# Rapid Communications

## Predictions and systematizations of the zinc-blende–wurtzite structural energies in binary octet compounds

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To systematize the wurtzite $(W)$ versus zinc blende (ZB) structural preferences among the binary octet compounds, we have calculated the corresponding energy difference $\Delta E_{W\text{-}ZB}^{LDF}(AB)$ for thirteen $AB$ compounds using the local-density formalism (LDF). We then uncovered a linear scaling between $\Delta E_{W\text{-}ZB}^{LDF}$ and an atomistic orbital-radii coordinate $\bar{R}(A,B)$ that can be simply calculated from the properties of the free $A$ and $B$ atoms. This permits perdictions of $W$-ZB energy differences for all binary compounds and exposes simple chemical trends, including the stabilization of the ZB form in the sequence $B = O \rightarrow S \rightarrow Se \rightarrow Te$ for $A^{II}B^{VI}$ and $A = Ga \rightarrow Al \rightarrow In$ for $A^{III}B^{V}$'s. We propose new structural assignments for the low-temperature ground state of CdSe (ZB) and MgTe (NiAs type).

Zinc blende (ZB) and wurtzite $(W)$ are the most common crystal structures of binary octet semiconductors.[1-5] While these structures belong to different crystal classes (cubic and hexagonal, respectively), the structural difference between them is subtle: $W$ and ZB differ only in the relative handedness of the fourth interatomic bond along the (111) chain [right and left for $W$ and ZB, respectively, in Figs. 1(a) and 1(b)] or, equivalently, in their dihedral conformation ["eclipsed" and "staggered" for $W$ and ZB, respectively, see Figs. 1(c) and 1(d)]. The structural similarity and the attendant small difference in
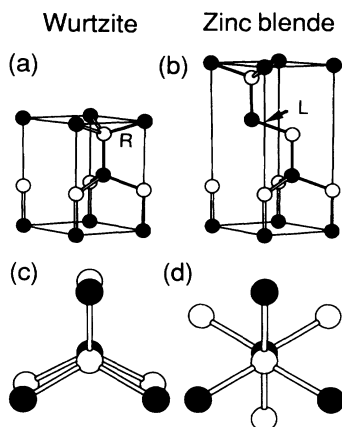


FIG. 1. Two views of the difference between the wurtzite and zinc-blende crystal structures. (a) and (b) show the handedness of the fourth interatomic bond: right $(R)$ for $W$ and left $(L)$ for ZB. (c) and (d) show the "eclipsed" and "staggered" dihedral conformations for $W$ and ZB.

internal energies $(\pm 20$ meV/atom) are manifested also by the well-known $W$-ZB polytypism:[2-5] Depending on the details of the growth parameters, a number of binary semiconductors (SiC, CdS, CdSe, ZnS, CuCl, and CuBr) can be prepared at ambient pressure in either forms.[4] In the few cases where the phase diagram was determined, the measured ZB-$W$ transition temperature was found to be rather low (well below the melting point), e.g., $95 \pm 5 \,°C$ in CdSe,[6] and 407, 386, and 396 $°C$ for CuCl, CuBr, and CuI, respectively.[7] Despite these structural and thermodynamic similarities between $W$ and ZB, their spectroscopic characteristics can be very different: For example, the minimum band gaps of SiC in the $W$ and ZB forms are 3.3 and $\sim 2.3$ eV, respectively,[8] and their phonon frequencies show large systematic variation.[8] Recent interest in optical application of wide-gap III-V and II-VI semiconductors[9] has therefore raised the need to systematize the $W$ vs ZB structural preferences among binary semiconductors. This goal was largely accomplished following the introduction of the nonclassical structural coordinate scales of Phillips[10] (the homopolar and heteropolar dielectric band gaps $E_h$ and $C$) and the orbital radii of St. John and Bloch,[11] Zunger and Cohen,[12,13] and Chelikowsky and Phillips.[14] The orbital radii coordinates are linear combinations,

$$R_\sigma(A,B) = |(r_p^A + r_s^A) - (r_p^B + r_s^B)| ,$$

$$R_\pi(A,B) = |r_p^A - r_s^A| + |r_p^B - r_s^B| ,$$

(1)

of the classical crossing points $r_l^{A,B}$ of the screened nonlocal atomic pseudopotentials of angular momentum $l$. It was previously demonstrated[11-14] that in the $R_\sigma(A,B)$ vs $R_\pi(A,B)$ plane there exists a separation into simple re-

gions occupied predominantly by compounds belonging to a single structure. The orbital radii determined from *ab initio* local-density formalism[12,13] were first applied to 565 binary (octet and nonoctet) 1:1 $AB$ compounds, achieving a >95% successful separation of 35 structure types. Later, these radii were incorporated into the three-coordinate scale of Villars and Hulliger[15] and used to systematize the crystal structures of nearly 6000 binary, ternary, and quaternary intermetallic compounds, binary oxides, and halides. Recent work include applications of these *ab initio* radii to quasicrystals and high-$T_c$ superconductors.[16]

As successful as these diagramatic structural maps are, they provide but a binary (yes/no) answer to the question: Is $X$ the stable crystal structure of a given compound? In the absence of a systematic data base of *structural energy differences* $\Delta E_{\alpha\beta}(AB)$ for a series of compounds $\{AB\}$ in different crystal structures $\alpha$ and $\beta$, it was impossible to establish whether the structural coordinates[10-16] actually scale with $\Delta E_{\alpha\beta}(AB)$. Indeed, *quantitative* structural regularities within homological chemical sequences such as AlN$\rightarrow$ CaN$\rightarrow$ InN or AlN$\rightarrow$ AlP$\rightarrow$ AlAs$\rightarrow$ AlSb cannot be established unless such a scaling is known. Furthermore, if neither $\alpha$ nor $\beta$ are the stable crystal structure of $AB$, structural diagrams provide no hint of the energy difference $\Delta E_{\alpha\beta}(AB)$ or the relative order of such unstable (or metastable) phases.

In order to address such questions in the present context we have calculated the $T=0$, $W$-ZB energy difference

$$\Delta E_{W-ZB}^{LDF}(AB) = E_W^{LDF}(AB) - E_{ZB}^{LDF}(AB) \tag{2}$$

for thirteen $AB$ compounds belonging to the IV-IV, III-V, and II-VI groups, using a numerically precise implementation[17,18] of the local-density formalism (LDF). We discover a simple *linear scaling between an "effective orbital ionicity"*

$$\tilde{R}(A,B) = \tilde{R}_\sigma(A,B) + \lambda \tilde{R}_\pi(A,B) \tag{3a}$$

and the $W$-ZB energy difference, i.e.,

$$\Delta E_{W-ZB}^{LDF}(AB) \cong \Delta E_{W-ZB}^M(AB) \equiv E_0 + a\tilde{R}(A,B), \tag{3b}$$

where $\tilde{R}_\sigma$ and $\tilde{R}_\pi$ are atomistic coordinates related to the orbital radii [Eq. (1)]. Like in Eq. (1), the determination of $\tilde{R}_\sigma(A,B)$ and $\tilde{R}_\pi(A,B)$ requires only the knowledge of *free atom* ($A$ and $B$) quantities; these can be calculated once and for all either from atomic wave functions or from nonlocal atomic pseudopotentials.[13] The model ($M$) of Eq. (3b) then permits predictions of the $W$-ZB energy differences for all binary octet compounds (including cases such as CaO, CdO, and C for which neither $W$ nor ZB are the ground states) and reveals clear chemical trends as a function of the position of $A$ and $B$ in the Periodic Table.

We first establish a data base of compounds for which $\Delta E_{W-ZB}^{LDF}$ is to be calculated by the LDF method. We include compounds that are known to be highly stable in the $W$ structure[4,5] (AlN, GaN, and InN) and compounds that occur at low temperatures only in the zinc blende (or diamond) phase[1-5] (Si, AlP, and AlAs; GaP, GaAs, and ZnTe). We then add compounds known to exhibit $W$-ZB

polytypism (ZnS, ZnSe, and CdS), and carbon, whose ground state (graphite) is neither $W$ nor ZB. The $W$-ZB total-energy difference of Eq. (2) was calculated in the LDF method using the Ceperley-Alder[19(a)] exchange correlation as parametrized by Perdew and Zunger.[19(b)] We used the plane-wave nonlocal pseudopotential method[17] for Si and the III-V's and the linearized augmented plane-wave (LAPW) method[18] for C and the II-VI's (that are difficult to converge in a pure plane-wave basis). A detailed convergence test[20] was performed with respect to Brillouin-zone k-point sampling and basis set size to assure a precision of 2 meV/atom in $\Delta E_{W-ZB}^{LDF}$.

To search for scaling between $\Delta E_{W-ZB}^{LDF}$ and atomistic coordinates, we note that the tendency towards stabilization of the $W$ structure increases[5] with the electronegativity difference $|\chi(A) - \chi(B)|$, and that the orbital ionization energy and, therefore, the orbital electronegativity $\chi_l(A)$ scales[13] as $1/r_l(A)$. This suggests a scaling [Eq. (3)] of $\Delta E_{W-ZB}(AB)$ with

$$\tilde{R}_\sigma(A,B) = \frac{R_\sigma(A,B)}{(r_p^A + r_s^A)(r_p^B + r_s^B)},$$

$$\tilde{R}_\pi(A,B) = \frac{R_\pi(A,B)}{(r_p^A + r_s^A)(r_p^B + r_s^B)}. \tag{4}$$

The simple linear scaling of Eqs. (3) and (4) give a rather small standard deviation $\sigma$ between the directly calculated $\{\Delta E_{W-ZB}^{LDF}(AB)\}$ and the fitted model $\{\Delta E_{W-ZB}^M(AB)\}$, using for $r_l^{A,B}$ either the position of the outer maximum of the valence atomic wave function $rR_{nl}(r)$ (giving $\sigma = 3.2$ meV), or the *ab initio*[13] LDF orbital radii (giving $\sigma = 2.8$ meV). Figure 2 shows the fit for the latter case. In either case, the fit error is comparable to the underlying precision with which $\Delta E_{W-ZB}^{LDF}$ can be calculated; we will hence use the model of Eq. (3) to predict the energy differences for all other binary octet compounds.

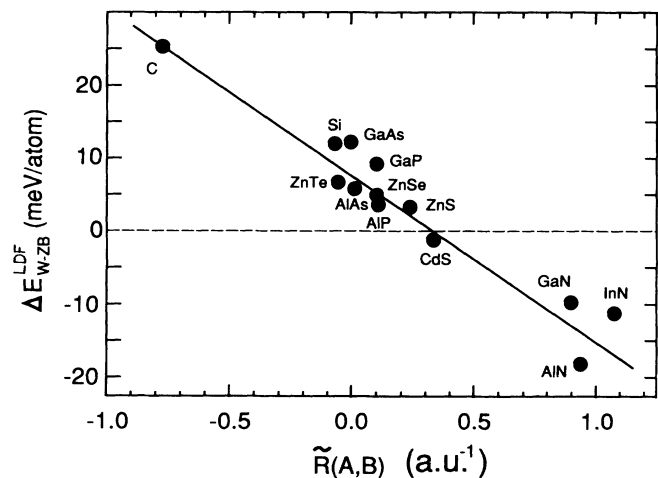Figure 3 shows the trends of $\Delta E_{W-ZB}^M$ within cation and

FIG. 2. The linear correction between the LDF-calculated $W$-ZB energy difference $\Delta E_{W-ZB}^{LDF}(AB)$ and the orbital coordinate $\tilde{R}(A,B)$ of Eq. (3), calculated from the orbital radii given in Ref. 13. The parameters of the fit (3b) are $E_0 = 8.137$ meV, $a = -22.152$, and $\lambda = -1.13$.
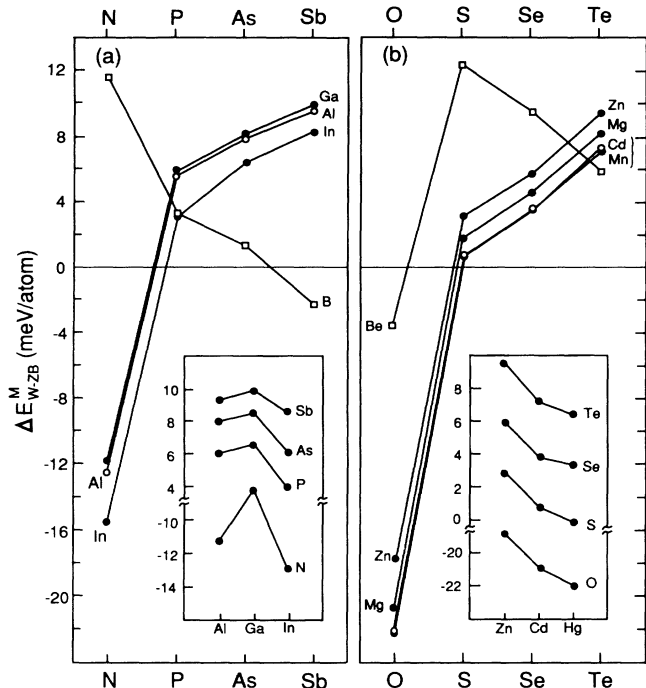
FIG. 3. Predicted $W$-ZB energy differences $\Delta E^M_{W\text{-ZB}}(AB)$ [Eq. (3)] for (a) the III-V series and (b) the II-VI series. The insets depict the trends with the cations.

anion chemical series of the III-V and II-VI compounds. Excluding for the moment those compounds for which $|\Delta E^M_{W\text{-ZB}}|$ is comparable to the standard deviation $\sigma$ of the fit, we find that our model correctly describes, with only a few exceptions, the overall $W$ vs ZB structural preferences established experimentally:[1-5] Column III nitrides and column IIB oxides tend to adopt the $W$ structure, whereas heavier anions stabilize the ZB structure. The exceptions relative to the previously accepted structural designations are CdSe, HgSe, and MgTe, believed[3-5,10-14] to have the $W$ ground state at low temperatures but found here to be more stable in the ZB structure. A recent careful examination of the ZB→ $W$ phase transition in CdSe (Ref. 6) established conclusively, however, that ZB is the stable low-temperature phase, in agreement with our result. Similarly HgSe was erroneously designated previously to have the $W$ ground state;[3,5,12,13] it is ZB at low temperatures.[1] The experimental assignment of MgTe as $W$ dates back to the 1927 work of Zachariasen[21] who obtained MgTe powder, finding hexagonal reflection patterns in this highly hygroscopic nonstoichiometric mixture of Mg+MgO+MgTe. However, it is not obvious from these experiments whether (i) $W$ is the stable low-temperature phase (in which case our prediction is incorrect) or (ii) $W$ is stable only as a high-temperature phase and another structure is stabler at low temperatures (in which case our result does not necessarily conflict with experiments[21]). To resolve this question we have calculated the LDF total energy of MgTe in the ZB, $W$, NaCl, and NiAs structures. We find that the energy differences relative to the ZB phase are 0, $-1.0$, $-1.3$, and $-15$ meV/atom, respectively. Hence, the $W$ and ZB forms of MgTe are predict-

ed to be unstable at low temperatures relative to the NiAs-type structure. Of the two metastable forms ($W$ and ZB) the orbital radii model shows that ZB is preferred. The situation here is analogous to what was found[22] in Mn chalcogenides, where MnO (like MgO) has the NaCl structure, but MnTe has the NiAs structure. Furthermore, the metastable ZB form of MnTe can be stabilized during growth.[22]

Considering next compounds for which $|\Delta E^M_{W\text{-ZB}}|$ is small ($\leq 3$ meV), we identify materials that exhibit strong $W$-ZB polytypism: CdS, CuCl, and ZnS with $\Delta E^M$ values of 0.7, 0.6, and 2.9 MeV, respectively.

The significance of the coordinates $\tilde{R}_\sigma, \tilde{R}_\pi$ [Eq. (4)] in the context of $W$-ZB structural preference can be appreciated in part by noting that (i) using the size coordinates $(R_\sigma, R_\pi)$ [Eq. (1)] instead of $(\tilde{R}_\sigma, \tilde{R}_\pi)$ leads to a twofold increase in the standard deviation of the fit and predicts incorrectly BeO to be ZB and ZnS, CdSe, CuCl, and InP to be $W$; (ii) using Phillip's coordinates[10] $E_h$ and $C$ in the fit of Eq. (3) leads also to a twofold increase in the standard deviation of the fit and predicts incorrectly ZnS, ZnSe, CuCl, CuBr, and CuI to be $W$. Hence, despite the fact that $(E_h, C)$ and $(R_\sigma, R_\pi)$ provide a good diagrammatic separation of different crystal structures, they do not exhibit a quantitative scaling with the energy difference $\Delta E_{\alpha\beta}(AB)$ as well as the $(\tilde{R}_\sigma, \tilde{R}_\pi)$ coordinates do. (iii) Omitting the orbital dependence of the coordinates (i.e., $r_s \neq r_p$) and using instead just the global atomic size difference $R_\sigma = |(r_s^A + r_p^A) - (r_s^B + r_p^B)|$ fails to distinguish between C, Si, and Ge as $R_\sigma(C) = R_\sigma(Si) = R_\sigma(Ge) = 0$. In fact (Fig. 2), $\Delta E^{LDF}_{W\text{-ZB}}(C) \gg \Delta E^{LDF}_{W\text{-ZB}}(Si)$.

The basic chemical rules pertaining to $W$-ZB stability that we deduce from our model are as follows.

(i) *The W-ZB boundaries*. We find that the stability of these phases is generally delineated by a single coordinate, i.e., $R(A,B)$ of Eq. (3a). When $\tilde{R}$ is between $\tilde{R}_c^{(1)} = 0.38$ [where $\Delta E^M(\tilde{R}_c^{(1)}) = 0$] and $\tilde{R}_c^{(2)} = -0.20$ the ZB structure is more stable, whereas for $\tilde{R}$ between $\tilde{R}_c^{(1)}$ and $\tilde{R}_c^{(3)} = 1.2$ the $W$ structure is more stable.

(ii) $\Delta E_{W\text{-ZB}}$ *for compounds that are unstable in the W or ZB structures*. We find that compounds whose ground state is the NaCl structure are divided into two groups in terms of the order of their metastable phases: MgO, CaO, MnO, and CdO are predicted to have metastable $W$ structure (with $\Delta E^M_{W\text{-ZB}}$ of $-19.7$, $-23.8$, $-21.2$, and $-21.0$ meV/atom, respectively), while CaTe and MgSe are predicted to have a metastable ZB structure (with $\Delta E^M_{W\text{-ZB}}$ of $+4.5$ meV/atom for both). For C (stable in the graphite form), we find that the metastable cubic (diamond) structure is considerably lower in energy than the $W$ form ($\Delta E^M_{W\text{-ZB}} = 25$ meV/atom). Both SiC and GeC are found on the $W$ side of the $W$/ZB border (the actual ground state of SiC is apparently the hexagonal $6H$ polytype[4]), while SiGe is predicted to be strongly ZB.

(iii) *Anion rules*. Except when the cation is a first-row element (B and Be) $\Delta E^M$ increases (e.g., ZB is stabilized) as the anion becomes heavier (i.e., going down in the column in the Periodic Table, see Fig. 3). For first-row cations the rule is reversed (except for BeO): heavy anions tend to stabilize the $W$ form. First-principles pseudopotential calculations indeed confirm that

$\Delta E_{W\text{-}ZB}(\text{BeS}) > \Delta E_{W\text{-}ZB}(\text{BeSe})$, in agreement with the model [Fig. 3(b)]. This reflects the fact that while atomic sizes $r = r_s + r_p$ generally increase as one moves down a column in the Periodic Table, first-row cations are particularly small. Hence, when the cation is a first-row element the global anion-cation size difference $|r_A - r_B|$ increases when the anion gets heavier (except for BeO), but for second-row cations and beyond this difference *decreases*. The anion dependence of $\Delta E^M$ is generally monotonic with respect to the anion position in a column.

(iv) *Cation rules.* As seen in the insets to Fig. 3, $\Delta E^M$ can be *nonmonotonic* with respect to the cation position in a column: For III-V's the $\Delta E^M_{W\text{-}ZB}$ energy sequence is $\text{In}X < \text{Al}X < \text{Ga}X$. Insofar as $\Delta E^M(A,B) \propto \tilde{R}(A,B)$ constitutes an orbital ionicity scale, this suggests Al$X$ to

be *more* ionic than Ga$X$, in agreement with the calculation of Christensen, Satpathy, and Pawlowska,[23] but in conflict with Phillips scale.[10]

In summary, we found that the $W$-ZB energy difference exhibits a remarkable linear scaling with the renormalized orbital radii [Eq. (4)]. This is used to unravel simple chemical trends within homological series. Apparent conflicts between this model and experiment lead to a suggested reassignment of the true ground state of MgTe (NiAs-type) and CdSe (ZB).

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[20]We have minimized the total energy of the $W$ structure with respect to the lattice constant $a$, the $c/a$ ratio, and the cell-internal parameter $u$. We used 14 and 10 special k points for structural optimization of $W$ and ZB, respectively, and as many as 42 and 60 special k points for the final-energy calculations. Use of too few k points tends to spuriously stabilize the ZB structure. The basis set cutoff for the pseudopotential calculation need to assure a $\leq$ 2-meV/atom precision in $\Delta E$ is 20 Ry for all compounds except the nitrides that require 50 Ry.

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