s-d coupling in zinc-blende semiconductors

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Most zinc blende semiconductors have a single anion-like *s* state near the bottom of the valence band, found in density-of-states (DOS) calculations, and seen in photoemission. Here, we discuss the case where *two s*-like peaks appear, due to strong *s-d* coupling. Indeed, away from the $\mathbf{k}=\mathbf{0}$ Brillouin zone center, cation *d* states and anion *s* states can couple in zinc blende symmetry. Depending on the energy difference $\Delta E_{sd}=E_s^{\text{anion}}-E_d^{\text{cation}}$, this interaction can lead to either a single or two *s*-like peaks in the DOS and photoemission. We find four types of behaviors. (i) In GaP, GaAs, InP, and InAs, ΔE_{sd} is large, giving rise to a single cation *d* peak well *below* the single anion *s* peak. (ii) Similarly, in CdS, CdSe, ZnS, ZnSe, and ZnTe, we see also a single *s* peak, but now the cation *d* is *above* the anion *s*. In both (i) and (ii) the *s-d* coupling is very weak. (iii) In GaN and InN, the local density approximation (LDA) predicts *two s*-like peaks bracketing below and above the cation *d*-like state. Correcting the too low binding energies of LDA by LDA+SIC (self-interaction correction) still leaves the two *s*-like peaks. The occurrence of two *s*-like peaks represents the fingerprint of strong *s-d* coupling. (iv) In CdTe, LDA predicts a single *s*-like peak just as in case (ii) above. However, LDA+SIC correction shifts down the cation *d* state closer to the anion *s* band, enhancing the *s-d* coupling, and leading to the appearance of *two s*-like peaks. Case (iv) is a remarkable situation where LDA errors cause not only quantitative energetic errors, but actually leads to a qualitative effect of a DOS peak that exists in LDA+SIC but is missing in LDA. We predict that the double-*s* peak should be observed in photoemission for GaN, InN, and CdTe.

Binary zinc blende semiconductors have a single anion

account final state effects (as in Refs. 22 and 23). Since the LDA treatment shows that in CdTe the anion-s to cation-d splitting is small (2.9 eV at Γ, compared with 4.5, 4.7, 6.5, 6.6, and 4.8 eV in CdS, CdSe, ZnS, ZnSe, and ZnTe, respectively) we also applied LDA+U$^{\text{SIC}}$ to CdTe. We apply a similar treatment for CdTe, where the Cd 4d band is shifted to the observed $E_v - 10.5$ eV value,[24,25] whereas the Te 5s state has according to GW Refs. 2 and 26 a negligible shift. The resulting DOS of LDA+U$^{\text{SIC}}$ is shown in the upper panel of Fig. 3 for GaN and CdTe. We see the following.

(a) *s-like and d-like states in GaN*. The double s peak seen in the LDA results for GaN *remains* when the self-interaction corrections of Ga 3d *and* of N 2s are included (Fig. 3). This is different than what was predicted by Lambrecht *et al.*[7] who got a single s peak by shifting only the Ga 3d LDA band, although they suggested that also a downward shift of the N 2s band is necessary. The main reason for the double s peak is the broad N 2s band which easily can be divided into

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is much deeper than that of P, As, and Sb, and so the ΔE_{sd} is smaller in nitrides leading to a bigger s-d coupling.

In summary, we find four types of behaviors in the DOS of zinc blende structures. (i) In GaP, GaAs, InP, and InAs, there is a single s peak well above the cation d band and ΔE_{sd} is large. (ii) In CdS, CdSe, ZnS, ZnSe, and ZnTe, we see also a single s peak, but now the cation d is above the anion s. In both (i) and (ii) the s-d coupling is very weak. (iii) In GaN and InN, LDA predicts two s-like peaks which remain when the SIC is included. (iv) In CdTe, LDA predicts a single s-like peak, whereas LDA+U^{SIC} yields two s-like peaks. We predict that the double-s peak should be observed in photoemission also for GaN and InN.

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