

# 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 (MnX/ZnX) 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 MnX depends weakly on X, while in conventional II-VI superlattices (e.g., Zn 3*d* in ZnX) there is a wider spread, and (iii) unlike the case for conventional common-anion II-VI superlattices, the mixed offset  $DE_V$  (ZnX/MnX) 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), be-

shifted relative to the unstrained values through the deformation potential. The change of  $E_{\text{VBM}}$  depends on the size and direction of the strain.<sup>22</sup> 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<sup>23,24</sup> -LSDA! as implemented by the general-potential, *relativistic*, all-electron, linearized-augmented-plane-wave -LAPW! method.<sup>25</sup> We used the Ceperley-Alder exchange and correlation potential<sup>23</sup> as parametrized by Perdew and Zunger.<sup>24</sup> 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.<sup>26</sup>

We have previously<sup>14</sup> noted that the LSDA underestimates the spin-exchange splitting in MnX. We corrected this<sup>26</sup> 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<sup>13,14</sup> 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  $d^1$  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  $G_{15}$  -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  $\|e_d - e_p\|$ . 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  $d^1$  and unoccupied Mn  $d^2$  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.

in MnTe is pushed down less than that in MnS, due to the weaker  $p$ - $d$  repulsion in the former. As a result,  $DE_{d^1}(\text{MnX})$  is only weakly dependent on  $X$ .

*Strong anion dependence in  $DE_V(\text{ZnX/MnX})$ :* The band offset  $DE_V\text{-ZnS/MnS}$  is 0, since the S  $3p$  to Mn  $d^1$  coupling is very strong due to the closeness of the respective energy levels. On the other hand,  $DE_V\text{-ZnTe/MnTe}$  is 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  $d^1$  and  $d^2$ .

The hybridization of  $d$  orbitals at VBM of zinc-blende compounds reduces the spin-orbit splitting  $D_0$ .<sup>13,14</sup> 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  $D_0$  in MnX is much larger than in ZnX -Table I!. This reduction of  $D_0$ -MnX! 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=Te, and smaller for X=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  $DE_V\text{-MgTe/MnTe}$  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<sup>27</sup> is compensated by its larger spin-orbit splitting - $D_0$  0.83 eV! relative to MnTe. This expectation is confirmed by our calculated value of  $DE_V\text{-MgTe/MnTe}$  0.17 eV, and is consistent with experimental observations,<sup>9,10,28</sup>  $DE_V\text{-MgTe/MnTe}$  > 0.

Our calculated band offsets given in Table I are in good agreement with a number of recent experimental measurements.<sup>3-10</sup> For example, our calculated band offset  $DE_V\text{-ZnSe/MnSe}$  0.22 0.1 eV -Table I! is consistent with the measured<sup>3-7</sup> values of  $DE_V\text{-ZnSe/MnSe}$  0.15 0.1 eV. Our calculated band offset<sup>14</sup> of  $DE_V\text{-CdTe/MnTe}$  0.44 0.1 eV -Table I! is also in good agreement with recently measured<sup>8-10</sup> values of  $DE_V\text{-CdTe/MnTe}$  0.48 0.1 eV using photoluminescence excitation spectroscopy. However, both the calculated

and measured results do not agree with previous prediction<sup>17</sup> based on the dielectric-midgap model, suggesting that the VBM of MnTe lies above that of CdTe -i.e.,  $DE_V\text{-CdTe/MnTe}$  1.06 eV#.

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- <sup>27</sup>Interestingly, the existence of a valence-band offset between the common-anion lattice-matched AlAs/GaAs pair is also ascribed @S.-H. Wei and A. Zunger, Phys. Rev. Lett. **59**, 144 -1987!# to an imbalance between difference  $p$ - $d$  repulsions: the -empty! Al  $d$  orbital pushes the VBM of AlAs *down* while the -occupied! Ga  $d$  pushes the VBM of GaAs -a bit! *up*.
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