

***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.

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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^{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^{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

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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²J.R. Chelikowsky and M.L. Cohen, Phys. Rev. B **14**, 556 (1976).