Electronic structure and band parameters for ZnX (X=O, S, Se, Te)

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First-principles density-functional calculations have been performed for zinc monochalcogenides with zinc-blende- and wurtzite-type structures. It is shown that the local-density approximation underestimates the band gap, misplaces the energy levels of the Zn-3d states, and overestimates the crystal-field splitting energy. Without spin-orbit coupling, the order of the states at the top of VB is found to be normal for all the ZnX phases considered. Upon inclusion of the spin-orbit coupling in calculations, ZnO in zinc-blende- and wurtzite-type phases become anomalous. It is shown that the Zn-3d electrons are responsible for the anomalous order. The effective masses of electrons and holes have been calculated and found that holes are much anisotropic and heavier than the electrons in agreement with experimental findings. The typical errors in calculated band gaps and related parameters originate from strong Coulomb correlations, which are found to be highly significant in ZnO. The LDA+U approach is found to correct the strong correlation of the Zn-3d electrons, and thus improves the agreement with the experimentally established location of the Zn-3d levels. Consequently, it increases significantly the parameters underestimated in the pure LDA calculations.

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I. INTRODUCTION

Investigation of properties of zinc monochalcogenides [ZnX (X=O, S, Se, Te)] with zinc-blende-(z-) and wurtzite-(w-)type structure has promoted much interest because of their numerous applications in optoelectronic devices such as visual displays, high-density optical memories, transparent conductors, solid-state laser devices, photodetectors, solar cells etc. Despite frequent studies over more than four decades many fundamental questions still remain open. One of them is the eigenvalue problem related to a severe underestimation of the band gap (Eg), energy levels of the Zn-3d electrons (E3d) for ZnO [1], ZnS [2], and ZnSe [2], splitting energies of the states at the top of the valence band (VB), spin-orbit (SO) coupling and crystal-field (CF) splitting energies (∆SO and ∆CF, respectively) calculated according to the density-functional theory (DFT) within the local-density approximation (LDA). These problems have been the subject of numerous studies with different methods such as the LDA plus self-interaction correction (LDA+SIC) [3], LDA plus the multiorbital mean-field Hubbard potential (LDA+U) [4] (which includes the on-site Coulomb interaction in the LDA Hamiltonian), and different version of GW approximation [5, 6]. In the latter approximation "G" stands for one-particle Green’s function as derived from many-body perturbation theory and "W" for Coulomb screened interactions. This approach takes into account both non-locality and energy-dependent features of correlations in many-body system. However, none of the above approaches has been able to remedy the eigenvalue problem except the combination of exact-exchange DFT calculations in the optimized-effective-potential approach with GW [7], which is found to give better agreement with the experimental band gaps and the location of the Zn-3d energy levels.

The order of the states at the top of the VB in ZnO-w is one of the topics which is still frequently debated [3, 8]. Another debated aspect is the effective masses of the charge carriers although these are more indefinite parameters for the ZnX phases. At present the effective masses from different ab initio packages and experiments scatter appreciably in publications on ZnO [3, 8, 10, 11, 12] and ZnTe [12]. In this work ZnX (X=O, S, Se, Te) in z- and w-type structural arrangements is studied by first-principles calculations within the LDA, generalized gradient approximation (GGA), and LDA+U approaches. See Ref. [14] for a more detailed account of our findings.

II. COMPUTATIONAL DETAILS

The electronic band structure of the ZnX phases is studied using the VASP–PAW package [15], which calculates the Kohn–Sham eigenvalues by the DFT [16] within the LDA [17], GGA [18], and LDA+U [19, 20] approximations. The exchange and correlation energy per electron have been described by the Perdew–Zunger parametrization [21] of the quantum Monte Carlo procedure of Ceperley–Alder [22]. The interaction between electrons and atomic cores is described by means of non-norm-conserving pseudopotentials implemented in the VASP package, which are generated in accordance to the projector-augmented-wave (PAW) method [23, 24]. Self-consistent calculations were performed using a 10 × 10 × 10 mesh frame according to Monkhorst–Pack scheme for
z-type phases and to Γ-centered grids for w-type phases. The completely filled semi-core-Zn-3d states have considered as valence states. Values for $\Delta_{\text{CF}}, \Delta_{\text{SO}}$ the average band gap $E_g$ are calculated within the cubic model $^{25, 26}$. For band-structure calculations used the experimentally determined crystal-structures for all ZnX phases considered.

Without SO coupling the top of the VB for phases w-type structure is split into a doublet $\Gamma_5$ and a singlet state by the crystal-field. Inclusion of SO coupling rise to three twofold degenerate valence bands, which denoted as $A$, $B$, and $C$ states. The symmetry of these three bands are of $\Gamma_7$ character and one of $\Gamma_8$ acter. Band gaps $E_A, E_B, E_C$ are defined difference between the conduction band (CB) and energy levels of the $A, B, C$ states, respectively. Without SO coupling the VB spectrum near the $\Gamma$ for the ZnX-z phases originates from the sixfold degenerate $\Gamma_{15}$ state. The SO interaction splits the $\Gamma_1$ into a fourfold degenerate $\Gamma_8$ and doubly degenerate $\Gamma_7$ levels.

### III. RESULTS AND DISCUSSION

#### A. Value of the parameters $U$ and $J$

The simplified rotationally invariant LDA+$U$ approach $^{19}$ used in this work requires knowledge of the values of the parameters $U$ and $J$. Since these parameters do not explicitly take into account the final state, values of $U$ and $J$ were found empirically from LDA+$U$ band structure calculations as a function of $U$ and $J$ such that the value of $E_d$ obtained for particular $U$ and $J$ fit with the experimentally determined location. For comparison, the values of $U$ and $J$ have been calculated for some of the compounds within the constrain DFT $^{30}$, showing that the calculated values to some extent agrees with those extracted semiempirically.

#### B. Eigenvalues

The results of the band structure calculations are listed in Table I. It is found that the band gaps ($E_g, E_A, E_B, E_C$) and the mean energy level $E_d$ severely underestimated in the LDA calculations. The error in the LDA calculated energies is quite pronounced for ZnO (see e.g. Fig. 1 for ZnO-z) compared to the other ZnX phases and the discrepancy exceeds the usual error for LDA calculations. Furthermore, compared to experimental data the CF splitting energy ($\Delta_{\text{CF}}$) is severely overestimated for ZnO-w by 2.4 times and underestimated for ZnS-w by around 1.2 times. $\Delta_{\text{SO}}$ is overestimated for ZnO-w to about 12.2 times, underestimated for ZnS-w by about 3.2 times, but agrees well with experimental data for ZnSe-z and ZnTe-z. Furthermore, $\Delta_{\text{SO}}$ is found to be negative for ZnO-z and -w phases in agreement with results of Refs. $^{3, 14}$ and $^{40, 41, 42}$ while it is positive for the other ZnX considered.

The GGA approach corrected the above mentioned LDA deficiency only to a little extent. However, LDA+$U$ significantly increased the values of $E_g, E_A, E_B, E_C$, and shifted the energy levels of the Zn-3d electrons up to experimentally determined limits, but only slightly changed the values of $\Delta_{\text{SO}}$ and $\Delta_{\text{CF}}$ for the ZnX phases except ZnO-z and -w. The dependence of $\Delta_{\text{CF}}, \Delta_{\text{SO}}$ on $U$ for ZnO-w is displayed in Fig. 2(a) and of $\Delta_{\text{SO}}$ for ZnO-z in Fig. 2(b). Analysis of these illustrations shows that $\Delta_{\text{SO}}$ remains negative for $U \leq 9.0$ eV for ZnO-w and for $U \leq 8.0$ eV for ZnO-z. For higher values of $U$, $\Delta_{\text{SO}}$ becomes a complex number for ZnO-w with a non-zero imaginary part (in itself physically meaningless), and changes sign for ZnO-z from negative to positive.

The SO splitting energy is much smaller than 1.0 eV for all phases except ZnSe-z ($\Delta_{\text{SO}} = 0.4$ eV) and ZnTe-z ($0.97$ eV). Regardless of the computational approach used, the numerical values of $\Delta_{\text{SO}}$ for all ZnX phases remained almost unchanged. The present values for $\Delta_{\text{SO}}$ for the ZnX-z phases are in good agreement with theoretical calculations $^{14}$ by the LAPW method and available experimental data.

The variation of the energy splitting between the $A, B, C$ states, viz. $E_A - E_B, E_A - E_C$, and $E_A - E_C$, at the top of the VB of ZnO-w is studied as a function of $U$ as shown in Fig. 2(c). For $U < 9.0$ eV the energy splitting decreases with increasing $U$. At higher values of $U$, $E_A - E_B$ becomes negative and decreases, $E_B - E_C$ increases, while $E_A - E_C$ stays more or less constant.

#### C. Density of states

The density of states corresponding to the Zn-3d levels according to the LDA calculations are inappropriately close to the CB (see e.g. Fig. 3 for ZnO-z), which contradicts the findings from XPS, XES, and UPS experiments $^{37, 58, 59}$. Furthermore, these states and the top of the

![FIG. 1: Band dispersion for ZnO-z calculated within LDA (solid lines) and LDA+$U$ (dotted lines) approaches. The Fermi level is set at zero of energy.](image-url)
TABLE 1: Band gaps \(E_0, E_g(A), E_g(B), E_g(C),\) and \(E_0,\) crystal-field (\(\Delta_{CF}^0, \Delta_{CF}\)) and spin-orbit (\(\Delta_{SO}\)) splitting energies (all in eV) for ZnX phases with z- and w-type structure calculated within LDA, GGA, and LDA+U approaches. \(E_g\) and \(\Delta_{CF}^0\) refer to calculations without the SO coupling, in all other calculations the SO interactions are accounted for. Experimental values are quoted when available.

| Phase   | Method | \(E_0\) | \(E_g(A)\) | \(E_g(B)\) | \(E_g(C)\) | \(E_g\) | \(\Delta_{CF}^0\) | \(\Delta_{CF}\) | \(\Delta_{SO}\) |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| ZnO-w   | LDA    | 0.7442 | 0.7328 | 0.7564 | 0.8385 | 0.773 | 5.091 | 0.0928 | -0.0429 |
| GGA     | 0.8044 | 0.7831 | 0.8165 | 0.9000 | 0.833 | 5.096 | 0.0944 | -0.0443 |
| LDA+U   | 1.9884 | 2.0080 | 2.0528 | 2.0530 | 2.038 | \(\sim 10.00\) | 0.0394 | -0.0035 |
| Expt.\[26\] | 3.4410 | 4.4434 | 3.4817 | 3.455 | 0.0688 | 0.0518 | 0.0269 |
| ZnS-w   | LDA    | 1.9896 | 1.9681 | 1.9947 | 2.0734 | 2.012 | 6.50 | 0.0661 | 0.0494 | 0.0249 |
| GGA     | 2.2322 | 2.2114 | 2.2361 | 2.3104 | 2.253 | 6.09 | 0.0588 | 0.0549 | 0.0256 |
| LDA+U   | 2.2828 | 2.2955 | 2.2858 | 2.3662 | 2.304 | 8.20 | 0.0580 | 0.0860 |
| Expt.\[43\] | 3.8643 | 3.8932 | 3.9808 | 3.907 | 0.0055 | 0.0920 |
| ZnSe-w  | LDA    | 1.0704 | 0.9389 | 1.0680 | 1.3789 | 1.109 | 6.50 | 0.1138 | 0.3243 | 0.0467 |
| GGA     | 1.3271 | 1.2004 | 1.2678 | 1.6243 | 1.364 | 6.50 | 0.1122 | 0.3105 | 0.0460 |
| LDA+U   | 1.4039 | 1.2708 | 1.3336 | 1.7209 | 1.442 | 9.30 | 0.1010 | 0.3465 | 0.0408 |
| Expt.\[13,43\] | 2.8600 | 2.8760 | 2.9260 | 2.903 | 0.0592 |
| ZnTe-w  | LDA    | 1.0519 | 0.7600 | 0.8200 | 1.6912 | 1.091 | 7.50 | 0.0857 | 0.8833 | 0.0332 |
| GGA     | 1.2577 | 0.9743 | 1.0319 | 1.8754 | 1.294 | 7.20 | 0.0835 | 0.8115 | 0.0320 |
| LDA+U   | 1.2826 | 0.9897 | 1.0434 | 1.8818 | 1.305 | 9.50 | 0.0754 | 0.8088 | 0.0296 |
| ZnO-z   | LDA    | 0.5732 | 0.5552 | 0.5883 | 0.577 | 4.60 | 0.0331 |
| GGA     | 0.6409 | 0.6152 | 0.6494 | 0.638 | 4.60 | 0.0342 |
| LDA+U   | 1.4859 | 1.4953 | 1.4973 | 1.496 | 7.90 | 0.0025 |
| ZnS-z   | LDA    | 1.8745 | 1.8516 | 1.9158 | 1.873 | 6.10 | 0.0642 |
| GGA     | 2.1134 | 2.0921 | 2.1513 | 2.112 | 6.00 | 0.0592 |
| LDA+U   | 2.3324 | 2.3007 | 2.3886 | 2.336 | 9.00 | 0.0789 |
| Expt.\[43\] | 3.6800 | 3.7400 | \(\geq 9.00\) | 0.0670 |
| ZnSe-z  | LDA    | 1.0793 | 0.9484 | 1.3409 | 1.079 | 6.60 | 0.3925 |
| GGA     | 1.3349 | 1.2089 | 1.5858 | 1.335 | 6.50 | 0.3769 |
| LDA+U   | 1.4214 | 1.2908 | 1.6995 | 1.427 | 9.05 | 0.4087 |
| Expt.\[43\] | 2.7000 | \(\geq 9.20\) | 0.4000 |
| ZnTe-z  | LDA    | 1.0607 | 0.7715 | 1.6681 | 1.070 | 7.10 | 0.3966 |
| GGA     | 1.2671 | 0.9862 | 1.8533 | 1.275 | 7.05 | 0.8671 |
| LDA+U   | 1.3287 | 1.0456 | 1.9561 | 1.349 | 9.90 | 0.9105 |
| Expt.\[43\] | 2.3941 | 9.84 | 0.9700 |
| Expt.\[43\] | 2.3941 | 9.84 | 0.9700 |

VB are hybridized. Distinct from the other ZnX phases considered, ZnO in both z- and w-type structure shows artificially widened Zn-3d states. These findings changed only slightly according to the GGA calculations.

The LDA+U approach was used to adjust the energy levels of the Zn-3d electrons derived bands to experimentally established positions using semiempirical methods for the parameters \(U\) and \(J.\) Consequently, the band gaps calculated by this approach become more reasonable than the pure LDA-derived band gaps. Further, the height of the peaks in the DOS corresponding to the Zn-3d states calculated by the LDA+U becomes much larger than those calculated by the pure LDA. This indicates that the semicore Zn-3d electrons have become more localized than according to the pure LDA. For ZnO-z and -w the width of the Zn-3d band calculated by LDA+U becomes much narrower than that calculated by LDA. For the other ZnX phases, however, LDA+U only slightly changed the width of the Zn-3d bands, which leads one to conclude that the Coulomb correlation effects for ZnO are more pronounced than that in other phases considered.

D. Order of states at the top of the VB

Optical and transport properties for semiconductors strongly depend on structure of the topmost VB. The order of states at the top of VB for ZnO-w is one of the topics which is frequently debated. It is found that the normal order \(\Gamma_5 > \Gamma_1\) is obtained by LDA without SO coupling for all ZnX phases. Calculations within GGA did not change the order. However, the order of the states at the top of VB for the ZnO-w is changed upon using the LDA+U approach with the semiempirical values of the parameter \(U,\) while there appears no change for the other ZnX phases. For ZnO with SO coupling, the order of states is \(\Gamma_7 > \Gamma_5 > \Gamma_9 > \Gamma_7\) which is referred to as anomalous order, resulting from a negative SO splitting.

The variation of the structure at the top of the VB on \(U\) with and without SO coupling is systematically studied for the ZnO-z- and -w-type phases. It is found that at around the above considered values of \(U\) (\(U \approx 9.0\) eV for ZnO-w and \(U \approx 8.0\) eV for ZnO-z), the LDA+U interchanges the sequence of the VB states from \(\Gamma_9 > \Gamma_7 > \Gamma_5 > \Gamma_7 > \Gamma_9\).

Since in theoretical calculations one can freeze interaction between the valence electrons and Zn-3d electrons by including the latter into the core, we studied this particular case for ZnO-z (with SO coupling) and -w (without SO coupling). It is found that the Zn-3d electrons are responsible for the order of the states. On comparing the top of the VB structures calculated within the LDA and GGA approaches it is found that only small quantitative
FIG. 2: (a) CF splitting, SO coupling energy for ZnO-w, (b) SO coupling energy for ZnO-z, and (c) splitting of the states at the top of VB a function of $U$ for ZnO-w. In panels a and c the solid and dotted lines represent calculated and experimental data, respectively.

FIG. 3: Total density of states for ZnO-z calculated from the LDA (solid line) and LDA+$U$ (dotted line) approaches. Fermi energy ($E_F$) is set at zero of energy.

changes have occurred. Hence, inhomogeneities in the electron gas do not affect the order of the states at the top of VB and only slightly changes the band dispersion.

E. Effective masses

The effective masses are calculated along $\Gamma \rightarrow A(\parallel)$, and $\Gamma \rightarrow M(\perp)$ with and without the SO couplings (Table III). According to the conventional notations, carrier masses for the ZnX-z phases are distinguished by the indices $e$ (electron), $hh$ (heavy-hole), $lh$ (light-hole), and $sh$ (split-off hole). The carrier masses for the ZnX-w phases are distinguished by the indices $e$, $A$, $B$, and $C$. The calculated CB masses $m_e$ for the ZnX-z phases are more isotropic than those for the ZnX-w phases. The numerical values of $m_e$ for ZnO-w, ZnS-w, ZnSe-z, and ZnTe-z obtained by the LDA is underestimated by about 50% compared to experimental findings [11, 12, 13], while those for the other ZnX phases agree fairly well with experimental data. GGA and LDA+$U$ calculations only slightly improved the LDA-derived $m_e$ values for all ZnX phases except ZnO, whereas for ZnO the $m_e$ values calculated from LDA+$U$ gives better agreement with experiment.

The heavy holes along all directions (see Table III and light holes along the $\Gamma \rightarrow A(\parallel)$ direction are much heavier than other holes and electrons. Hence, the carrier transport in ZnX is dominated by electrons, while that by holes can in practice be ruled out. This in turn can be the reason for the experimentally established large disparity between electron and hole mobilities [13], and also for the large optical nonlinearity in ZnO [8]. The hole effective masses are more anisotropic than those of electrons. On comparison of the values for $m_e$ in Table III, one sees that the influence of SO coupling on $m_e$...
is very important for ZnSe-z and ZnTe-z, while for the other phases its effect is small.

IV. CONCLUSION

Electronic structure and band parameters for ZnX-w and -z phases are studied by first-principles calculations within the LDA, GGA, and LDA+U approaches. It is found that LDA underestimates the band gaps, the actual positions of the energy levels of the Zn-3d states as well as splitting energies between the states at the top of VB, but overestimates the crystal-field splitting energy. The spin-orbit coupling energy is overestimated for ZnO-w, underestimated for ZnS-w, and comes more or less accurate for ZnS-z, ZnSe-z, and ZnTe-z.

The LDA+U calculation as a function of U and J has been used to adjust the Zn-3d band derived from LDA to the experimentally established location of the Zn-3d levels determined from X-ray emission spectra. Using the U values corresponding to the experimentally found Ed location the calculated band gaps and band parameters are improved compared to pure LDA approach.

The order of the states at the top of VB is systematically examined for ZnO-z and -w phases. It is shown that without SO coupling the band order is normal, it becomes anomalous and $\Delta_{SO}$ goes negative upon inclusion of SO coupling. It is found that in the LDA+U calculations the anomalous order is maintained until $U \approx 8.0$ eV for ZnO-z and $U \approx 9.0$ eV for ZnO-w. Above these $U$ values, the band order is inverted and becomes normal and $\Delta_{CF}$ for ZnO-w goes from positive to negative, whereas $\Delta_{SO}$ converts to a complex quantity. It indicates that either the quasiconic model, within which $\Delta_{CF}$ and $\Delta_{SO}$ are calculated, do not work for this particular case or such order is unphysical.

Upon excluding the interaction between the Zn-3d and other valence electrons by including the former in the core, the order becomes anomalous. Based on these analyses one can conclude that the Zn-3d electrons are responsible for the anomalous order of the states at the top of VB in ZnO.

Effective masses of electrons at the conduction-band minimum and of holes at the valence-band maximum have been calculated. The heavy holes in the VB are found to be much heavier than the CB electrons. The calculations, moreover, indicate that effective masses of the holes are much more anisotropic than those of the electrons. CB electron masses for ZnO-w, ZnS-w, ZnSe-z, and ZnTe-z calculated within LDA are underestimated by about 50 % compared with experimental data, while those for the other ZnX phases considered agree with experimental data.

The GGA approach does not remedy the LDA derived error in energy gaps and band parameters. We found that SO coupling is important for calculation of the parameters for the $z$-ZnSe and $z$-ZnTe phases, while it is not significant for other ZnX phases. However, the calculated $\Delta_{CF}$ values within the different approaches do not differ much except for ZnO emphasizing that Coulomb correlation effects are more pronounced for ZnO than ZnS, ZnSe, and ZnTe.

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[1] M. Usuda, N. Hamada, T. Kotani, and M. Schilfgaarde, Phys. Rev. B 66 (2002) 12 5101.
[2] W. Luo, S. Ismail-Beigi, M. L. Cohen, and S. G. Louie, Phys. Rev. B 66 (2002) 19 5215.
[3] W. R. L. Lambrecht, A. V. Rodina, S. Limpijumnong, B. Segall, and B. K. Meyer, Phys. Rev. B 65 (2002) 07 5207.
[4] D. Vogel, P. Krüger, and J. Pollmann, Phys. Rev. B 54 (1996) 5495.
[5] C. L. Dong, C. Persson, L. Vaysierles, A. Augustsson, T. Schmitt, M. Mattesini, R. Aluja, C. L. Chang, and J.-H. Guo, Phys. Rev. B 70 (2004) 19 5325.
[6] X. Feng, J. Phys.: Condens. Matter 16 (2004) 4251.
[7] P. Rimke, A. Queishi, J. Neugebauer, C. Freysoldt, and M. Scheffler, arXiv:cond-mat/0502404 1 (2005) 1.
[8] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. Cantwell, and W. C. Harsch, Phys. Rev. B 60 (1999) 2340.
[9] Y.-N. Xu and W. Y. Ching, Phys. Rev. B 48 (1993) 4335.
[10] L. C. Lew Yan Voon, M. Willatzen, and M. Cardona, Phys. Rev. B 53 (1996) 10 703.
[11] K. Hümmer, Phys. Status Solidi B 56 (1973) 249.
[12] Y. Imanaka, M. Oshikiri, K. Takehana, T. Takamatsu, and G. Kido, Physica B 298 (2001) 211.
[13] O. Madelung, ed., Data in Science and Technology. Semiconductors: Other than Group IV Elements and III-V Compounds (Springer, Berlin, 1992).
[14] S. Z. Karazhanov, P. Ravindran, U. Grossner, A. Kjekshus, H. Fjellvåg, and B. G. Svensson, Phys. Rev. B, submitted (2005).
[15] G. Kresse and J. Furthmüller, Phys. Rev. B 54 (1996) 11 169.
[16] P. Hohenberg and W. Kohn, Phys. Rev. 136 (1964) B864.
[17] W. Kohn and L. J. Sham, Phys. Rev. 140 (1965) A1133.
[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[19] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B 48 (1993) 16 929.
[20] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57 (1998) 1505.
TABLE II: Effective masses of electrons and holes (in units of the free-electron mass $m_0$) for Zn-X-z and -w phases calculated within LDA, GGA, and LDA+$U$ approaches. The results are compared to calculated and experimentally determined data cited in Ref. [13] and those calculated by FP-LMTO [8], LCAO [9] and determined experimentally [13]. For ZnO-w labelling of the effective masses was not changed with changing the order of the top VB states.

|       | $m_{lh}^{0}$ | $m_{lh}^{10}$ | $m_{lh}^{11}$ | $m_{lh}^{111}$ | $m_{lh}^{100}$ | $m_{lh}^{110}$ | $m_{lh}^{1110}$ | $m_{lh}^{101}$ | $m_{lh}^{1111}$ |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| ZnO-z | LDA         | 0.110       | 0.390       | 0.571       | 0.385       | 1.520       | 1.100       | 1.330       | 0.174       |
|       | GGA         | 0.120       | 0.409       | 0.579       | 0.492       | 1.505       | 1.250       | 1.281       | 0.188       |
|       | LDA+$U$    | 0.193       | 1.782       | 2.920       | 1.972       | 0.968       | 1.392       | 1.669       | 0.250       |
| ZnSe-z | LDA         | 0.150       | 0.775       | 1.766       | 2.755       | 0.224       | 0.188       | 0.188       | 0.355       |
|       | GGA         | 0.172       | 0.783       | 1.821       | 2.544       | 0.233       | 0.210       | 0.202       | 0.378       |
|       | LDA+$U$    | 0.176       | 1.023       | 1.227       | 1.087       | 0.268       | 0.252       | 0.218       | 0.445       |
|       | Expt. [13] | 0.184       |            | 1.760       |            |            |            |            | 0.230       |
| ZnTe-z | LDA         | 0.077       | 0.564       | 1.310       | 1.924       | 0.164       | 0.100       | 0.094       | 0.250       |
|       | GGA         | 0.094       | 0.568       | 0.922       | 1.901       | 0.126       | 0.122       | 0.111       | 0.271       |
|       | LDA+$U$    | 0.100       | 0.636       | 1.670       | 1.920       | 0.129       | 0.120       | 0.117       | 0.287       |
|       | Expt. [13] | 0.130       | 0.570       | 0.750       |            |            |            |            | 0.309       |
| ZnO-w | LDA         | 0.064       | 0.381       | 0.822       | 1.119       | 0.071       | 0.067       | 0.066       | 0.254       |
|       | GGA         | 0.078       | 0.418       | 0.638       | 1.194       | 0.093       | 0.086       | 0.081       | 0.261       |
|       | LDA+$U$    | 0.081       | 0.483       | 0.929       | 1.318       | 0.096       | 0.088       | 0.085       | 0.288       |
|       | Expt. [13] | 0.130       |            | 0.690       |            |            |            |            | 0.292       |

[21] J. P. Perdew and A. Zunger, Phys. Rev. B 23 (1981) 5048.
[22] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45 (1980) 566.
[23] P. E. Blöchl, Phys. Rev. B 50 (1994) 17953.
[24] G. Kresse and D. Joubert, Phys. Rev. B 59 (1999) 1758.
[25] J. J. Hopfield, J. Phys. Chem. Solids 15 (1960) 97.
[26] A. Mang, K. Reimann, and S. Rubenacke, Solid State Commun. 94 (1995) 251.
[27] Inorganic Crystal Structure Database (Gmelin Institut, Karlsruhe, 2001).
[28] M. J. Weber, ed., Handbook of Laser Science and Technology, vol. III (CRC, Cleveland, 1986).
[29] O. Zakharov, A. Rubio, X. Blase, M. L. Cohen, and S. G. Louie, Phys. Rev. B 50 (1994) 10780.
[30] N. Lakshmi, N. M. Rao, R. Venugopal, D. R. Reddy, and B. K. Reddy, Mater. Chem. Phys. 62 (2000) 275.
[31] V. N. Tomashik, G. S. Oleinik, and I. B. Mizetskaya, Inorg. Mater. 14 (1978) 1119.
[32] W. H. Bragg and J. A. Darbyshire, J. Met. 6 (1954) 238.
[33] K.-H. Hellwege and O. Madelung, eds., Numerical Data and Functional Relationships in Science and Technology, vol. 17a and 22a of Landolt-Börnstein, New series. Group III (Springer, New York, 1982).
[34] R. C. Weast, D. R. Lide, M. J. Astle, and W. H. Beyer, eds., CRC Handbook of Chemistry and Physics, 70th ed. (Chemical Rubber, Boca Raton, 1990).
[35] B. K. Agrawal, P. S. Yadav, and S. Agrawal, Phys. Rev. B 50 (1994) 14881.
[36] W. E. Pickett, S. C. Erwin, and E. C. Ethridge, Phys. Rev. B 58 (1998) 1201.
[37] L. Ley, R. A. Pollak, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B 9 (1974) 600.
[38] C. J. Vesely and D. W. Langer, Phys. Rev. B 4 (1971) 451.
[39] M. Ruckh, D. Schmid, and H. W. Schock, J. Appl. Phys. 76 (1994) 5045.
[40] J. E. Rowe, M. Cardona, and F. H. Pollak, Solid State Commun. 6 (1968) 239.
[41] D. G. Thomas, J. Phys. Chem. 15 (1960) 86.
[42] K. Shindo, A. Morita, and H. Kamimura, J. Phys. Soc. Jpn. 20 (1965) 2054.
[43] O. Madelung and M. Schulz, eds., Numerical Data and Functional Relationships in Science and Technology. New Series. Group III: Crystal and Solid State Physics. Semiconductors. Supplements and Extensions to Volume III/17. Intrinsic Properties of Group IV Elements and III-V, II-VI and I-VII Compounds, vol. 22a (Springer, Berlin, 1982).
[44] P. Carrier and S.-H. Wei, Phys. Rev. B 70 (2004) 035212.