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

Chin-Yu Yeh, Z. W. Lu, S. Froyen, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401
(Received 9 January 1992)

To systematize the wurtzite (W) versus zinc blende (ZB) structural preferences among the binary octet compounds, we have calculated the corresponding energy difference \( \Delta E_{\text{W-ZB}}(AB) \) for thirteen \( AB \) compounds using the local-density formalism (LDF). We then uncovered a linear scaling between \( \Delta E_{\text{W-ZB}} \) and an atomistic orbital-radii coordinate \( R(A, B) \) that can be simply calculated from the properties of the free \( A \) and \( B \) atoms. This permits predictions 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 \( A^{\text{IV}} \) and \( A=\text{Ga}\rightarrow \text{Al}\rightarrow \text{In} \) for \( A^{\text{III}} \). 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 internal energies (\( \pm 20 \text{ meV/atom} \)) 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 \( \pm 5 ^\circ \text{C} \) in CdSe,\(^6\) and 407, 386, and 396 \( ^\circ \text{C} \) 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 \( \sim 2.3 \text{ eV} \), 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 \( E_p \) 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,

\[
R_s(A, B) = |(r_p^A + r_i^A) - (r_p^B + r_i^B)|, \tag{1}
\]

\[
R_s(A, B) = |r_p^A - r_i^A| + |r_p^B - r_i^B|,
\]

of the classical crossing points \( r_1^A, B \) of the screened nonlocal atomic pseudopotentials of angular momentum \( l \). It was previously demonstrated\(^11\)–\(^14\) that in the \( R_s(A, B) \) vs \( R_s(A, B) \) plane there exists a separation into simple re-
gions occupied predominantly by compounds belonging to a single structure. The orbital radii determined from \textit{ab initio} local-density formalism\textsuperscript{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 Villar and Hulliger\textsuperscript{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 \textit{ab initio} radii to quasicrystals and high-\(T_c\) superconductors.\textsuperscript{16}

As successful as these diagrammatic 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 \textit{structural energy differences} \(\Delta E_{ab}(AB)\) for a series of compounds \{\(AB\)\} in different crystal structures \(a\) and \(b\), it was impossible to establish whether the structural coordinates\textsuperscript{10–16} actually scale with \(\Delta E_{ab}(AB)\). Indeed, \textit{quantitative} structural regularities within homologous chemical sequences such as \(\text{AlN} \rightarrow \text{CaN}\) \(-\rightarrow \text{InN}\) or \(\text{AlN} \rightarrow \text{AlP} \rightarrow \text{AlAs} \rightarrow \text{AlSb}\) cannot be established unless such a scaling is known. Furthermore, if neither \(a\) nor \(b\) are the stable crystal structure of \(AB\), structural diagrams provide no hint of the energy difference \(\Delta E_{ab}(AB)\) 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

\[
\Delta E_{W-ZB}(AB) = E_{W}^{\text{LDF}}(AB) - E_{ZB}^{\text{LDF}}(AB) \tag{2}
\]

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

\[
\bar{R}(A,B) = \bar{R}_o(A,B) + \omega \bar{R}_e(A,B) \tag{3a}
\]

and the \(W\)-\(ZB\) energy difference, i.e.,

\[
\Delta E_{W-ZB}^{\text{LDF}}(AB) \approx \Delta E_{W-ZB}^{\text{M}}(AB) = E_0 + \sigma \bar{R}(A,B) \tag{3b}
\]

where \(\bar{R}_o\) and \(\bar{R}_e\) are atomistic coordinates related to the orbital radii [Eq. (1)]. Like in Eq. (1), the determination of \(\bar{R}_o(A,B)\) and \(\bar{R}_e(A,B)\) requires only the knowledge of \textit{free atom} \((A\) and \(B)\) quantities; these can be calculated once and for all either from atomic wave functions or from nonlocal atomic pseudopotentials.\textsuperscript{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 \(\text{CaO}, \text{CdO},\) and \(\text{C}\) 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 \(\Delta E_{W-ZB}^{\text{LDF}}\) is to be calculated by the LDF method. We include compounds that are known to be highly stable in the \(W\) structure,\textsuperscript{4,5} (\(\text{AlN}, \text{GaN},\) and \(\text{InN}\)) and compounds that occur at low temperatures only in the zinc blende (or diamond) phase\textsuperscript{1–3} (\(\text{Si}, \text{AlP}, \text{AlAs}, \text{GaP}, \text{GaAs},\) and \(\text{ZnTe}\)). We then add compounds known to exhibit \(W\)-\(ZB\) polytypism (\(\text{ZnS}, \text{ZnSe},\) and \(\text{CdS}\)), 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\textsuperscript{19a,b} exchange correlation as parametrized by Perdew and Zunger.\textsuperscript{19b}

We used the plane-wave nonlocal pseudopotential method\textsuperscript{17} for \(\text{Si}\) and the III-V's and the linearized augmented plane-wave (LAPW) method\textsuperscript{18} for \(C\) and the II-VI's (that are difficult to converge in a pure plane-wave basis). A detailed convergence test\textsuperscript{20} was performed with respect to Brillouin-zone \(k\)-point sampling and basis set size to assure a precision of 2 meV/atom in \(\Delta E_{W-ZB}^{\text{LDF}}\).

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

\[
\bar{R}_o(A,B) = \frac{R_o(A,B)}{(r_o^A + r_o^B)(r_o^A + r_o^B)} \tag{4}\]

\[
\bar{R}_e(A,B) = \frac{R_e(A,B)}{(r_e^A + r_e^B)(r_e^A + r_e^B)} \tag{4}\]

The simple linear scaling of Eqs. (3) and (4) give a rather small standard deviation \(\sigma\) between the directly calculated \(\Delta E_{W-ZB}^{\text{LDF}}(AB)\) and the fitted model \(\Delta E_{W-ZB}^{\text{M}}(AB)\), using for \(r_i(B)\) the position of the outer maximum of the valence atomic wave function \(r_{va}(r)\) (giving \(\sigma = 3.2\) meV), or the \textit{ab initio}\textsuperscript{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 \(\Delta E_{W-ZB}^{\text{LDF}}\) 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 \(\Delta E_{W-ZB}^{\text{M}}\) within cation and...
FIG. 3. Predicted W-ZB energy differences $\Delta E_{MZB}^W(AB)$ [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 $|\Delta E_{MZB}^W|$ 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 IIIB 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\(^1\)\(^-\)\(^5\)\(^,\)\(^10\)\(^-\)\(^12\)\(^,\)\(^13\)\(^,\)\(^15\)\(^-\)\(^17\)\(^,\)\(^20\)\(^,\)\(^21\)\(^,\)\(^22\) 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 $ZB \rightarrow W$ 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;\(^13\),\(^15\)\(^,\)\(^17\)\(^,\)\(^21\) it is ZB at low temperatures.\(^3\) 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-
\[ \Delta E_{W,ZB}(\text{BeS}) > \Delta E_{W,ZB}(\text{BeSe}) \], in agreement with the model [Fig. 3(b)]. This reflects the fact that while atomic sizes \( r = r_1 + r_p \) 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 \( \Delta E_{W,ZB}^M \) energy sequence is \( \text{InX} < \text{AlX} < \text{GaX} \). Insofar as \( \Delta E^M(A,B) \propto R(A,B) \) constitutes an orbital ionicity scale, this suggests \( \text{AlX} \) to be more ionic than \( \text{GaX} \), in agreement with the calculation of Christensen, Satpathy, and Pawlow ska,\(^{23}\) but in conflict with Phillips scale.\(^9\)

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 homologous 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).

This work was supported by the Office of Energy Research (OER) [Division of Materials Science of the Office of Basic Energy Science (BES)], U.S. Department of Energy, under Contract No. DE-AC02-77-CH00178.


\(^{5}\)E. Parthe, *Crystal Chemistry of Tetrahedral Structures* (Gordon and Breach, New York, 1964).


\(^{20}\)We have minimized the total energy of the \( W \) structure with respect to the lattice constant \( a \), the \( c/a \) ratio, and the cellinternal 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 \( \leq 2 \text{-meV/atom precision in } \Delta E \text{ is 20 Ry for all compounds except the nitrides that require 50 Ry.} \)


\(^{22}\)S.-H. Wei and A. Zunger, Phys. Rev. Lett. 56, 2392 (1986), and references therein.