angle-resolved photoemission data. Somewhat larger differences are observed for the electronic structure of CdSe, where spin-orbit and many-body corrections might be more important. Specific features of the calculated band structures related to the cationic d bands and their rigid shifts relative to experiment are in common with our results for hexagonal ZnO and ZnS discussed in Ref. 1.

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