s-*d* coupling in zinc-blende semiconductors

Clas Persson and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401, USA

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 $\Delta E_{sd} = E_s^{\mathrm{anion}} - E_d^{\mathrm{cation}}$, 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 valence *s* orbital, and are thus expected to exhibit a single anion *s* peak in the calculated density-of-states (DOS) and in measured photoemission. This expectation is borne out by tight binding[1] as well as by pseudopotential calculations,[2] showing a single anion *s*-like DOS peak at −10 to −13 eV below the valence-band maximum (E_v) in GaAs and −11 to −12 eV in ZnSe.[2] However, the calculated electronic structure of zinc blende GaN (Ref. 3) via the local density approximation (LDA) reveals in the DOS *two* anion *s* peaks at about $E_v−13$ and $E_v−17$ eV, around the Ga 3*d* band ($E_v−15$ eV). We have reproduced these results qualitatively in our LDA calculations in GaN and InN [Figs. 1(a), 1(b)][4] via an all-electron full-potential linearized augmented plane wave approach (FPLAPW).[5,6] The two anion *s* peaks in GaN are at first surprising because GaP and GaAs exhibit [Figs. 1(c), 1(d)] a strong single anion *s* peak even in an all-electron representation, as ZnSe and CdTe do [Figs. 1(e), 1(f)]. This was noted early on by Fiorentini *et al.*[3] and Lambrecht *et al.*[7,8] Hence, we generalize this study to a series of materials and investigate cases where the effect is due to LDA errors.

The resolution to this puzzle is as follow. In zinc blende materials at the Brillouin zone center, the point group symmetry is T_d, supporting the irreducible representations a_1, a_2, e, t_1, and t_2. The cation *d* orbitals support the representations e and t_2, whereas the anion *s* orbitals give the a_1 representation. Since there are no representations with the same symmetry for anion *s* and for cation *d*, the *s*-*d* coupling $V_{s-d}(\Gamma)$ is zero. However, at the *X* point in the zinc blende Brillouin zone, the point-group symmetry is reduced to D_{2d}, having the representations a_1, a_2, b_1, b_2, and e. Now, the cation *d* orbitals ($a_1 \oplus a_2 \oplus e$) and the anion *s* orbital ($a_1 \oplus b_2$) have a common representation (a_1) and can thus couple, so $V_{s-d}(X) \neq 0$. The same is true for other **k** points away from the Γ point. This coupling creates an a_1-a_1 repulsion, splitting off an *s*-*d*-like (actually, a_1) state *above* the main cation *d* band (the coupled states are neither pure *s* nor *d*, but both). The splitting depends on the strength $V_{s-d}^2(X)$ of the coupling and on the eigenvalue difference $E_s^{\mathrm{anion}} - E_d^{\mathrm{cation}} \equiv \Delta E_{sd}$. Thus, we have a lower band (a_1^l) and an upper band (a_1^u) with the main cation *d* band usually in between [Figs. 1(a), 1(b)].

Figure 1 shows the energy bands and the total DOS as obtained in LDA (Refs. 4,6,5,9) for six zinc blende systems, demonstrating three types of behavior.

(a) In materials exhibiting anion-*s* band well above cation-*d* such as GaP, GaAs, [Figs. 1(c), 1(d)] InP, and InAs with $\Delta E_{sd} \sim 2$ eV the *s*-*d* coupling is so weak that we see no split-off a_1^u DOS peak.

(b) In materials where the LDA yields the anion-*s* band close to the cation-*d* band as in GaN and InN [Figs. 1(a), 1(b)] with $\Delta E_{sd} \approx 0$ eV we see *two s*-like DOS peaks due to a strong *s*-*d* coupling. The separation of a_1^l and a_1^u depends inversely on ΔE_{sd}.

(c) In the II-VI's (CdS, CdSe, CdTe, ZnS, ZnSe, and ZnTe) the LDA yields the anion-*s* well below the cation-*d* band, and the *s*-*d* coupling is again so weak that we only see one *s*-like DOS peaks [Figs. 1(e), 1(f)].

The existence of a split-off second anion *s*-like state has important implications on LDA computations, since if such a state is physical (suggesting strong *s*-*d* coupling) one should perhaps not pseudize the cation *d* state but keep it instead as an active valence state in pseudopotential calculations. This
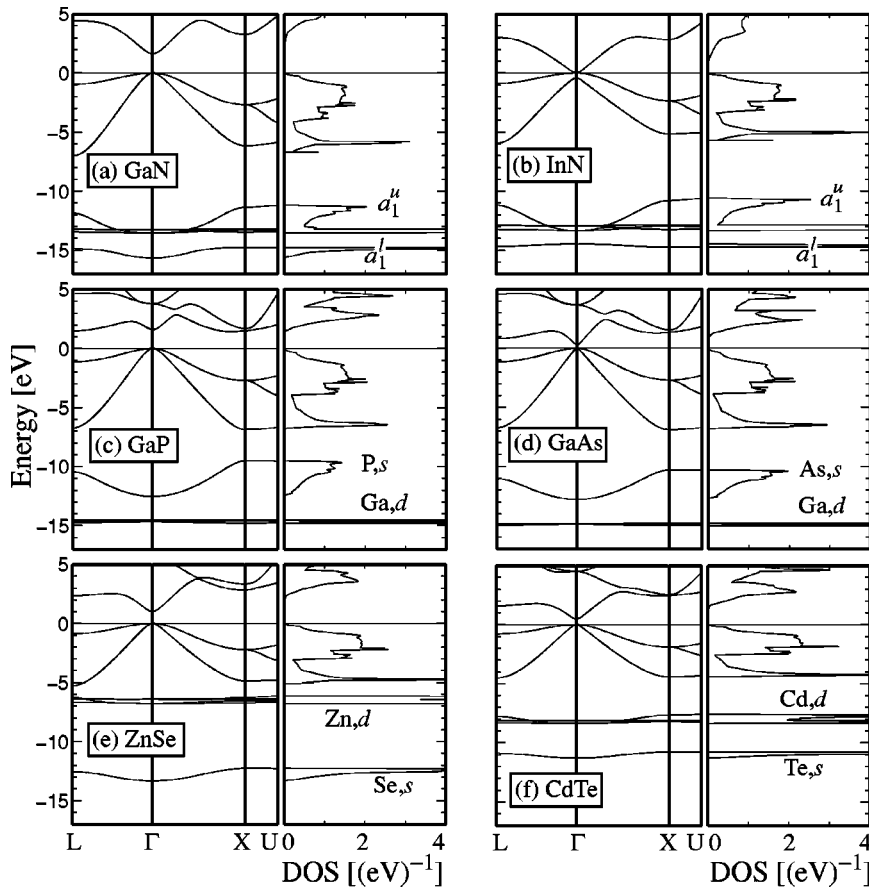
FIG. 1. LAPW-calculated electronic band structure and total DOS. We use the zinc blende structures with experimental lattice constant (Ref. 4) and the exchange-correlation potential of Perdew and Wang (Ref. 6).

means that the cation d state has to be retained *explicitly* (as a band, as suggested by Fiorentini *et al.*,[3] Wei *et al.*,[10] and Lambrecht *et al.*[7]), not just *implicitly* (e.g., via the "core correction"[11]). Indeed, LDA computations show [Figs. 1(a), 1(b)] that in GaN and InN there is a strong a_1^u split-off state, whereas in the remaining III-V materials and in all II-VI's it is weak or negligible, suggesting small s-d coupling. However, LDA is known to suffer from a self-interaction problem,[12] which leads to an underestimate of the binding energies of valence state with respect to the valence-band maximum. This underestimate scale with the orbital localization,[13] and is thus smaller for s orbitals than for d orbitals. The LDA error is illustrated in Fig. 2 which gives the positions of the Ga, $3d$ levels with respect to the valence-band maxima in GaN, GaP, and GaAs as obtained here from all-electron LDA, and from photoemission.[14,15] In this plot we have aligned the valence-band maxima according to the calculated[16] (unstrained) band offset. We see that as suggested by the "vacuum pinning rule"[17] the d states approximately align when displayed on an absolute energy scale. Furthermore, LDA eigenvalues are too high by ~ 4 eV. Thus, even in the case where LDA gives the band order "anion-s below cation-d," it is possible that once corrected, the new order will change the existence or nonexistence of a split-off a_1^u state. Indeed, Lambrecht *et al.*[7] find that the Ga $3d$ band is well separated from the N $2s$ band after they corrected the self-interaction of Ga $3d$.

In order to investigate this, we apply an on-site Coulomb interaction to correct the self-interactions of the cation-d and anion-s states, as described by a rotational invariant LDA $+\mathrm{U}^{\mathrm{SIC}}$ method.[18,19] In this approach we empirically assign U_d^{SIC}(cation) and U_s^{SIC}(anion) values to shift the LDA Ga d band to the photoemission-observed positions of GaN (Fig. 3) $E_v - 17.0$ eV (Refs. 7,15,20) (a shift of 3.7 eV with respect to LDA), and we lower the N $2s$ band by 1.5 eV according to GW results[21] compared with LDA. This lowering of the N $2s$ is consistent with the fact that LDA in general underestimates the valence-band width. However, we do not view this LDA$+\mathrm{U}^{\mathrm{SIC}}$ approach as being rigorous, since U is here a fitting parameter and does not explicitly take into
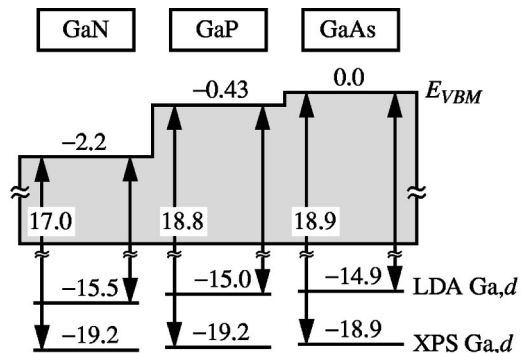

FIG. 2. Position of the Ga $3d$ as obtained from photoemission (Refs. 14,15) (XPS) and LDA calculations. The valence-band maxima are aligned using calculated (Ref. 16) (unstrained) offsets. Note the approximate alignment of Ga, $3d$ levels in different materials, when placed on an absolute energy scale.
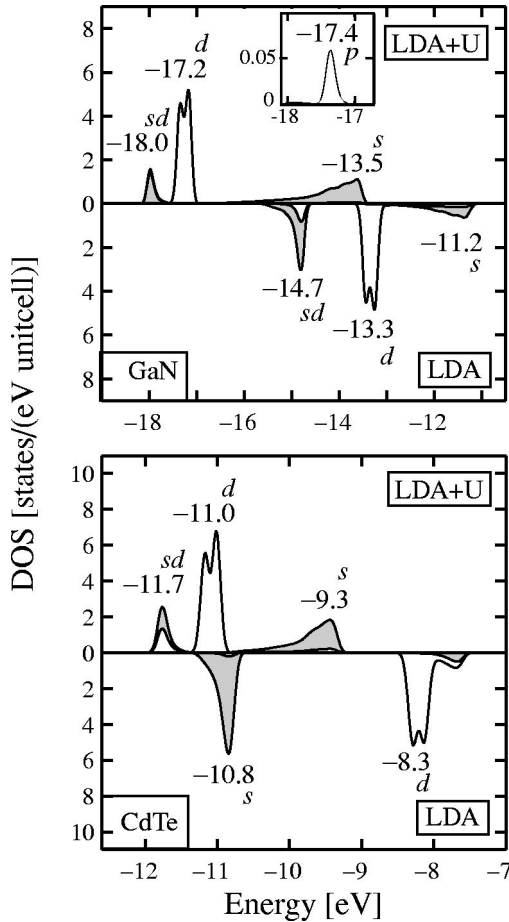
FIG. 3. l-decomposed DOS for (a) GaN and (b) CdTe obtained with (upper panels) and without (lower panels) correction to the LDA self-interaction error. The DOS are normalized by the factor of $1/(2l+1)$, and we have used a Gaussian broadening of 50 meV.

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 a_1^l and a_1^u. Since zinc blende InN as well as corresponding wurtzite GaN and InN have similar electronic structures as zinc blende GaN, we expect that these materials will also reveal strong s-d coupling. The photoemission spectrum of thin-film wurtzite GaN by Maruyama *et al.*[29] shows a high-

energy shoulder of the Ga $3d$ peak which was considered to correspond from interaction between the N $2s$ band[29] and surface Ga $3d$ core levels. Further examination of the s-d band in bulk GaN and InN via photoemission experiments are called for. We also find that the s-d coupling creates a N $2p$-like state within the Ga $3d$ band (see the inset of Fig 3). This is the reason why Smith *et al.*[20,27] see a low-intensity peak in their soft x-ray N K-emission measurements of wurtzite GaN which arises from N $2p\to1s$ transitions, although the authors assign this peak to be below the Ga $3d$ band.

(b) *s-like and d-like states in CdTe*. At the LDA level, CdTe exhibits a distinct cation d peak in the DOS at $E_v-8.3$ eV and a single anion s-like peak at $E_v-10.8$ eV (Fig. 3). The reason for the absence of two s-like peaks in LDA is the large ΔE_{sd} splitting of ~ 2.6 eV. However, the SIC correction shifts the Cd d band to deeper energies bringing it inside the Te s band. This leads to the appearance of a strong double-s peak at $E_v-9.3$ and $E_v-11.7$ eV in LDA+U^{SIC}. This is the only known case where the LDA-error is not merely an inaccurate value of the band gap, but misses a qualitatively new state in the DOS.

Photoemission measurements by Löher *et al.*[24] of CdTe films shows *two* Cd $4d$ peaks (at about $E_v-10.8$ and $E_v-11.5$ eV) consistent with our findings of d peaks at $E_v-11.0$ and $E_v-11.8$ eV for LDA+U^{SIC}, whereas corresponding CdS films show a single peak. Also photoemission measurements by Fritcshe *et al.*[25] of CdTe films reveal increasing double-peak behavior as CdTe film thickness increases. The experimental spectra[24,25] also show a low-intensity "shoulder" (with binding energies of 9.5–10.0 eV) on the high-energy side of the Cd $4d$ peak for CdTe, which can be identified as the broad $E_v-9.3$ eV to $E_v-10.9$ eV peak in Fig. 3. These experimental results indicate that s-d coupling is strong in CdTe, whereas it is absent (or weak) in CdS and CdSe. Our LDA+U^{SIC} calculations of CdS and CdSe show very weak s-d coupling due to the large ΔE_{sd} energy difference. In LDA this difference is more than 1.6 eV larger in CdSe and CdS than in CdTe (at the Γ point).

The reason for the strong s-d coupling in III-V nitrides, relative to phosphides and arsenides can be appreciated from considerations of anion-s to cation-d energy separation. Figure 2 shows that *on an absolute energy scale* the energies of the Ga, $3d$ level are nearly the same for GaN, GaP, and GaAs. (Similarly, the energies of In are all nearly the same on an absolute scale in InN, InP, and InAs.) In contrast, the energy of the anion-s state in zinc blende solids, in tight-binding approximation[28] is given (also on an absolute scale) by

$$E_{\Gamma_{1v}} = \frac{E_a^s + E_c^s}{2} + \sqrt{\left(\frac{E_a^s - E_c^s}{2}\right)^2 + (4V_{ss})^2},\qquad(1)$$

where E_a^s and E_c^s are anion and cation s energies and V_{ss} is the coupling. The atomic orbital energies E_a^s for N$\to$P $\to$As$\to$Sb move rapidly towards lower binding energy (see Chaps. 2, 3, and 6 in Ref. 28 for orbital energies and the coupling term). Thus, the anion s level of nitrogen in nitrides

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$^{\text{SIC}}$ yields two s-like peaks. We predict that the double-s peak should be observed in photoemission also for GaN and InN.

[1] H.P. Hjalmarson, P. Vogl, D.J. Wolford, and J.D. Dow, Phys. Rev. Lett. **44**, 810 (1980).

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

[3] V. Fiorentini, M. Methfessel, and M. Scheffler, Phys. Rev. B **47**, 13 353 (1993).

[4] *Numerical Data and Functional Relationships in Science and Technology*, New Series, Vol. III/17a,b, edited by O. Madelung *et al.* (Springer, Berlin, 1982).

[5] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2K, *An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Technische Universität Wien, Austria, 2001).

[6] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[7] W.R.L. Lambrecht, B. Segall, S. Strite, G. Martin, A. Agarwal, H. Morkoç, and A. Rockett, Phys. Rev. B **50**, 14 155 (1994).

[8] W.R.L. Lambrecht and B. Segall, in *Wide Ban-Gap Semiconductors*, Mater. Res. Soc. Symp. Proc. No. 242 (Materials Research Society, Pittsburgh, 1992), p. 367.

[9] We use the zinc blende structures with experimental lattice constant (Ref. 4), the exchange-correlation potential of Perdew and Wang (Ref. 6), and 20 **k** points (including inversion symmetry) in the irreducible Brillouin zone. The plane wave cutoff K_{max} is given by $R_{mt}K_{\text{max}}=9.0$–9.6, where R_{mt} is the anion sphere radius.

[10] S.-H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 (1988).

[11] S.G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[12] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[13] A. Zunger and A.J. Freeman, Phys. Rev. B **17**, 4850 (1978).

[14] N.J. Shevchick, J. Tejeda, and M. Cardona, Phys. Rev. B **9**, 2627 (1971).

[15] G. Martin, A. Botchkarev, A. Rockett, and M. Morkoç, Appl. Phys. Lett. **68**, 2541 (1996).

[16] S.-H. Wei and A. Zunger, Appl. Phys. Lett. **72**, 2011 (1998).

[17] M.J. Caldas, A. Fazzio, and A. Zunger, Appl. Phys. Lett. **45**, 671 (1984).

[18] V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyzyk, and G.A. Sawatzky, Phys. Rev. B **48**, 16 929 (1993).

[19] A.I. Liechtenstein, V.I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).

[20] K.E. Smith, L.C. Duda, C.B. Stagarescu, J. Downes, D. Korakakis, R. Singh, T.D. Moustakas, J.H. Guo, and J. Nordgren, J. Vac. Sci. Technol. B **16**, 2250 (1998).

[21] A. Rubio, J.L. Corkill, M.L. Cohen, E.L. Shirley, and S.G. Louie, Phys. Rev. B **48**, 11 810 (1993).

[22] S.B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. **52**, 13 975 (1995).

[23] A. Zunger, Phys. Rev. Lett. **50**, 1215 (1983).

[24] T. Löher, Y. Tomm, C. Pettenkofer, A. Klein, and W. Jaegermann, Semicond. Sci. Technol. **15**, 514 (2000).

[25] J. Fritsche, A. Thißen, A. Klein, and W. Jaegermann, Thin Solid Films **387**, 158 (2001).

[26] O. Zakharov, A. Rubio, X. Blase, M.L. Cohen, and S.G. Louie, Phys. Rev. B **50**, 10 780 (1994).

[27] C.B. Stagarescu, L.-C. Duda, K.E. Smith, J.H. Guo, J. Nordgren, R. Singh, and T.D. Moustakas, Phys. Rev. B **54**, R17 335 (1996).

[28] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1989).

[29] T. Maruyama, Y. Miyajima, S.H. Cho, K. Akimoto, and H. Kato, Physica B **262**, 240 (1999).