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Ionicity scale based on the centers of maximally localized Wannier functions

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The maximally localized Wannier functions (MLWFs) of 32 A^NB^{8-N} compounds, ranging from elemental group-IV solids to I-VII compounds, have been constructed according to the method of Marzari and Vanderbilt [Phys. Rev. B **56**, 12847 (1997)]. The considered systems crystallize in the diamond, zinc-blende, or rocksalt structures. A different bond ionicity scale has been introduced based on the deviation of the centers of the MLWFs from the corresponding bond centers, which involves only physical constants. The present bond ionicity of the considered compounds can be considered, to a very good approximation, as the best fit to the previous empirical and self-consistent ionicity scales. The critical value of the bond ionicity that separates the fourfold and sixfold coordinate structures is found to be of about 0.7, which is smaller than previous theoretical values of about 0.8. The volume variation of the bond ionicity is found to be much smaller than previously thought, except for SiC.

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I. INTRODUCTION

Modern electronic structure methods based on the density-functional theory are well established techniques to accurately calculate various physical and chemical properties of a wide range of materials, ranging from isolated atoms to some biological systems. However, concepts such as valency, electronegativity, and bond ionicity are still very useful in understanding the differences in the properties of different systems and in seeking trends of these properties. Focusing on A^NB^{8-N} compounds, where N is the valency of the A atom, various empirical[1,2] and first-principles[3,4] ionicity scales have been introduced. The main aim of this work is to introduce a different first-principles ionicity scale based on the center of the maximally localized Wannier functions (MLWFs).[5] It is constructive to first provide a critical review of the previous ionicity scale and to briefly describe MLWFs.

The most famous empirical ionicity scales are those of Pauling[1] and Phillips.[2] Based on thermodynamical arguments, Pauling[1] has developed an electronegativity scale (X) for the elements according to the relation

$$D(AB) = \frac{1}{2}[D(AA) + D(BB) + c(X_A - X_B)], \tag{1}$$

where D denotes the formation energy of the AA, BB, and AB bonds; X is the electronegativity of the A and B atoms; and c is a constant with the dimension of energy. Then, he introduced an ionicity scale based on the empirically obtained electronegativity difference. For molecules, the Pauling ionicity scale is

$$P_i = 1 - \exp\left(-\frac{1}{4}|X_A - X_B|^2\right). \tag{2}$$

For crystalline A^NB^{8-N} compounds, a modified form is used:

$$P_i = 1 - \frac{N}{M}\exp\left(-\frac{1}{4}|X_A - X_B|^2\right). \tag{3}$$

Here, M denotes the coordination number, and the $\frac{N}{M}$ prefactor takes into account the sharing of the N valence electrons by the M bonds (known as resonant bonds). The Phillips[2] ionicity scale is based on the dielectric theory of Phillips and Van Vechten. This ionicity scale is defined as

$$f_i = \frac{C^2}{E_g^2} = \frac{C^2}{E_h^2 + C^2}, \tag{4}$$

where E_h is the homopolar gap due to the symmetric part of the potential, $\frac{1}{2}(V_A+V_B)$, while C is the ionic or charge transfer gap resulting from the antisymmetric part, $\frac{1}{2}(V_A-V_B)$. The average band gap of the crystal E_g is equal to $(E_h^2+C^2)^{1/2}$. The two Phillips ionicity scale parameters are obtained empirically as follows. E_h is obtained by scaling the optical band gap of diamond or Si according to the relation

$$E_h = E_h(\mathrm{Si})\left(\frac{a(\mathrm{Si})}{a}\right)^{2.5}, \tag{5}$$

where a denotes the lattice constant. C is obtained from E_g which, in turn, is obtained from the dielectric constant (ε_∞). A remarkable feature of the Phillips ionicity scale is the existence of a critical value of f_i, 0.79, that separates fourfold from sixfold coordination compounds.

Christensen *et al.*[3] introduced an *ab initio* approach for the bond ionicity. They have carried out a tight-binding parametrization of the band structures of many A^NB^{8-N} compounds in the zinc-blende (ZB) phase, calculated by employing a linear-muffin-tin orbital (LMTO) method. This parametrization has enabled them to express the Phillips ionicity scale parameters (E_h and C) in terms of LMTO band structure parameters. The so-obtained bond ionicity (denoted as f_i^*) is found to be, generally speaking, higher than the corresponding values of f_i. Interestingly, the investigations of Christensen *et al.*[3] have confirmed the existence of a critical ionicity value that separates fourfold from sixfold coordination compounds, in accord with the value suggested by Phillips (see above). This critical ionicity value has also been confirmed by Chelikowsky and Burdett.[6] The second first-principles ionicity scale is introduced by Garcia and Cohen[4] based on the asymmetry of the charge-density distribution. By defining the symmetric and antisymmetric charge densities as $n_S(\mathbf{r})=[n(\mathbf{r})+n(-\mathbf{r})]/2$ and $n_A(\mathbf{r})=[n(\mathbf{r})-n(-\mathbf{r})]/2$, this bond ionicity scale is given as

$$g=\sqrt{\frac{S_A}{S_S}}, \tag{6}$$

with

$$S_A=\frac{1}{V_{cell}}\int n_A^2(\mathbf{r})d\mathbf{r} \tag{7}$$

and

$$S_S=\frac{1}{V_{cell}}\int n_S^2(\mathbf{r})d\mathbf{r}, \tag{8}$$

where V_{cell} is the unit-cell volume. The obtained values of g are found to correspond quite well with f_i, except for compounds involving first row elements for which g is found to be larger than f_i. The largest discrepancy (of about 0.3) is in the case of group-III nitrides. It is worth noting that the above two first-principles bond ionicity scales are extracted from the properties of the whole crystal—not directly from a bond property.

An attempt to extract the bond ionicity from a bond property is made by Coulson *et al.*[7] In this approach, the σ-bond orbital is written as

$$\psi=\phi_A+\lambda\phi_B, \tag{9}$$

where ϕ_A and ϕ_B are sp^3 hybrid atomic orbitals centered on atoms A and B, respectively, and λ is determined by total-energy minimization. Under the assumption that atomic wave functions used in Eq. (9) are orthogonal, the bond ionicity is given as

$$c_i=\frac{(\lambda^2-1)}{(\lambda^2+1)}. \tag{10}$$

As noted by Phillips,[2] this approach probably gives about as good a definition of the ionicity as can be obtained. However, the major problem of this approach lies in the extremely poor representation of wave functions of the A^NB^{8-N} compounds.

The Wannier function representation of the electron wave functions in periodic crystalline solids has recently received considerable interest. This is because of the elegant method provided by Marzari and Vanderbilt[5] to construct MLWFs (see Sec. II A for a brief description). For elemental group-IV solids in the diamond structure, there is a symmetric MLWF associated with each bond and centered at the bond center. By going to A^NB^{8-N} compounds crystallizing in the ZB phase, the MLWFs become asymmetric and their centers are shifted toward the anions. The magnitude of this shift is obviously proportional to the bond ionicity and, hence, it can be used as a measure for the bond ionicity. As noted by Marzari and Vanderbilt,[5] the MLWFs of the valence bands of the considered compounds have roughly the character of the σ-bond orbitals (i.e., a linear combination of the sp^3 hybrids of the two neighboring atoms projected toward the bond center). In this sense, the present approach is similar in spirit to the method of Coulson *et al.*[7] However, unlike the latter approach, the MLWFs provide an exact representation of the wave functions of the A^NB^{8-N} compounds.

In this work, we first used the method of Marzari and Vanderbilt[5] to calculate the MLWFs of 32 A^NB^{8-N} compounds, with $N=1$, 2, 3, and 4, in their ground-state phases [diamond, ZB, or rocksalt (RS)]. The MLWFs of the A^NB^{8-N} compounds in the RS phase possess different features from those of the ZB structures because of the difference in the coordination number. To the best of our knowledge, MLWFs for systems that crystallize in the RS form have not been previously reported. Then, a first-principles bond ionicity scale is introduced based on the center of the MLWFs and some physical constants.

The rest of the paper is organized as follows. In Sec. II, we present a brief description of the MLWFs and the computational details. The results are presented and discussed in Sec. III. Finally, Sec. IV contains a summary of our main results and conclusions.

II. METHODOLOGY

A. Maximally localized Wannier functions

The electronic states in periodic systems are usually described in terms of extended Bloch orbitals

$$\psi_{n,\mathbf{k}}(\mathbf{r})=u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{11}$$

where $u_{n,\mathbf{k}}(\mathbf{r})$ are periodic functions with the periodicity of the crystal. The Bloch orbitals are characterized by two quantum numbers: the wave vector inside the first Brillouin zone (BZ), $\mathbf{k}$, and the band index n. An alternative representation is in terms of localized real-space orbitals or Wannier functions (WFs), $|\mathbf{R}n\rangle$, which are characterized by real-space translation vectors $\mathbf{R}$ and n. The WFs can be constructed from the extended Bloch orbitals according to

$$|\mathbf{R}n\rangle=\frac{V_{cell}}{(2\pi)^3}\int_{\mathrm{BZ}}|\psi_{n,\mathbf{k}}\rangle e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}}d\mathbf{k}, \tag{12}$$

where $\varphi_n(\mathbf{k})$ is an arbitrary periodic phase factor in the reciprocal lattice. Such phase factors, which do not affect the physical properties extracted from Bloch's orbitals, lead to the nonuniqueness of the WFs, which has dramatically limited their applications.

Marzari and Vanderbilt[5] have used the above nonuniqueness property to construct MLWFs. This has been done by writing

$$|\mathbf{R}n\rangle=\frac{V_{cell}}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_{m=1}^{N}U_{mn}^{(\mathbf{k})}|\psi_{n,\mathbf{k}}\rangle e^{-i\mathbf{k}\cdot\mathbf{R}}d\mathbf{k}, \tag{13}$$

where $U_{mn}^{(\mathbf{k})}$ are unitary matrices of dimension N (number of occupied states). Then, the optimal set of $U_{mn}^{(\mathbf{k})}$ is obtained by minimizing a spread function given as

$$\Omega=\sum_n[\langle 0n|r^2|0n\rangle-\langle 0n|\mathbf{r}|0n\rangle^2]. \tag{14}$$

The expectation value $\mathbf{r}_n=\langle 0n|\mathbf{r}|0n\rangle$ defines the centers of the MLWFs. An elegant iterative scheme for minimizing Ω has been introduced by Marzari and Vanderbilt.[5]

TABLE I. Structure, lattice parameter (a), spread of the MLWF's (Ω_{min}) and β (see text), and bond ionicity (w_i) for the considered $A^N B^{8-N}$ compounds. Also shown are the ionicities of Phillips (Ref. 2) (f_i), Garcia and Cohen (Ref. 4) (g), and Christensen *et al.* (Ref. 3) (f_i^*). D here denotes the diamond structure.

Compound	Structure	a (Å)	Ω_{min}	β	w_i	f_i	g	f_i^*
Si	D	5.431	8.232	0.500	0.000	0.000	0.000	0.000
Ge	D	5.658	10.116	0.500	0.000	0.000	0.000	0.000
Sn	D	6.490	13.801	0.500	0.000	0.000	0.000	0.000
SiC	ZB	4.360	4.651	0.654	0.308	0.177	0.475	0.394
BP	ZB	4.540	5.479	0.516	0.077	0.006	0.085	0.001
BAs	ZB	4.777	6.211	0.526	0.107	0.002	0.116	0.002
GaSb	ZB	6.100	11.527	0.577	0.246	0.261	0.169	0.108
InSb	ZB	6.480	12.251	0.610	0.321	0.321	0.294	0.303
AlSb	ZB	6.140	10.135	0.614	0.330	0.250	0.230	0.163
GaAs	ZB	5.650	8.871	0.618	0.339	0.310	0.316	0.310
InAs	ZB	6.060	10.138	0.651	0.407	0.357	0.450	0.553
AlAs	ZB	5.660	8.090	0.655	0.415	0.274	0.375	0.367
GaP	ZB	5.450	7.637	0.620	0.342	0.327	0.371	0.361
InP	ZB	5.870	8.492	0.654	0.413	0.421	0.506	0.534
AlP	ZB	5.460	7.146	0.657	0.419	0.307	0.425	0.421
BN	ZB	3.620	2.820	0.658	0.421	0.256	0.484	0.383
GaN	ZB	4.531	4.109	0.729	0.557	0.500	0.780	
InN	ZB	4.980	5.032	0.753	0.599	0.578	0.853	
AlN	ZB	4.370	3.711	0.760	0.612	0.449	0.794	
ZnS	ZB	5.410	5.784	0.714	0.654	0.623	0.673	0.764
ZnSe	ZB	5.658	6.192	0.723	0.668	0.630	0.597	0.740
CdS	ZB	5.818	6.287	0.740	0.693	0.685		0.794
CdSe	ZB	6.052	6.706	0.743	0.698	0.699		0.841
MgS	ZB	5.629	5.543	0.759	0.720			0.828
MgS	RS	5.203	6.022	0.884	0.916	0.786	0.788	
MgSe	RS	5.451	6.456	0.890	0.920	0.790	0.732	
CaS	RS	5.690	6.170	0.895	0.924	0.902	0.906	
CaSe	RS	5.910	6.418	0.899	0.928	0.900	0.872	
NaBr	RS	5.925	4.247	0.904	0.965	0.934	0.935	
NaCl	RS	5.640	4.150	0.907	0.966	0.935	0.958	
KBr	RS	6.541	4.303	0.914	0.969	0.952	0.976	
KCl	RS	6.290	4.241	0.917	0.970	0.953	0.986	

B. Computational details

In this work, we followed the procedure of Ref. 5 to construct the MLWFs of 32 $A^N B^{8-N}$ compounds, with $N=1$, 2, 3, and 4, in their ground-state phases (diamond, ZB, or RS). The considered compounds are listed in Table I, together with their adopted (ground-state) crystal structures and lattice parameters. The list includes 3 of group-IV elemental solids in the diamond structure, the cubic phase of SiC, 15 III–V compounds in the ZB structure, 4 IIB–VI compounds in the ZB structure, 4 IIA–VI compounds in the RS structure, and 4 I–VII compounds in the RS structure.

The used norm-conserving scalar-relativistic pseudopotentials are generated by using the Troullier-Martins optimization method,[8] employing the FHI98PP code.[9] Then, the generated pseudopotentials are transformed to the separable Kleinman-Bylander form.[10] The ground-state configuration is used for all the involved atoms. The cation semicore d electrons of the IIB–VI and some III–V compounds are treated as part of the frozen core, and nonlinear exchange-correlation core corrections[11] are included for all the considered systems. The used pseudopotentials are carefully tested, and are found to have good transferability and to be free of ghost states.[12]

The calculations are performed by employing an *ab initio* pseudopotential plane-wave technique using the SPHINX code.[13] The local-density approximation has been used for the exchange and correlation potential, employing the Ceperley-Alder[14] exchange-correlation data as parametrized by Perdew and Zunger.[15] A plane-wave energy cutoff of 60 Ry has been used for the compounds involving first row elements (B, N, and C), and that of 25 Ry for all other com-

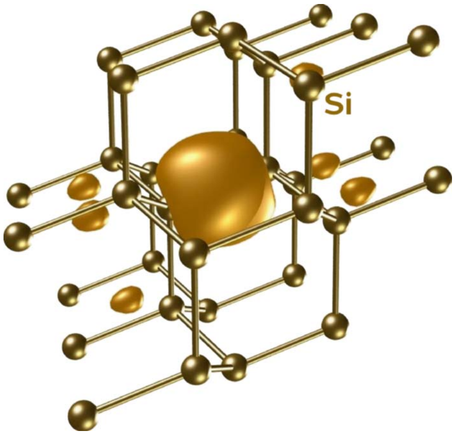

FIG. 1. (Color online) An isosurface of a maximally localized Wannier function of Si in the diamond structure.

pounds. The ground-state charge density and potential are obtained first by using a regular $4\times4\times4$ Monkhorst-Pack (MP) mesh,[16] while the required Bloch's wave functions [Eq. (11)] to construct the MLWFs are then calculated on a regular $8\times8\times8$ MP mesh (see Ref. 5 for details). It has been shown that the adopted meshes provide well converged $\mathbf{r}_n$.[5]

III. RESULTS AND DISCUSSION

A. MLWFs of $A^N B^{8-N}$ compounds

The MLWFs of the considered $A^N B^{8-N}$ compounds were constructed as described in Sec. II. In Table I, we also list the spread of the MLWFs, Ω_{min}, and the parameter $\beta = r_n/d$, where r_n is the distance between $\mathbf{r}_n$ and the position of the cation of the associated bond and d is the bond length. As representatives, we show in Figs. 1–3 an isosurface of a MLWF of Si, GaN, and NaCl, respectively.

Let us first start with the elemental group-IV solids (Si, Ge, and α-Sn) in the diamond structure. For such systems, there are four bonding MLWFs per primitive unit cell since there are eight valence electrons filling completely four valence bands. This means that there is a symmetric MLWF associated with each bond, as shown in Fig. 1. The center of the MLWF coincides with that of the corresponding bond (i.e., $\beta=0.5$). For Si, the obtained value of Ω_{min} (8.232 Å^2) is in very good agreement with the previously reported value[5] (8.192 Å^2). The spread of MLWFs in these systems increases by increasing the atomic number of the involved atoms (see Table I) because of the increase of the bond length.

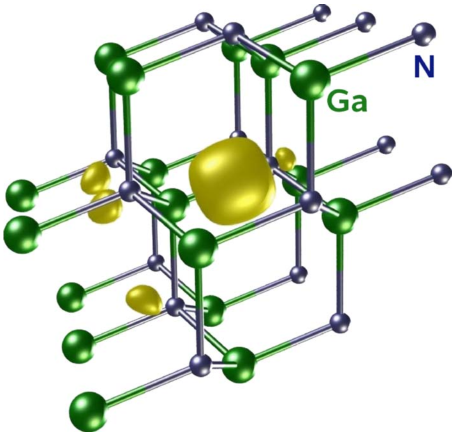

FIG. 2. (Color online) An isosurface of a maximally localized Wannier function of GaN in the zinc-blende structure.

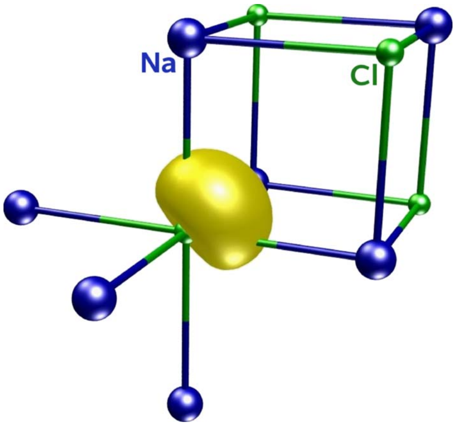

FIG. 3. (Color online) An isosurface of a maximally localized Wannier function of NaCl in the rocksalt structure.

For the $A^N B^{8-N}$ compounds crystallizing in the ZB structure, the mean features of the MLWFs are quite similar to those of the elemental group-IV solids. However, in the ZB form, the two atoms at the ends of each bond have different electronegativities, which leads to a partial charge transfer from the cation to the anion regions. This, in turn, shifts the center of the MLWFs away from the center of the bond toward the anion, as illustrated in Fig. 2, in the case of GaN. Therefore, the values of β of these systems are larger than 0.5 (see Table I). Both Ω_{min} and β of GaAs (8.871 Å^2 and 0.618, respectively) are in good agreement with the reported results in Ref. 5 (8.599 Å^2 and 0.617). As expected, there is a strong correlation between $(\beta-0.5)$ and the bond ionicity, as illustrated in Fig. 4. Based on this fact, an ionicity scale will be introduced in the next section.

The Si-C bond is also partially ionic because of the large difference in size between the C and Si atoms. This makes the MLWFs in cubic SiC similar to those in the III–V com-

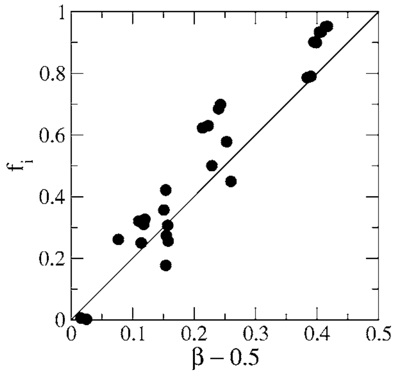

FIG. 4. The Phillips bond ionicity vs $(\beta-0.5)$ for the considered $A^N B^{8-N}$ compounds. Those of the elemental group-IV solids are not shown.

pounds, with the center of the MLWFs closer to the C atom. The obtained value of β of SiC is very close to that of GaAs.

For the more ionic compounds crystallizing in the sixfold coordinate RS phase, namely, the I–VII and IIA–VI compounds, the situation is quite different: the one-to-one correspondence between the bonding MLWFs and bonds breaks down. In the RS structure, the four bonding MLWFs, per primitive unit cell, correspond to six bonds. Because of the large bond ionicity of these compounds, one expects the MLWFs to be centered around the anions. Our calculations have shown that the center of the MLWFs lies along four of the eight $\langle 111 \rangle$ directions of the cubic crystals, very close to the anions, as shown in Fig. 3 in the case of NaCl. It is interesting to note that, with respect to the anions, the MLWFs in the RS phase have the same orientation as those in the ZB phase (along the bonds of the latter structure). Moreover, it is meaningful to consider that each MLWF is a superposition of three somehow "optimized" σ-bond orbitals of the three neighboring bonds (see Fig. 3). Thus, each bond yields two-thirds of a MLWF, which is the same ratio between the number of MLWFs and the bonds in the RS structure. To find the value of β of the relevant compounds, reported in Table I, we consider one of the above "optimized" σ-bond orbitals and take its center to be the component of the center of any of the two associated MLWFs along the corresponding bond.

B. Bond ionicity

As noted in the previous section, there is a strong correlation between the deviation of $\mathbf{r}_n$ from the bond center [expressed by $(\beta-0.5)$] and the bond ionicity (see Fig. 4 and Table I). This, in turn, shows that $(\beta-0.5)$ can be used as a measure for the bond ionicity, as we will show below.

To devise a bond ionicity scale based on $(\beta-0.5)$, it is important to realize that we are dealing with a bond property, in the solid phase of the material. Therefore, the concept of resonant bonds of Pauling[1] (see Sec. I) also applies to the present case. This implies that such an ionicity scale should also depend on the valency N and coordination number M. After several attempts, we have found that the best ionicity scale takes the form

$$w_i = (2\beta - 1.0)^{N/M}. \tag{15}$$

A remarkable feature of this ionicity scale is that it involves only physical constants.

A comparison between the present ionicity scale and previous empirical and *ab initio* ones is shown in Fig. 5. The important features to note from this figure are as follows. (i) For the quite large scattering of the previous values of bond ionicity, the largest deviation of about 0.3 is obtained in the case of group-III nitrides, between f_i and g. It has been noted by Garcia and Cohen[4] that g is appreciably larger than f_i for the compounds involving first row elements, namely, SiC and B and N based compounds. Table I shows that w_i is also larger than f_i for these compounds and comparable to g, except for the group-III nitrides where the values of w_i are closer to f_i than to g. This indicates that the bond ionicity of the group-III nitrides provided by g is exaggerated. The discrepancy between g and w_i for these systems is intrinsic, since our calculated values of g are found to compare very well with those of Ref. 4. (ii) The w_i provides almost a best fit to the previously available values. This reflects the accuracy and reliability of this bond ionicity scale.

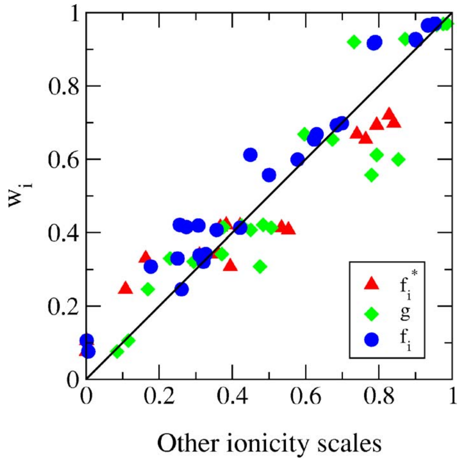

FIG. 5. (Color online) The present bond ionicity w_i vs those of Phillips (Ref. 2), f_i, Garcia and Cohen (Ref. 4), g, and Christensen *et al.* (Ref. 3), f_i^*.

An important achievement of the Phillips ionicity scale is the existence of a critical ionicity value that separates the ZB from the RS structures. The existence of such a critical ionicity value has been confirmed by Chelikowsky and Burdett[6] and Christensen *et al.*[3] by investigating the ionicity dependence of the critical pressure (p_t) of the ZB to RS structural phase transformation under high pressure. To determine such a critical ionicity value employing w_i ($w_{i,c}$), it is important to point out two things: (i) The phase diagrams of the $A^N B^{8-N}$ compounds are much more complicated than previously thought. Stable phases such as the cinnabar (a hexagonal phase with 6-atom unit cell) and SC16 (a simple cubic phase with 16-atom unit cell) have been observed below RS (Refs. 17 and 18): only few $A^N B^{8-N}$ compounds transform directly from the ground-state ZB (or wurtzite) phase to the RS structure. (ii) $w_{i,c}$ should lie within the bond ionicity gap between the IIB–VI and IIA–VI compounds (roughly between 0.7 and 0.9, see Table I). Thus, to determine $w_{i,c}$, we plot in Fig. 6 the experimental values of p_t (Refs. 17 and 18) as a function of

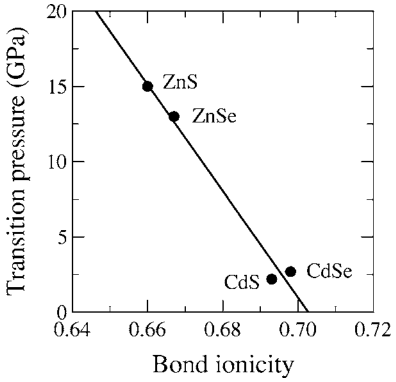

FIG. 6. The transition pressure (p_t) of the ZB to RS phase transformation of some IIB-VI compounds vs bond ionicity w_i.

TABLE II. Volume variation of the bond ionicity.

Compound	$dw_i/d\ln V$	$dg/d\ln V$ (Ref. 4)	$df_i^*/d\ln V$ (Ref. 3)
SiC	−0.129	−0.008	−0.114
GaAs	0.036	0.134	0.342
AlP	0.012	0.149	0.235
AlN	0.055	0.155	0.200
BN	−0.008	0.096	

w_i of the considered IIB–VI compounds. This figure shows that $w_{i,c}$ is about 0.7. It should be stressed that the main difference between the present value and the previous ones,[2,3,6] of about 0.8, arises mainly from the difference in the calculated values of bond ionicity of the IIB–VI compounds in these approaches (see Table I). As a check for the obtained value of $w_{i,c}$, we have calculated w_i of the ZB phase of MgS, which has RS as the ground-state structure. The obtained value of 0.72 strongly supports our value of $w_{i,c}$.

The volume variation of the bond ionicity of some A^NB^{8-N} compounds has been investigated. In this work, we have considered only the systems studied in Ref. 4. The results are listed in Table II, together with the other available theoretical values.[3,4] The important features to note from this table are as follows. (i) The $dw_i/d\ln V$ of SiC compares well with the other self-consistent approaches, especially with $df_i^*/d\ln V$.[3] (ii) For the other studied systems, the volume variation of w_i is much weaker than previously reported:[3,4] the $dg/d\ln V$ and $df_i^*/d\ln V$ are larger than $dw_i/d\ln V$ by about 0.1 and 0.2, respectively. (iii) For BN, the $dw_i/d\ln V$ and $dg/d\ln V$ have different signs. However, this can be understood because of its small value of $dg/d\ln V$ and the above difference between $dw_i/d\ln V$ and $dg/d\ln V$, in the case of the considered III–V compounds. The significant discrepancies between the calculated volume dependence of the bond ionicity arise from differences in volume dependence of the physical quantities from which the bond ionicity is extracted in the different approaches.

IV. SUMMARY

The maximally localized Wannier functions (MLWFs) have been constructed for 32 A^NB^{8-N} compounds, ranging from elemental group-IV solids to I–VII compounds, which crystallize in the diamond, zinc-blende, or rocksalt (RS) structures. In the case of the RS phase, where we have four MLWFs and six bonds per primitive unit cell, the orientation of the MLWFs is found to be the same as those of the other studied systems. The MLWFs of the RS structure can be thought of as superpositions of some kind of "optimized" σ-bond orbitals of the surrounding three bonds. Based on the deviation of the center of the MLWFs from the bond center, a different bond ionicity scale has been introduced, which involves only physical constants. In the case of the RS structure, the centers of the optimized σ-bond orbitals have been considered instead of those of the MLWFs. The so-obtained ionicity of the considered compounds provides almost a best fit to previous values of the empirical and self-consistent bond ionicity. The present ionicity scale has a further advantage of being extracted directly from a bond property. Within our ionicity scale, the critical value of the ionicity that separates the fourfold and sixfold coordinate structures is found to be of about 0.7, which is smaller than previous values of about 0.8. Finally, the volume variation of the bond ionicity is found to be much smaller than previously thought, except for SiC.

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