Application of the bond valence method in the non-isovalent semiconductor alloy \((\text{GaN})_{1-x}(\text{ZnO})_x\)

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Abstract
This paper studies the bond valence method (BVM) and its application in the non-isovalent semiconductor alloy \((\text{GaN})_{1-x}(\text{ZnO})_x\). Particular attention is paid to the role of short-range order (SRO). The theoretical standing of the BVM is examined by density-functional theory (DFT) calculations. Combining the BVM with Monte-Carlo simulations and a DFT-based cluster expansion model, bond-length distributions and bond-angle variations are predicted. The connection between bond valence and bond stiffness is also discussed. Finally, the BVM is extended to the modelling of an interatomic potential.

Keywords: bond valence method, non-isovalent semiconductor alloy, short-range order

(Some figures may appear in colour only in the online journal)

1. Introduction

Isovalent semiconductor alloys are extensively studied since their structural, electronic and optical properties can be tuned by varying the alloy composition [1–3]. More recently, non-isovalent semiconductor alloys are gaining attention [4]. For example, the pseudobinary \((\text{GaN})_{1-x}(\text{ZnO})_x\) alloy is attractive for its high efficiency in photocatalytic water splitting [5]. Strong short-range order (SRO) was recently predicted in the \((\text{GaN})_{1-x}(\text{ZnO})_x\) alloy arising from its non-isovalent nature [6]. SRO has an important role in determining the atomic, electronic and vibrational properties. To keep local charge neutrality, the substitutional SRO is accompanied with and compensated by atomic deviation from the ideal lattice positions. Therefore, it is imperative to study the composition (x), temperature (T) and SRO (\(\Pi\)) dependent (x, T, \(\Pi\)) structural relaxations. In [6] the \((\text{GaN})_{1-x}(\text{ZnO})_x\) alloy is efficiently represented...
by a SRO-modified version of the special quasirandom structure (SQS) [7] approach. This approach, denoted SQoS for special quasiordered structure, ‘mimics’ the statistical correlations of the short-range ordered alloys. The present study aims for statistically reliable predictions of bond-length distribution and bond-angle variation.

The bond valence method (BVM) is widely adopted in solid state chemistry for various applications including prediction of molecular geometry [8], construction of interatomic potentials for perovskite oxides [9, 10], and calculation of the acidity constant \( pK_a \) [11, 12]. The concept of the scalar bond valence is also vectorized to describe the geometry of crystal structures [13–15]. Its power in predicting the energetics for non-isovalent semiconductor alloys is recently demonstrated [16, 17]. In inorganic chemistry the BVM is commonly used as an empirical tool, the underlying physics of which is not widely discussed. For example, the fact that bond valence correlates strongly with bond length [8] suggests a connection between bond valence and bond-length-dependent transferable force constant [18]. Also the correlation between total energy and bond valence [8] is not yet fully understood. Brown [8] proposed a ‘more rigorous but less physical’ analogy of the Kirchhoff circuit law which treated the bond valence network as a capacitive electric circuit. Burdett and Hawthorne [19] interpreted the BVM from the molecular orbital basis. There is also some similarity between the bond valence and the Mayer bond order [20]. In the present study, particular attention is paid to the theoretical standing of the BVM. Density-functional theory (DFT) calculations are performed wherever necessary.

Inclusion of vibrational entropy in the first-principles alloy phase diagram calculation is a long-standing challenge. For non-isovalent semiconductor alloys, a large supercell is favored in order to include the statistical fluctuations. As large structural relaxations are expected, accurate DFT total energy and force calculations are computationally expensive. The problem is partly alleviated by the SQS approach [6, 21, 22]. Another idea is to use a bond-length-dependent transferable force constant [1, 18], where the bond stiffness is predicted from the bond length and the chemical identity of the bond. The present study reveals the strong correlation between bond valence and bond length, which indicates the possibility of using bond valence instead of bond length as a predictor for bond stiffness. Such an extension will release the estimation of nearest-neighbor force constants from the requirement for the relaxed geometry of a configuration.

2. The bond valence method

The BVM is extensively discussed in [23]. The strength of the BVM lies in its simplicity and robustness. Given only the site occupancies of configurations, total energy and structural properties can be predicted. Each nearest-neighbor cation–anion bond is assigned a bond valence \( v_{IJ} \). Next nearest-neighbor cation–cation/anion–anion interactions are neglected. The bond valence sum (BVS) of an atom is defined as the sum of the bond valences surrounding the atom. Each atom has an ionic valence \( V_I \) equal to its corresponding formal ionic charge. By convention, \( V_{Ga} = +3 \), \( V_{N} = -3 \), \( V_{Zn} = +2 \), \( V_{O} = -2 \), \( v_{H} = -v_{H} \). Of crucial importance for non-isovalent semiconductor alloys are two rules: (1) the valence sum rule \( V_I = \sum_J v_{IJ} \), and (2) the valence loop rule \( \sum_{loop} v_{IJ} = 0 \). The valence sum rule is an equivalent statement of the principle of local charge neutrality, where \( |v_{IJ}| \) correlates with the Mulliken overlap population \( P_{IJ} \) [24, 25]. The ‘valence loop rule’ is also known as the ‘equal valence rule’, since the zero circulation condition is equivalent to the minimization of \( \sum_{d,J} v_{dJ}^2 \) (see for example the appendix in [17]). The solution is a set of \( \{v_{IJ}\} \) which minimizes the measure of the total energy \( E = \alpha \sum_{d,J} v_{dJ}^2 \) (\( \alpha \) is the correlation constant) under the constraint of the valence sum rule.
As for the measure of the total energy, in solid state language, a perturbation expansion of the orbital interaction energy reads \[19\]

\[
E_i = \sum_{i,I,J} \epsilon_i = \sum_{i,I,J} \left( \epsilon_i^0 + \sum_{j,J} \frac{\langle \phi_i^0 | H | \phi_j^0 \rangle^2}{\epsilon_i^0 - \epsilon_j^0} \right)
\]

where \(\phi_i^0\) denotes its orbital and \(\epsilon_i^0\) denotes its energy, respectively. Capital \(I, J\) and lowercase \(i, j\) refer to atomic and orbital indices, respectively. In the next section it will be shown by DFT calculations that the matrix element \(H_{ij} \langle \phi_i^0 | H | \phi_j^0 \rangle\) is proportional to the orbital overlap integral \(S_{ij} \langle \phi_i^0 | \phi_j^0 \rangle\). The total relaxation energy \(E_r = \sum_{i,I} \epsilon_i\) is then approximately equal to \(\alpha_{IJ} \sum_{i,I,J} S_{ij}^2\), where the denominator \(\epsilon_i^0 - \epsilon_j^0\) is reduced into a bond-specific constant \(\alpha_{IJ}\). The overlap integral \(S_{ij}(r, \theta, \phi)\) can be expressed in a separable form \(S_{ij}(r)f(\theta, \phi)\) \[19\]. The angular dependence is lifted after summing \(\sum_{i,I,J} f^2(\theta, \phi)\) over all the interacting orbital pairs. The summation over orbital pairs then reduces to the summation over atom pairs. Finally, the measure of the total energy \(E = \alpha \sum_{i,I,J} v_{ij}\) is obtained, with the assumptions \(v_{ij} \sim S_{ij} \equiv \sqrt{\sum_{i,I,J} S_{ij}^2}\) and \(\alpha_{IJ} = \alpha\), while \(\alpha\) is to be fitted by DFT total energy calculations. In analogy to the Kirchoff circuit law, the bond capacitances are all equal \[8\], which is equivalent to assuming \(\alpha_{IJ}\) is equal for different types of atomic pairs.

The radial dependence of \(S_{ij}(r)\) leads naturally to the empirical exponential correlation between bond valence and bond length

\[
v_{ij} = \exp(r_{ij}^0 - r)b_{ij}
\]

where \(r\) is the observed bond length while \(r_{ij}^0\) and \(b_{ij}\) are empirically fitted bond valence parameters for \(I-J\) bond. \(b_{ij}\) measures the bond softness and is usually taken as a universal constant of 0.37 Å, while \(r_{ij}^0\) is experimentally determined from the structural data of related materials \[26\]. The bond-angle variation is predicted using an empirical relation \[23\]

\[
\theta_{ICJ} = 109.5 + k(v_{CI} + v_{CJ} - V_c/2)
\]

where \(k\) is an empirical constant (equal to 15.3° per valence unit in \[23\]), \(v_{CI}\) and \(v_{CJ}\) are the bond valences of the two ligand bonds, and \(V_c\) is the ionic valence of the central cation. In the present study, the disordered alloy offers abundant structural data. Therefore \(r_{ij}^0, b_{ij}\) and \(k\) are fitted to DFT calculations instead.

### 3. Computational methodology

For completeness a brief outline of the computational methods is given. An Ising-type model Hamiltonian for the (GaN)$_{1-x}$(ZnO)$_x$ alloy was constructed by Li et al \[27\] using a DFT-based cluster expansion method \[28–30\]. Monte-Carlo simulations are then performed on the constructed cluster expansion model using the ATAT package \[31–33\]. For each \((x, T)\) of interest, a thermodynamic ensemble of configurations is generated. Details are in \[6\]. For each configuration the bond valences are determined using the BVM. At this stage only the site occupancies are needed. An iterative scheme \[34\] enforcing the equal valence rule is used to obtain the set of bond valences \(\{v_{ij}\}\) which minimizes the measure of the total energy \(E = \alpha \sum_{i,I,J} v_{ij}^2\). Finally, the bond-length distribution and bond-angle variation are obtained using the empirical correlations (equations (2) and (3)).
Ga-3d and Zn-3d electrons are treated explicitly as valence electrons. The \( k \)-point mesh is chosen to be equivalent to a \( 6 \times 6 \times 4 \) mesh for the 4-atom wurtzite unit cell. DFT calculations are performed for two reasons: (1) The correlations \( P_{IJ} \propto v_{IJ} \), \( H_{ij} \propto S_{ij} \) and \( v_{IJ} \sim S_{IJ} \) are crucial for the theoretical standing of the BVM and are therefore examined first; (2) The BVM parameters \( r_{IJ} \), \( b_{IJ} \) and \( k \) are to be fitted to DFT calculations. For the former purpose (figures 1–3), three representative 432-atom supercells at \( x = 0.25 \), 0.5 and 0.75 are constructed. Kohn–Sham wavefunctions are expanded in a variationally optimized double-\( \zeta \) polarized (DZP) basis set, as implemented in the SIESTA package [35]. The Perdew–Burke–Ernzerhof (PBE) [36] version of the exchange-correlation functional is used. Pseudopotentials

Figure 1. The correlation between the DFT-calculated Mulliken population \( P_{IJ} \) and the BVM-predicted bond valence \( v_{IJ} \) for different types of bonds.

Figure 2. The correlation between the DFT-calculated off-diagonal Hamiltonian matrix element \( H_{ij} \) and the DFT-calculated orbital overlap integral \( S_{ij} \) between the first \( \zeta \) numerical atomic orbitals of different species.
are available from the SIESTA homepage [37]. The Mulliken population $P_{IJ}$, the off-diagonal Hamiltonian matrix elements $H_{ij}$ and the orbital overlap integral $S_{ij}$ are all ingredients of the SIESTA method with localized basis sets. For the latter purpose (figures 4, 5 and 10–12), a thermodynamic ensemble equilibrated at the experimental synthesis temperature $T = 1123$ K [5] with 72-atom supercells is used. Total energy and force calculations are performed using the QUANTUM ESPRESSO package [38] with the PBEsol functional [39]. Pseudopotentials are available from the PSlibrary [40].

4. Results and discussions

4.1. Examination of the BVM

In figure 1 the correlations between the Mulliken population $P_{IJ}$ and the bond valence $v_{IJ}$ for different types of bonds are shown. Although $P_{IJ}$ has no strict physical sense due to its sensitivity to the atomic basis sets used in the projection, the linearity of the correlations indicate that the bond valence $v_{IJ}$ resembles the Mulliken bond population $P_{IJ}$. While the valence sum $\sum_{I} v_{IJ}$ equals the formal ionic charge $V_{I}$, the sum of Mulliken population $\sum_{I} P_{IJ}$ differs from $V_{I}$ by the Mulliken charge $P_{II}$. In figure 2 the correlation between the off-diagonal Hamiltonian matrix element $H_{ij}$ and the orbital overlap integral $S_{ij}$ is shown for the first $\zeta$ numerical atomic orbitals of different species. In the extended Hückel method [41], $H_{ij}$ is approximated by the corresponding diagonal Hamiltonian matrix elements and $S_{ij}$ through $H_{ij} \propto S_{ij}(H_{ii} + H_{jj})/2$. Since Ga and O are more electronegative than Zn and N, respectively, Ga-4s and O-2p orbitals have deeper atomic energy levels than Zn-4s and N-2p orbitals. Therefore the Ga-O and Zn-N curves have the largest and smallest slope in magnitude, respectively. In figure 3 the approximate bond valence $S_{IJ}$ (defined as $\sum_{i=1}^{N} S_{ij}^{2}$ in the present study) is compared with the BVM-predicted $v_{IJ}$ for different types of bonds. A qualitative agreement is found. The linearity of the correlation supports the interpretation of the BVM proposed in the present study.

The empirical correlations between the DFT-calculated bond lengths and the BVM-predicted bond valences are fitted according to equation (2) and plotted in figure 4. While the exponential dependence is correctly described, the correlation shows a half width (uncertainty) of roughly 0.2 Å for the bond lengths and 0.05 v.u. for the bond valences. In table 1, the original (tabulated in [26]) and fitted-to-DFT bond valence parameters are listed. Bond lengths of compound GaN and ZnO (labeled as R) calculated with the two sets of bond valence parameters are also listed. Since the fitting procedure releases the freedom of the bond softness $b_{IJ}$, an overall improvement is found for the fitted-to-DFT set of bond valence parameters. The correlation between the DFT-calculated bond angles and the BVM-predicted bond valences shows linear dependence with larger uncertainty, as is shown in figure 5. The fitted bond valence parameters $k$ for Ga and Zn are 18.1° v.u.$^{-1}$ and 20.1° v.u.$^{-1}$, respectively, slightly larger than the universal empirical constant 15.3° v.u.$^{-1}$ [23].

4.2. Bond-length distribution and bond-angle variation

Reference [6] shows that there is strong SRO in the (GaN)$_{1-x}$(ZnO)$_{x}$ alloy. Although a completely random alloy may not be achievable under common experimental conditions, the degree of SRO introduced is influenced by the experimental methods adopted in growing the samples [44]. Given the site occupancies of each configuration in the thermodynamic ensemble at ($x$, $T$), bond-length distribution and bond-angle variation are predicted using the fitted-to-DFT bond valence parameters. Temperatures of 1123 K, 2000 K, 5000 K and 20000 K are
chosen to represent the degree of SRO in short-range ordered (SRO), disordered (DIS1 and DIS2) and random (RAN) alloys respectively. Figure 6 shows the total bond-length distributions at various temperatures. As the temperature is raised, the peak of the bond-length distribution shifts slightly in the direction of shorter bond length while its width becomes broader. The small shift could be easily overwhelmed by thermal expansion, which is not considered in the present study. In figure 7, bond-length distributions of different types of bonds are shown. Upon mixing, the Ga-N bond shrinks while the Zn-O bond expands relative to the bond lengths in the corresponding pure compounds. From SRO alloy to RAN alloy, the shift
is toward shorter bond length for Ga-N, barely temperature-dependent for Ga-O and Zn-N, and toward longer bond length for Zn-O. This unusual tendency of bond-length distribution is a consequence of the non-isovalent nature of the alloy. One consequence of elevating the degree of randomness is to enhance the statistical presence of the energetically unfavored valence-mismatched Ga-O and Zn-N pairs. In the language of BVM, for a cation–anion pair, enhancing the presence of N(O) neighbors around the cation and Ga(Zn) neighbors around

**Table 1.** Bond valence parameters.

|                  | Original BVM [26] | Fitted to DFT |
|------------------|------------------|---------------|
|                  | GaN  | GaO  | ZnN  | ZnO  | GaN  | GaO  | ZnN  | ZnO  |
| $r_0^+ (\text{Å})$ | 1.84 | 1.73 | 1.77 | 1.704 | 1.844 | 1.755 | 1.831 | 1.756 |
| $b_0 (\text{Å})$  | 0.37 | 0.357 | 0.391 | 0.268 | 0.312 |
| $R (\text{Å})$    | 1.946 | — | 1.960 | 1.947 | — | 1.972 |
| Expt. ($\text{Å}$) [43] | 1.95 | — | 1.977 | 1.95 | — | 1.977 |

**Figure 5.** Correlations between the DFT-calculated bond angles and the BVM-predicted bond valences. The solid red lines represent the fitted correlations according to equation (3). In each figure the number of data points drawn is reduced by a factor of ten.

**Figure 6.** Temperature dependence of the total bond-length distribution at $x = 0.5$. 

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the anion will drain(pour) bond valence from(into) the cation–anion pair and as a result the bond is lengthened(shortened). Of particular importance is the Zn-N bond-length distribution due to the decisive role of Zn3d-N2p repulsion on the top of the valence band. In [6], an almost linear band gap reduction upon increasing the ZnO content for the short-range ordered alloy is observed. Upon increasing the ZnO content, a shorter Zn-N bond-length distribution is expected, which is confirmed by the BVM prediction shown in figure 8. The shorter Zn-N bond lengths result in the stronger Zn3d-N2p repulsion, which pushes the top of the valence band and therefore reduces the band gap. Figure 9 shows the anion–cation–anion bond-angle variation of short-range ordered alloy at x = 0.5. The N-Ga-N angle expands while the O-Zn-O angle shrinks relative to the ideal tetrahedral angle 109.5°, due to the fact that the bond valence

Figure 7. Bond-length distributions of short-range ordered alloy and random alloy at x = 0.5. The vertical dotted lines mark the bond lengths of the corresponding pure compounds.

Figure 8. Composition dependence of the Zn-N bond-length distribution.
of the ligand cation-O bond is generally smaller than that of the ligand cation-N bond. The BVM-predicted bond-length distribution and bond-angle variation (figures 7–9) agree well with more reliable but less statistical DFT calculations [6].

4.3. Energetics

As for the energetics, 170 structures are selected from a $T = 1123$ K thermodynamic ensemble over the full range of compositions. The formation energies calculated with DFT agree well with those predicted by the BVM (i.e. the measure of energy $E = \alpha \sum_{\alpha} v_\alpha^2$), as is shown in figure 10. The fitted parameter $\alpha = 1.07$ is consistent with that of [16]. However, since only the nearest-neighbor cation–anion bond valences are considered, the wurtzite and zincblende structures are indistinguishable from each other in the BVM. Due to this short-range nature, the BVM fails to reproduce the ordered (GaN)$_1$(ZnO)$_1$ ground state superlattice structure at $x = 0.5$ [27]. The formation energy of (GaN)$_1$(ZnO)$_1$ predicted by the BVM is positive, while that predicted by DFT is slightly negative [27]. This discrepancy does not affect any conclusion drawn in the present study since only the disordered alloy is concerned.

The bond stiffness is defined as the force constant $\phi_{\alpha\beta}$ in the bond direction. Figure 11 shows the dependence of bond stiffness $\phi_{\alpha\alpha}$ and $\phi_{\alpha\beta}$ on bond length, where $\alpha$ refers to the bond direction and $I, J$ are nearest neighbors. The bond stiffness is calculated with a displacement of 0.02 Å from the relaxed 72-atom supercell structures along each bond direction. While a linear correlation between bond stiffness and bond length is suggested in the bond-length-dependent transferable force constant approach [1, 18], an exponential dependence for nearest neighbors seems to fit better according to the DFT calculations. The ionic Zn-O bond is softer than the covalent Ga-N bond.

For isovalent III–V semiconductor alloys, the widely used Keating valence force field (KVFF) model [45] yields generally good accuracy [46–51]. In the KVFF model, the force constants are related to the macroscopic elastic constants, which can be accurately determined experimentally. Also the isovalent nature of III–V semiconductor alloys guarantees good transferability from pure compound semiconductors to the corresponding alloy. For the non-isovalent semiconductor alloys, the transferability no longer holds, for the apparent reason that there exists no wurtzite GaO or ZnN. The non-isovalent nature is well described by the BVM. In the present study, the BVM is extended to the modelling of an interatomic potential. The relaxation energy is assumed to consist of three parts.

Figure 9. The anion–cation–anion bond-angle variation of short-range ordered alloy at $x = 0.5$. 
The first term is the measure of the total energy, and the second term is the harmonic angle potential. The third term accounts for large lattice relaxations by penalizing deviations from the bond valence conservation \([9, 10, 52]\). This interatomic potential is fitted to DFT calculations where each relaxed structure is expanded and contracted by 1%. Fitting parameters \(k_{N,O}\) and \(\beta_{Ga,Zn}\) are found to be negligible. In figure 12 the comparison is shown. The energetics is faithfully reproduced by the proposed interatomic potential.
Discussion and conclusions

The theoretical standing of the BVM is discussed from a computational perspective. The underlying assumptions within the BVM are revealed by DFT calculations on the non-isovalent semiconductor alloy (GaN)$_{1-x}$(ZnO)$_x$. Bond-length distribution and bond-angle variation are predicted by fitting BVM empirical relations to reliable DFT-calculated structural data. Particular attention is paid to the role of SRO. The present study also offers an alternative way of accurately reproducing the energetics of non-isovalent semiconductor alloys with the BVM, where only site occupancies are needed. The connection between bond valence and bond stiffness is discussed. Finally a tentative interatomic potential is proposed. In principle, the discussions in the present study should also be applicable for other non-isovalent semiconductor alloys.

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