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Chemical trends in band offsets of Zn- and Mn-based II-VI superlattices: *d*-level pinning and offset compression

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Calculation of the unstrained band offsets between conventional zinc-blende II-VI superlattices (ZnS/ZnSe/ZnTe), or between magnetic II-VI superlattices (MnS/MnSe/MnTe) or combinations thereof (Mn*X*/Zn*X*) show that (i) the range of offsets spanned by different magnetic II-VI superlattices is compressed by a factor of 2 relative to the range of offsets spanned by conventional II-VI superlattices, (ii) the distance between the Mn *d* band and the valence-band maximum in Mn*X* depends weakly on *X*, while in conventional II-VI superlattices (e.g., Zn 3*d* in Zn*X*) there is a wider spread, and (iii) unlike the case for conventional common-anion II-VI superlattices, the mixed offset ΔE_V(Zn*X*/Mn*X*) depends strongly on *X*. We show that all three effects have a simple and common physical origin.

Superlattices and heterojunctions between common-cation conventional II-VI superlattices (e.g., ZnS/ZnSe/ZnTe), between common-cation magnetic II-VI superlattices (e.g., MnS/MnSe/MnTe), and combinations thereof (e.g., Zn*X*/Mn*Y*) have been studied extensively.[1,2] Of particular interest to optical and transport studies are experimental[3–12] and theoretical[13–17] investigations of the band offsets in these systems. We have systematically studied via *ab initio* theoretical methods the various unstrained, ''natural'' valence-band offsets ΔE_V in these systems, finding the following three interesting effects.

(i) Both the magnitude and the range of the offsets ΔE_V(Mn*X*/Mn*Y*) between *magnetic* II-VI superlattices with different anions *X*,*Y*=S, Se, and Te are reduced relative to the magnitude and range of ΔE_V(Zn*X*/Zn*Y*) in the analogous *nonmagnetic* II-VI superlattices. The calculated nonmagnetic offsets are 0.53, 0.73, and 1.26 eV for the S/Se, Se/Te, and S/Te pairs, respectively, while for the magnetic systems the offsets are 0.22, 0.42, and 0.64 eV, respectively.

(ii) The one-electron energy separation ΔE_{d^+}(Mn*X*) $=E_{\mathrm{VBM}}-E_{d^+}$ between the valence-band maximum (VBM) and the center of the occupied Mn d^+ band depends only weakly on the identity of the anion *X*: the values of ΔE_{d^+}(Mn*X*) are 2.4, 2.6, and 2.9 eV for *X*=S, Se, and Te, respectively. This result parallels the trend observed in a related[18] quantity, namely, the pinning of the Mn d^+-band *binding energies* in photoemission experiment of Mn*X*.[11] In contrast, in conventional II-VI compounds, the calculated distance ΔE_d(Zn*X*) varies in a wider range, being 6.4, 6.8, and 7.5 eV for ZnS, ZnSe, and ZnTe, respectively.[18]

(iii) The unstrained band offset ΔE_V(Zn*X*/Mn*X*) between magnetic and nonmagnetic II-VI superlattices depends *strongly* on the identity of the anion *X*. The offset is positive for *X*=S, but changes to negative values for *X*=Se and Te. This is unlike the case of conventional (nonmagnetic) common-anion heterostructures where the ''new common anion rule''[13,14] and the data[19] show that the unstrained offset $\Delta E_V(AX/BX)$ depends only weakly on the identity of the anion *X*.

In the following, we will describe our calculations and show that all three effects (i)–(iii) share a simple and common physical origin: they emerge from the fact that the anion *p* levels of S, Se, and Te in Mn*X* lie between the spin-up and spin-down Mn 3*d* states, while in Zn*X*, the Zn 3*d* band is systematically *below* the anion *p* levels.

To calculate the valence-band offset $\Delta E_V(AX/BX)$ between two compounds *AX* and *BX* we follow the procedure used in photoemission core-level spectroscopy,[20] where the band offset is given by

$$\Delta E_V(AX/BX)=\Delta E^{BX}_{\mathrm{VBM},C'}-\Delta E^{AX}_{\mathrm{VBM},C}+\Delta E_{C,C'}(AX/BX). \tag{1}$$

Here,

$$\Delta E^{AX}_{\mathrm{VBM},C}=E^{AX}_{\mathrm{VBM}}-E^{AX}_{C} \tag{2}$$

(and similarly for $\Delta E^{BX}_{\mathrm{VBM},C'}$) are the core-level valence-band-maximum energy separations for pure *AX* (and similarly for pure *BX*), while

$$\Delta E_{C,C'}(AX/BX)=E^{BX}_{C'}-E^{AX}_{C} \tag{3}$$

is the difference in core-level binding energy between *AX* and *BX* in the *AX*/*BX* heterojunction. To obtain the *unstrained* ''natural'' offsets, the core-to-VBM one-electron energy difference $\Delta E_{\mathrm{VBM},C}$ is calculated for *AX* and *BX* at their respective *equilibrium* cubic lattice constants[1] (Table I), thus the VBM is not split by a crystal field. The core-level difference $\Delta E_{C,C'}(AX/BX)$ is obtained here from the calculation for the $(AX)_n/(BX)_n$ superlattices with (001) orientation. The superlattice layer thickness *n* is increased until the core levels of the innermost layer on each side of the superlattice are bulklike. The structural parameters of the superlattice are fully relaxed, so interface effects on the band offset are taken into account. The lattice constant mismatch between *AX* and *BX* causes some relaxation, hence shift, in the core levels.[21] The effect on the difference $\Delta E_{C,C'}(AX/BX)$ is estimated to be smaller than 0.05 eV for all systems studied here. Therefore, our calculated results represent ''relaxed and unstrained natural band offsets.'' If one is interested instead in the case where the compounds form a *coherently strained* interface, the band-edge energy E_{VBM} of each compound is split and

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TABLE I. Relative energies E_{VBM} of eight cubic II-VI compounds calculated at their respective measured cubic equilibrium lattice constants a_{eq} (from Ref. 1). We give calculated results using the standard LSDA and using the corrected LSDA (LSDA+C). The energy zero is placed arbitrarily at the VBM of ZnS. The energy difference between any of the two compounds gives the unstrained natural band offset. The calculated spin-orbit splittings Δ_0 (included in the present relativistic calculation) are also given.

Compounds	a_{eq} (Å)	Δ_0 (eV)	E_{VBM} (eV) LSDA	E_{VBM} (eV) LSDA+C
ZnS	5.409	0.07	0.00	0.00
ZnSe	5.668	0.40	0.53	0.53
ZnTe	6.089	0.89	1.26	1.26
MnS	5.606	0.00	0.43	0.09
MnSe	5.904	0.14	0.55	0.31
MnTe	6.330	0.42	0.86	0.73
CdTe	6.480	0.85	1.17	1.17
HgTe	6.460	0.78	1.53	1.53

shifted relative to the unstrained values through the deformation potential. The change of E_{VBM} depends on the size and direction of the strain.[22] We find that the total uncertainty due to the neglect of core-level deformation potential and the choice of magnetic ordering (see below) is about 0.1 eV.

The band-structure calculation is performed using the local-spin-density-functional approximation[23,24] (LSDA) as implemented by the general-potential, *relativistic*, all-electron, linearized-augmented-plane-wave (LAPW) method.[25] We used the Ceperley-Alder exchange and correlation potential[23] as parametrized by Perdew and Zunger.[24] For MnX we assume a type-I antiferromagnetic spin arrangement. The electronic properties of type-I MnX are similar to those of the type-III ground state.[26]

We have previously[14] noted that the LSDA underestimates the spin-exchange splitting in MnX. We corrected this[26] via addition to the LSDA of a fitted parametric external potential, finding that this also improves considerably the agreement with experiment of many other band-structure-related properties. Here we calculate the band offset using both the standard LSDA and the LSDA-corrected (LSDA+C) approaches. Eight systems (ZnS/MnS, ZnSe/MnSe, ZnTe/MnTe, ZnS/ZnSe, ZnSe/ZnTe, ZnS/ZnTe, CdTe/MnTe, and MnS/MnSe) were computed directly in the present study. Our calculated unstrained valence-band offsets are given in Table I, together with our previously[13,14] computed band offsets for ZnTe/CdTe, ZnTe/HgTe, and CdTe/HgTe. We find that transitivity is well satisfied for these *unstrained*, "natural" offsets. Hence, in Table I all of the VBM energies are related to that of ZnS. The trends (i)–(iii) noted in the Introduction are evident in our results.

To understand these trends, we provide in Fig. 1 a schematic diagram showing how the atomic anion p orbitals and the cation d orbitals (both shown as dashed horizontal lines) interact to produce the VBM and the occupied d^+ bands (solid horizontal lines) in the crystal. In the zinc-blende compound with T_d site symmetry both the anion p and the cation d orbitals transform (among others) as the Γ_{15} (or t_2) representation. These two equal-symmetry states can interact with each other. The interaction between the p and d states results in a level repulsion, inversely proportional to the unperturbed energy difference $|\epsilon_d-\epsilon_p|$. The key aspect of Fig. 1 is that due to the large exchange splitting between the Mn spin-up and spin-down d orbitals, the S, Se, and Te p orbitals lie *between* the occupied Mn d^+ and unoccupied Mn d^- levels, while the Zn d levels are systematically well *below* the anion p levels. This explains effects (i)–(iii) noted in the Introduction as follows.

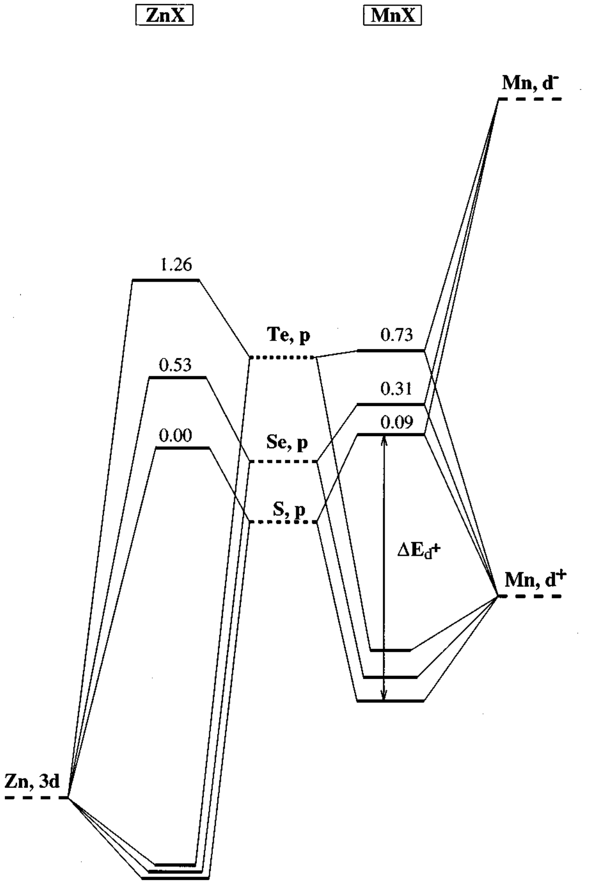

FIG. 1. Schematic plot of p-d repulsion in MnX (X=S, Se, and Te) and ZnX. Atomic orbitals are shown as horizontal dashed lines, while the VBM and the occupied d states in the solids are shown as solid lines. Note that the anion p orbitals lie between the occupied Mn d^+ and the unoccupied Mn d^- orbitals, while the Zn 3d is well below the anion p orbitals. Values refer to natural band offsets (LSDA+C) with respect to ZnS.

(i) *Spectral compression* in *E_V(MnX)*: The valence-band maximum of MnX is pushed *upwards* by the Mn d^+ and *downwards* by the Mn d^-. This results in a spectral *compression* of the VBM energies of MnS, MnSe, and MnTe into a narrow range. In contrast, ZnX compounds do not exhibit this "balancing act," since all the valence-band maxima are pushed systematically *upwards* by the deep-lying Zn 3d band. As a result, the spread in the VBM energies is larger, mainly reflecting the natural spread of the anion p energies.

(ii) *d-level pinning:* The *range* of VBM to occupied cation d^+ energy differences ΔE_d(ZnX) reflects primarily the large spread in the VBM energies (Fig. 1). In contrast, in the magnetic II-VI superlattices, not only is there a narrower spread in the VBM energies [effect (i)], but there also exists a compensating spread in the energies of Mn d^+: the Mn d^+ level in MnTe is pushed down less than that in MnS, due to the weaker p-d repulsion in the former. As a result, $\Delta E_{d^+}(\mathrm{Mn}X)$ is only weakly dependent on X.

(iii) *Strong anion dependence* in $\Delta E_V(\mathit{ZnX/MnX})$: The band offset $\Delta E_V(\mathrm{ZnS/MnS})>0$, since the S $3p$ to Mn d^+ coupling is very strong due to the closeness of the respective energy levels. On the other hand, $\Delta E_V(\mathrm{ZnTe/MnTe})<0$, because the VBM of ZnTe is pushed up by the p-d repulsion, while in MnTe the net shift of VBM due to the p-d repulsion is very small, since the Te p orbital energy is almost in the middle between Mn d^+ and d^-.

The hybridization of d orbitals at VBM of zinc-blende compounds reduces the spin-orbit splitting Δ_0.[13,14] In MnX, the d orbital mixing at the VBM is large (due to the small anion p to cation d energy difference), thus the reduction of Δ_0 in MnX is much larger than in ZnX (Table I). This reduction of $\Delta_0(\mathrm{Mn}X)$ also reduces the upwards shift of VBM in MnX, thus enhancing effects (i)–(iii) above. This spin-orbit contribution to (i)–(iii) is maximal for $X=\mathrm{Te}$, and smaller for $X=\mathrm{S}$.

The trends discussed above are general for all II-VI superlattices and can thus be used to estimate the band offset between other related systems. For example, we expect that the band offset $\Delta E_V(\mathrm{MgTe/MnTe})$ should be small and positive. This is because the VBM shift due to p-d repulsion is very small in MnTe [effect (i)], while the downward shift of the VBM in zinc-blende MgTe by the unoccupied, high-energy Mg d orbital[27] is compensated by its larger spin-orbit splitting ($\Delta_0=0.83$ eV) relative to MnTe. This expectation is confirmed by our calculated value of $\Delta E_V(\mathrm{MgTe/MnTe})=0.17$ eV, and is consistent with experimental observations,[9,10,28] $\Delta E_V(\mathrm{MgTe/MnTe})\geqslant 0$.

Our calculated band offsets given in Table I are in good agreement with a number of recent experimental measurements.[3–10] For example, our calculated band offset $\Delta E_V(\mathrm{ZnSe/MnSe})=-0.22\pm0.1$ eV (Table I) is consistent with the measured[3–7] values of $\Delta E_V(\mathrm{ZnSe/MnSe})=-0.15\pm0.1$ eV. Our calculated band offset[14] of $\Delta E_V(\mathrm{CdTe/MnTe})=-0.44\pm0.1$ eV (Table I) is also in good agreement with recently measured[8–10] values of $\Delta E_V(\mathrm{CdTe/MnTe})=-0.48\pm0.1$ eV using photoluminescence excitation spectroscopy. However, both the calculated and measured results do not agree with previous prediction[17] based on the dielectric-midgap model, suggesting that the VBM of MnTe lies *above* that of CdTe [i.e., $\Delta E_V(\mathrm{CdTe/MnTe})=+0.6$ eV].

There are two interesting inconsistencies between experiment and our theory.

(a) The inferred large positive offsets $\Delta E_V(\mathrm{Zn}X/\mathrm{Mn}X)>0$ for *all X* obtained by Weidemann and co-workers[11] from photoemission measurement is inconsistent with our predicted trends (Fig. 1). In interpreting their measurement, however, the authors[11] assumed that the Zn $3d$ orbitals behave as constant corelike states in ZnX compounds and in ZnMnX alloys. However, since the Zn $3d$ orbitals are energetically close to Mn $3d$, the ensuing coupling between Mn d^+ and Zn $3d$ states in ZnMnX alloys pushes the Zn $3d$ state to higher binding energy, making them noncorelike. This could be the reason for the discrepancy. We thus suggest that for magnetic semiconductors, accurate photoemission measurement of the band offset requires using as reference energies chemically inert (i.e., deeper than Zn $3d$, Cd $4d$, etc.) core levels.

Recently, Wang *et al.*,[12] using photoelectron spectroscopy, found a positive band offset $\Delta E_V(\mathrm{ZnSe/MnS})=+0.15$ eV for relatively thick MnS layers strained on ZnSe. This is in contradiction to our calculated unstrained band offset of -0.44 ± 0.1 eV for this system. Coherent strain has little effect (0.02 eV reduction) on this system due to the small lattice mismatch (Table I). Hence, the discrepancy between present theory and the experiment[12] is not understood at this time.

In summary, using theoretical band-structure calculation we have studied the general trends of band offsets between MnX ($X=\mathrm{S}$, Se, and Te) and other "normal" II-VI compounds. We find that the p-d repulsion mechanism can be used to understand most of the interesting results observed in these systems. Our calculated results agree well with the majority of the recent experimental measurements. The discrepancy between the present results and some of the calculated and measured systems are discussed.

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