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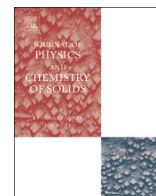


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The bond ionicity in $A^N B^{8-N}$ compounds from maximally localized Wannier functions

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ABSTRACT

The bond ionicity in seventy two $A^N B^{8-N}$ compounds is investigated according to the recently introduced first-principles ionicity scale, based on the centers of the maximally localized Wannier functions, which has several interesting features. The obtained bond ionicities (q_i) are found to exhibit the expected trends, according to electronegativity arguments. In particular, the bond ionicity in the alkaline-earth oxides increases by going from MgO to BaO. A strong crystal structure dependence of q_i is observed. A critical value of q_i (of 0.91) that separates between the tetrahedrally and octahedrally coordinated systems is inferred directly from the calculated values of q_i . The volume dependence of q_i is investigated for all the considered compounds and found to reduce by volume decrease for most of the studied systems. The adopted ionicity scale is established as a very strong competitor to the most widely accepted Phillips and Pauling ionicity measures.

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1. Introduction

Electronegativity (χ) and bond ionicity are very important concepts in chemistry, physics and other branches of science. As defined by Pauling [1], χ is the ability of the atom to attract an electron to itself, when interacts with other atoms to form molecules or solids. Therefore, χ is not a property of the atom in isolation, and hence it lacks a precise definition. Several approaches are introduced to measure χ [2]. The most widely cited χ scale is that of Allred and Rochow [3] based on the electrostatic force between the effective nucleus charge of the atom and an electron at its covalent radius. As for the bond ionicity, one can also say that it lacks a precise definition (or an absolute scale) [4]. In fact, a meaningful description of the valence charge distribution in heteropolar compounds by a single parameter (i.e. bond ionicity) poses a big challenge, and this has been a subject of interest and debate since the pioneer work of Pauling [5]. However, over the past 80 years, various bond ionicity scales have been introduced, based on thermochemistry (the original Pauling ionicity scale [1,5]), spectroscopy (the famous Phillips ionicity scale [6]), ensemble of effective charges (see Ref. [4]), charge density [7], electronic band structure parameters [8] and centers of the maximally localized Wannier functions (MLWFs) [9].

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The elegant approach introduced by Marzari and Vanderbilt [10] to construct MLWFs is a very important development in condensed matter theory, as already proved by their many interesting applications [11]. Based on the centers of the MLWFs, Abu-Farsakh and Qteish [9] have recently introduced an ionicity scale that has several advantages. First, it is based on a bond property: the MLWFs 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) [10]. Thus, it can be considered as a direct ionicity measure, unlike the other ionicity scales which are mainly based on bulk or molecule properties. Second, it is a fully self-consistent approach – the ionicity is expressed solely in terms of physical parameters. Third, the obtained ionicities in 32 $A^N B^{8-N}$ systems considered in Ref. [9] provide a best fit to previous values of the empirical [1,6] and self-consistent ionicity scales [7,8].

In this work the Abu-Farsakh and Qteish approach [9] is used to determine the ionicity (q_i) in an extensive list of $A^N B^{8-N}$ compounds. These compounds constitute a very important family of semiconductors that has a wide range of technological applications. For this reason, these compounds are widely studied both experimentally and theoretically. In spite of some serious attempts [7–9], a self-consistent study of the bonding in an extensive list of these semiconductors is still lacking. In addition to this important aim, this study enhances the usefulness of the above ionicity scale and allows for a better comparison with other most frequently used ionicity scales [namely, those of Pauling [1] (p_i) and Phillips [6] (f_i)]. The volume dependence of q_i is also studied, for all the

considered compounds. Moreover, the effects of the relaxation of the semicore electrons and the crystal structure on q_i are investigated.

The rest of the article is organized as follows. The methodology is described in Section 2, which contains a brief description of the MLWFs, a brief introduction to the ionicity scales considered in this work, and the computational details. The obtained results are presented and discussed in Section 3. Finally, a summary of the main results and conclusions is provided in Section 4

2. Methodology

2.1. Maximally localized Wannier functions

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

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (1)$$

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 wavevector 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

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

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

Marzari and Vanderbilt [10] have used the above non-uniqueness property to construct MLWFs. This has been done by writing

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

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

$$\Omega = \sum_n [\langle 0n | r^2 | 0n \rangle - \langle 0n | r | 0n \rangle^2]. \quad (4)$$

An elegant iterative scheme for minimizing Ω has been introduced in Marzari and Vanderbilt [10]. The centers of these MLWFs are defined as

$$\mathbf{r}_n = \langle 0n | \mathbf{r} | 0n \rangle. \quad (5)$$

The \mathbf{r}_n are the key quantities in the development of Abu-Farsakh and Qteish [9] ionicity scale, introduced in the following subsection.

2.2. Ionicity scales

Because of space limitations, only the two most famous empirical ionicity scales [1,6] and the two most promising first-principles measures [8,7] are considered, in addition to the adopted one [9].

We start with the empirical ionicity scale of Pauling [1] based on thermodynamical arguments. Pauling has developed an electronegativity scale for the elements according to the relation:

$$D(\text{AB}) = \frac{1}{2} \left\{ D(\text{AA}) + D(\text{BB}) + c(\chi_A - \chi_B) \right\}, \quad (6)$$

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

$$p_i = 1 - \exp \left(-\frac{1}{4}(\chi_B - \chi_A)^2 \right). \quad (7)$$

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

$$p_i = 1 - \frac{N}{M} \exp \left(-\frac{1}{4}(\chi_B - \chi_A)^2 \right). \quad (8)$$

Here, M denotes the coordination number, and the N/M prefactor takes into account the sharing of the cation N valence electrons by the M bonds (known as resonant bonds). Instead of Eq. (8), the formula [12]

$$p_i = 1 - \frac{N}{M} \exp \left(-(\chi_B - \chi_A)^{3/2} / \chi_{GM}^{3/2} \right) \quad (9)$$

is used, which provides a best matching with the experimental molecular electric dipole charge [13,14]. Here, χ_{GM} is the geometrical mean of χ_A and χ_B . As for χ , the Allred–Rochow scale [3] is adopted in this work. A detailed account for the performance of the various χ scales and the electronegativity–ionicity relations will be reported elsewhere [15].

The Phillips [6] ionicity scale is based on the dielectric theory of Phillips and Van Vechten. This ionicity scale is defined as

$$f_i = \frac{C^2}{E_g^2} = \frac{C^2}{E_h^2 + C^2}, \quad (10)$$

where E_h is the homopolar gap due to the symmetric part of the potential $\frac{1}{2}(V_A + V_B)$, and 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:

$$E_h = E_h(\text{Si}) \left(\frac{a(\text{Si})}{a} \right)^{2.5}, \quad (11)$$

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

We now turn to the first-principles ionicity scales, and start with that of Christensen et al. [8]. They have carried out a tight-binding parameterization of the band structures of many $A^N B^{8-N}$ compounds in the ZB phase, calculated by employing a linear-muffin-tin orbital (LMTO) method. The Phillips ionicity scale parameters are given as $C = \Delta E_{sp^3}$ (E_{sp^3} is the sp^3 hybrid energy) and $E_h = -2h$ (h is the hopping integral), with both E_{sp^3} and h are expressed in terms of LMTO band structure parameters. The so-obtained ionicity (denoted as f_i^*) in the considered compounds are found to be, generally speaking, higher than the corresponding values of f_i . Interestingly, the Christensen et al. [8] investigations have confirmed the existence of a critical ionicity value that separates between the fourfold and sixfold coordinated compounds, in accord with the value suggested by Phillips, see above. This critical ionicity value has also been confirmed by Chelikowsky and

Burdett [16].

The second first-principles ionicity scale is that of Garcia and Cohen [7] 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 ionicity scale is given as

$$g_i = \sqrt{\frac{S_A}{S_S}}, \quad (12)$$

with

$$S_A = \frac{1}{V_{\text{cell}}} \int n_A^2(\mathbf{r}) d\mathbf{r}, \quad (13)$$

and

$$S_S = \frac{1}{V_{\text{cell}}} \int n_S^2(\mathbf{r}) d\mathbf{r}, \quad (14)$$

The obtained values of g_i are found to correspond quite well with f_i , except for compounds involving first row elements for which g_i 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 ionicity scales are based on properties of the whole crystal – not directly on a bond related property.

An attempt to extract the ionicity from a bond property is made by Coulson et al. [17]. In this approach the σ -bond orbital is written as

$$\psi = \phi_A + \lambda \phi_B, \quad (15)$$

where ϕ_A and ϕ_B are respectively the sp^3 hybrids of atoms A and B, and λ is determined by total energy minimization. Under the assumption that atomic wavefunctions used in the Eq. (15) are orthogonal, the ionicity is given as

$$c_i = \frac{(\lambda^2 - 1)}{(\lambda^2 + 1)}. \quad (16)$$

As noted by Phillips [6], 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 wavefunctions of the $A^N B^{8-N}$ compounds.

Recently, Abu-Farsakh and Qteish [9] have introduced an ionicity scale based on the centers of the MLWFs (\mathbf{r}_n , see Eq. (5)). For elemental group-IV solids in the diamond structure, there is a symmetric MLWF associated with each bond, centered at the middle of the bond. By going to the $A^N B^{8-N}$ compounds crystallizing in the ZB phase, the MLWFs become asymmetric with their \mathbf{r}_n shifted towards the anions (as illustrated in Fig. 1) and located at a fixed distance from bond center. The MLWFs of the $A^N B^{8-N}$ compounds have roughly the character of the σ -bond orbitals [10]. To measure the shift in \mathbf{r}_n of these systems, away from the bond center, a parameter β is defined as $\beta = r_n/d$, where r_n is the magnitude of the displacement between \mathbf{r}_n and the cation position, and d is the bond length. In the case of the RS phase, there are four MLWFs and six bonds per primitive unit cell. The orientation of the MLWFs is found to be similar to those of the ZB phase (i.e., along four of the [111] directions), and their centers are located very close to the anions, as shown in Fig. 2. Thus, the MLWFs in this case are thought of as superpositions of some kind of “optimized” σ -bond orbitals of the surrounding three bonds. The parameter β is calculated from centers of the “optimized” σ -bond orbitals – not directly from those of the MLWFs. For a MLWF oriented along the [111] direction, for example, the three associated “optimized” σ -bond orbitals correspond to the surrounding three A–B bonds along the [100], [010] and [001] directions. Therefore, the r_n used to calculate β (see above) is taken to be the component of \mathbf{r}_n along

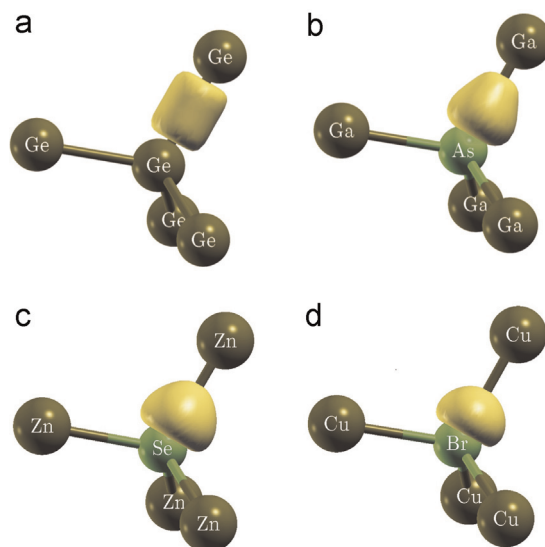


Fig. 1. An isosurface of a MLWF of Ge (a), GaAs (b), ZnSe (c) and CuBr (d). The centers of these MLWFs (calculated according to Eq. (5)) are expected to be very close to the center of gravity of the shown isosurfaces.

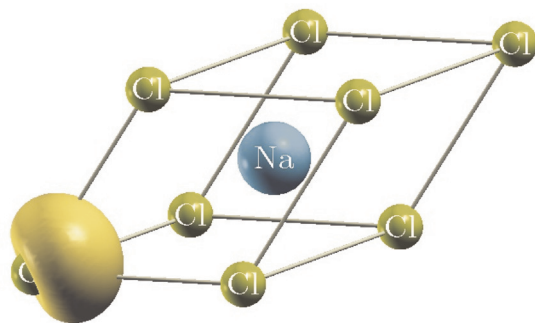


Fig. 2. As in Fig. 1, but of a MLWF of NaCl, in the rocksalt structure.

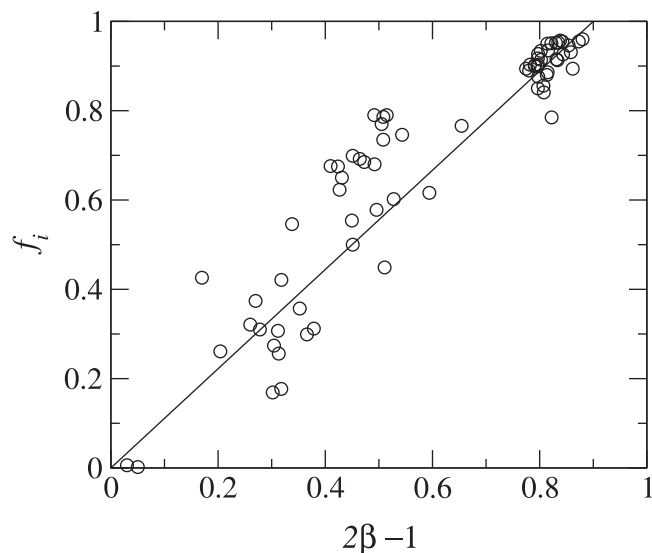


Fig. 3. The correlation between $(2\beta - 1)$ and the Phillips ionicity scale (f_i).

one of these three bonds. Before introducing this ionicity scale, it was first demonstrated that there is a strong correlation between $(\beta - 0.5)$ and f_i . Fig. 3 shows the correlation between $(2\beta - 1)$ and f_i for the extensive set of $A^N B^{8-N}$ compounds considered in this

Table 1

Structure, lattice parameter (a), N/M factor, β (see text), ionicity (q_i) and volume dependence of q_i ($dq_i^*/d \ln V$) for the considered group-IV solids and III–V compounds. Also shown are Phillips [6] (f_i) and Pauling [1] (p_i) ionicities. The reported values of p_i are obtained using Eq. (9) and Allred–Rochow [3] χ scale.

Compound	Structure	$a(\text{\AA})$	N/M	β	q_i	f_i	p_i	$dq_i^*/d \ln V$
SiC	ZB	4.360	4/ 4	0.659	0.318	0.177	0.197	−0.125
SiGe	ZB	5.537	4/ 4	0.510	0.020	0.002	0.056	−0.104
BN	ZB	3.620	3/ 4	0.657	0.419	0.221 ^a	0.432	0.055
BP	ZB	4.540	3/ 4	0.515	0.072	0.032 ^a	0.253	0.389
BAs	ZB	4.777	3/ 4	0.525	0.106	0.044 ^a	0.270	0.292
AlN	ZB	4.370	3/ 4	0.755	0.604	0.449	0.610	−0.007
AlP	ZB	5.460	3/ 4	0.656	0.417	0.307	0.384	0.015
AlAs	ZB	5.660	3/ 4	0.652	0.410	0.274	0.421	0.026
AlSb	ZB	6.140	3/ 4	0.585	0.265	0.250 ^a	0.321	−0.328
GaN	ZB	4.531	3/ 4	0.726	0.551	0.500	0.489	0.016
GaP	ZB	5.450	3/ 4	0.635	0.375	0.327 ^a	0.282	0.144
GaAs	ZB	5.650	3/ 4	0.639	0.383	0.310	0.310	0.114
GaSb	ZB	6.100	3/ 4	0.602	0.304	0.261	0.250	0.255
InN	ZB	4.980	3/ 4	0.748	0.591	0.578	0.603	−0.012
InP	ZB	5.870	3/ 4	0.659	0.423	0.421	0.377	0.114
InAs	ZB	6.060	3/ 4	0.676	0.457	0.357	0.413	0.177
InSb	ZB	6.480	3/ 4	0.630	0.364	0.321	0.314	0.272

work. The linear correlation coefficient is found to be of 0.93, which confirms the very strong correlation between these two quantities. An ionicity scale that based on $(2\beta - 1)$ is then devised [9] as

Table 3

As in Tables 1 and 2, but for the considered I–VII compounds.

Compound	Structure	$a(\text{\AA})$	N/M	β	q_i	f_i	p_i	$dq_i^*/d \ln V$
CuF	ZB	4.255	1/ 4	0.827	0.899	0.766	0.890	0.030
CuCl	ZB	5.424	1/ 4	0.772	0.859	0.746	0.822	0.090
CuBr	ZB	5.691	1/ 4	0.754	0.844	0.735	0.816	0.147
valence					0.754	0.844		0.147
CuI	ZB	6.055	1/ 4	0.732	0.826	0.692	0.777	0.136
AgF	RS	4.936	1/ 6	0.931	0.976	0.894	0.948	0.009
AgCl	RS	5.546	1/ 6	0.903	0.965	0.856	0.908	0.014
AgBr	RS	5.772	1/ 6	0.898	0.963	0.850	0.904	0.016
AgI	ZB	6.473	1/ 4	0.753	0.843	0.770	0.814	−0.211
LiF	RS	4.028	1/ 6	0.916	0.970	0.915	0.977	0.011
LiCl	RS	5.140	1/ 6	0.898	0.963	0.903	0.949	0.014
LiBr	RS	5.502	1/ 6	0.898	0.963	0.899	0.946	0.014
LiI	RS	6.000	1/ 6	0.890	0.960	0.890	0.924	0.016
NaF	RS	4.634	1/ 6	0.927	0.974	0.946	0.974	0.009
NaCl	RS	5.650	1/ 6	0.908	0.967	0.935	0.945	0.012
NaBr	RS	6.004	1/ 6	0.901	0.964	0.934	0.942	0.014
NaI	RS	6.474	1/ 6	0.899	0.963	0.927	0.919	0.014
KF	RS	5.348	1/ 6	0.936	0.978	0.955	0.980	0.008
KCl	RS	6.294	1/ 6	0.917	0.970	0.953	0.955	0.011
KBr	RS	6.596	1/ 6	0.915	0.970	0.952	0.952	0.012
KI	RS	7.066	1/ 6	0.907	0.966	0.950	0.931	0.013
RbF	RS	5.630	1/ 6	0.940	0.979	0.960	0.981	0.007
RbCl	RS	6.582	1/ 6	0.921	0.972	0.955	0.957	0.010
RbBr	RS	6.890	1/ 6	0.919	0.971	0.957	0.954	0.011
RbI	RS	7.342	1/ 6	0.911	0.968	0.951	0.933	0.012

$$q_i = (2\beta - 1.0)^{N/M}. \quad (17)$$

Table 2

As in Table 1, but for the considered II–VI compounds. The results obtained by including the semicore electrons as part of the frozen core are referred to by “valence”.

Compound	Structure	$a(\text{\AA})$	N/M	β	q_i	f_i	p_i	$dq_i^*/d \ln V$
ZnO	ZB	4.557	2/ 4	0.797	0.771	0.616	0.743	0.042
ZnS	ZB	5.410	2/ 4	0.713	0.653	0.623	0.607	0.086
ZnSe	ZB	5.658	2/ 4	0.709	0.646	0.630 ^a	0.613	0.088
valence					0.705	0.640		0.070
ZnTe	ZB	6.089	2/ 4	0.669	0.581	0.609 ^a	0.540	0.116
CdO	RS	4.696	2/ 6	0.911	0.937	0.785	0.859	0.020
CdS	ZB	5.818	2/ 6	0.736	0.779	0.685	0.656	0.105
CdSe	ZB	6.052	2/ 6	0.726	0.767	0.699	0.662	0.114
CdTe	ZB	6.529	2/ 6	0.712	0.751	0.717 ^a	0.583	0.239
HgS	ZB	5.852	2/ 4	0.757	0.717	0.790 ^a	0.661	0.229
HgSe	ZB	6.084	2/ 4	0.746	0.701	0.680 ^a	0.668	0.257
HgTe	ZB	6.394	2/ 4	0.716	0.656	0.650 ^a	0.588	0.284
BeO	ZB	3.808	2/ 4	0.764	0.726	0.602	0.786	0.070
BeS	ZB	4.862	2/ 4	0.689	0.615	0.312	0.653	0.131
BeSe	ZB	5.139	2/ 4	0.683	0.605	0.299	0.660	0.136
BeTe	ZB	5.626	2/ 4	0.651	0.549	0.169	0.581	0.172
MgO	RS	4.212	2/ 6	0.904	0.931	0.841	0.894	0.022
MgS	RS	5.203	2/ 6	0.885	0.916		0.814	0.030
	ZB	5.620	2/ 4	0.754	0.713	0.786	0.721	0.037
MgSe	RS	5.451	2/ 6	0.885	0.917		0.818	0.032
	ZB	5.910	2/ 4	0.746	0.701	0.790	0.727	0.035
MgTe	RS	5.886	2/ 6	0.877	0.910		0.765	0.032
	ZB	6.420	2/ 4	0.725	0.671	0.554	0.647	0.059
CaO	RS	4.797	2/ 6	0.917	0.941	0.913	0.923	0.019
CaS	RS	5.691	2/ 6	0.896	0.925	0.902	0.854	0.026
CaSe	RS	5.910	2/ 6	0.895	0.925	0.900	0.857	0.027
CaTe	RS	6.350	2/ 6	0.887	0.918	0.894	0.808	0.030
SrO	RS	5.130	2/ 6	0.922	0.945	0.926	0.930	0.018
SrS	RS	6.024	2/ 6	0.901	0.929	0.914	0.865	0.025
SrSe	RS	6.236	2/ 6	0.898	0.927	0.917	0.868	0.032
valence					0.901	0.929		0.026
SrTe	RS	6.659	2/ 6	0.891	0.921	0.903	0.820	0.033
BaO	RS	5.524	2/ 6	0.929	0.950	0.878 ^b	0.933	0.017
BaS	RS	6.389	2/ 6	0.907	0.934	0.886 ^b	0.869	0.022
BaSe	RS	6.595	2/ 6	0.907	0.933	0.880 ^b	0.872	0.025
BaTe	RS	7.005	2/ 6	0.899	0.927	0.876 ^b	0.825	0.026

^a Taken from Ref. [30].

^b Taken from Ref. [31].

This ionicity scale takes into account thus the resonant bond concept of Pauling [1], see above. Since the MLWFs of the $A^N B^{8-N}$ can be thought of as σ -bond orbitals, this approach is similar in spirit to the Coulson et al. [17] method. But unlike the latter approach, the MLWFs provide an exact representation of the wavefunctions of the above compounds.

2.3. Computational details

In this work, the MLWFs of an extensive list of $A^N B^{8-N}$ compounds, with $N=1, 2, 3$ and 4 are constructed, following the procedure of Ref. [10]. The considered compounds are listed in Tables 1–3, together with their adopted crystal structures (ZB or RS) and the used experimental lattice parameters. It should be noted that some of these compounds (such as, GaN and CdS) have the wurtzite phase as the ground state structure, and their ZB phase is metastable. The ZB and wurtzite structures however have almost the same local tetrahedral structures, and, as expected, very close values of β are obtained for CdS, CdSe and CdTe in these two crystal structures [18]. Such small differences in β yield discrepancies in the corresponding values of q_i of less than 0.01. Therefore, the simpler metastable ZB structure is considered in this work to calculate the ionicity of the compounds that crystallize in the wurtzite phase. The bonding in the group-IV elemental solids (diamond, Si, Ge and α -Sn) is purely covalent ($q_i=0$), and hence are not listed in the above tables.

The first-principles calculations are performed by employing an ab-initio pseudopotential plane-wave approach as implemented in the ABINIT code [19,20]. The MLWFs are constructed by using the Wannier90 code [21]. For the compounds considered in Ref. [9], the present values of q_i are almost identical to the previously reported values obtained by using the S/PHI/nX package [22]. The local density approximations (LDA) has been used for the exchange and correlation potential, employing the Ceperley-Alder [23] exchange-correlation data as parameterized by Perdew and Zunger [24]. The valence-bands states of the above considered compounds, used to construct the relevant MLWFs, are of sp character and hence are well described by the LDA calculations. A plane-wave energy cutoff of 60 Ryd has been used for the compounds involving first row elements (B, N and C) and/or elements with semicore electrons, and of 25 Ryd for all other compounds. Both the self-consistent calculations and the construction of the MLWFs are performed by using a regular $8 \times 8 \times 8$ Monkhorst-Pack (MP) mesh [25], which provides well converged \mathbf{r}_n . [10] In Ref. [9], we used norm-conserving scalar-relativistic pseudopotentials (PPs), generated by using the Troullier–Martins optimization method [26] as implemented in the FHI98PP code [27]. The used set of PPs is found however to have negligible effects on the calculated values of \mathbf{r}_n . In this work, the Hartwigsen et al. [28] PPs (provided by the ABINIT code) are employed.

3. Results and discussion

The ionicity, q_i , in seventy two $A^N B^{8-N}$ compounds with $N=1, 2, 3$ and 4 , calculated as described in Section 2, are listed in Tables 1 (for group-IV and III–V compounds), II (for II–VI compounds) and III (for I–VI compounds). These results will be discussed below, among each other and in comparison with mainly the ionicity measures of Phillips [6] and Pauling [1] (also shown in Tables 1–3). The present results are compared with those of Phillips [6] and Pauling [1] in Fig. 4, and with the self-consistent results of Christensen et al. [8] and Garcia and Cohen [7] in Fig. 5.

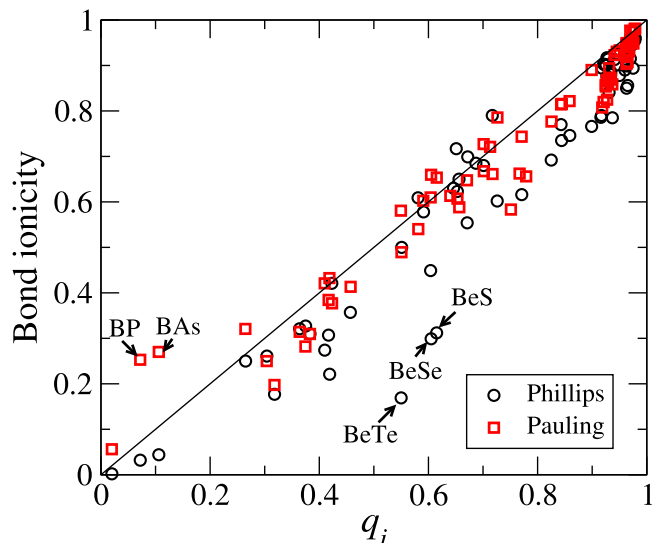


Fig. 4. The ionicity, q_i , versus those of Pauling [1] (p_i) and Phillips [6] (f_i).

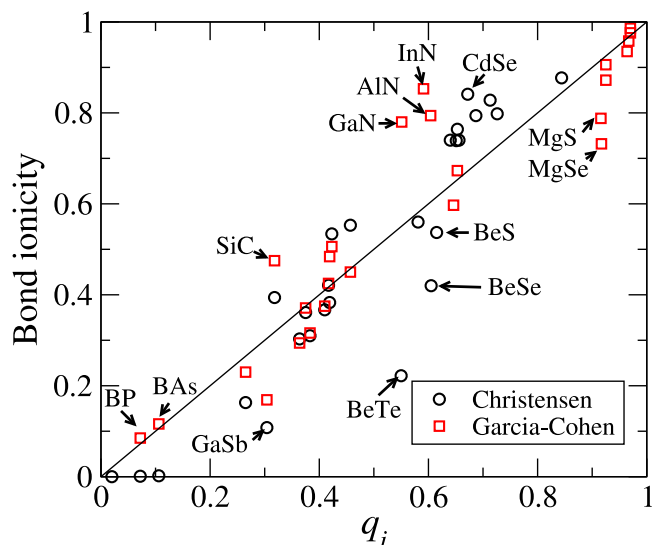


Fig. 5. The ionicity, q_i , versus those of Christensen et al. [8] (f_i^*) and Garcia and Cohen [7] (g_i).

3.1. General features

The above three tables show that q_i of the considered $A^N B^{8-N}$ systems exhibit, generally speaking, the expected ionicity trends: (i) q_i declines by increasing N . (ii) q_i of the group IA (IIA) based compounds are larger than the corresponding values of the group IB (IIB) based materials. (iii) For a given cation, q_i reduces by increasing the atomic number of the anion. (iv) Finally, for a fixed anion, q_i increases by increasing the atomic number of the cations. These trends originate from the period and group trends of χ : increases by going towards the noble gas element in the period of the Periodic Table, and decreases by going down the group [29]. Some exceptions however do exist. For example, the electronegativities of Ga, Ge and As are larger than those of the corresponding elements above them. This feature can be understood to arise from the weak shielding of the nuclear charge by the highly localized 3d electrons, which increases the effective charge and reduces the size of these elements. These exceptions have direct consequences on the calculated ionicities, as will be described below.

To investigate the effects of the relaxation of the semicore

electrons on the calculated ionicity, the q_i of ZnSe, SrSe and CuBr are calculated with and without including the semicore states of Zn (3d), Cu (3d) and Sr (4s and 4p) as valence. It is evident from Tables 2 and 3 that the relaxation of these electrons have negligible effects on the calculated ionicity, and the slight increase of q_i by the semicore calculations (for ZnSe and SrSe) suggests that the valence electrons are slightly pushed away toward the anions by including these electrons as part of the valence states.

As for the effects of the crystal structure on the ionicity, it is worth noting that the bonding in crystalline solids depends on the hybridization between the states of the involved atoms, in addition to the electronegativity difference. Such a hybridization differs by going from one crystal structure to another. To account for this fact, Pauling [1] has introduced the N/M prefactor in Eq. (8), which enhances the ionicity in the crystal structures with larger coordination number. It has been noted by Phillips [6] that the difference in the Pauling measure of ionicity between the RS and ZB phases of MgS and MgSe (which are found to exist in both phases) is about 0.12, which he considered as an artifact of the Pauling ionicity scale. According to the Phillips ionicity scale, this ionicity difference is very small (of order of 0.01) [6]. To shed more light on this issue, q_i is calculated for MgS, MgSe and MgTe in both the RS and ZB structures. Moreover, the relative stability of the ZB and RS phases of these three compounds is investigated. The total energy versus volume curves are shown in Fig. 6. This figure clearly shows that the RS phase is more stable than the ZB form for MgS and MgSe, and the two phases have almost the same ground state total energy for MgTe. These results are in good agreement with a recent study by Gökoglu et al. [32]. For MgTe, the NiAs structure is found however to be more stable than both RS and ZB (or wurtzite) phases [32,33]. The results reported in Table 2 show that the ionicity in the RS phase is about 0.2 larger than that in the ZB structure. Such a large difference is not mainly due to the N/M power in Eq. 17, since there are large differences in the obtained values of β (of about 0.15). This clearly shows that a significant difference in ionicity exists between crystal structures with different coordination number, even when such crystal structures have comparable relative stabilities.

Fig. 4 shows that, q_i is larger than f_i for the majority of the considered systems, in agreement with the trend observed for f_i^* [8]. As for p_i , the adopted combination of the Allred–Rochow χ scale and Eq. (9), see Section 2.3, leads to results that are, generally speaking, in good agreement with q_i . On the other hand, Fig. 5

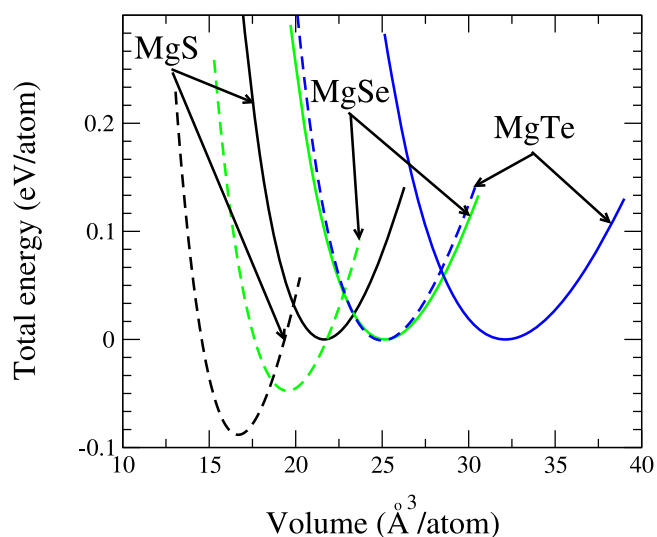


Fig. 6. The total energy versus volume of the zincblende (solid lines) and rocksalt (dashed lines) phases of MgS, MgSe and MgTe.

shows that q_i provides an excellent fitting to the f_i^* and g_i results. In the following subsection, the ionicity in the considered group-VI, III–V, II–VI and I–VII will be discussed in more details.

3.2. Ionicity in group-IV, III–V, II–VI and I–VII compounds

The bonding in the elemental group-IV solids crystallizing in the diamond structure (diamond, Si, Ge and α -Sn) is purely covalent ($q_i=0$). Among these elements, only C and Si are known to form ordered structures (polytypes), and SiGe systems exist only in the form of alloys. The lack of p states in the core of the first row elements (B, C, N and O) leads to rather strong effective potentials seen by valence electrons, which, in turn, yields large electronegativity values for these elements. For this reason, appreciable electronic charge transfer is expected to go from the Si to C atoms. The obtained value of q_i (of 0.318) is in the ionicity range of the III–V compounds. This value is larger than those of the Phillips [6] and Pauling [1] ionicity scales. It has been argued by Christensen et al. [8] that there are evidences (such as the value of the transverse effective charge) that the ionicity in SiC is larger than obtained by Phillips (of 0.177). Our value is in good agreement with that of Ref. [8] of 0.39, and appreciably smaller than that of Ref. [7] of 0.475. According to the Si electronegativity rule [34], $\chi(\text{Ge})$ is larger than that of Si, and hence electronic charge transfer from Si to Ge atoms is expected. By considering the cubic ZB structure as a model for $\text{Si}_x\text{Ge}_{1-x}$ alloy with $x=0.5$, the resulting value of q_i is of 0.020, which is consistent with the small difference between $\chi(\text{Ge})$ and $\chi(\text{Si})$, which are respectively of 2.02 and 1.74 [3].

For the III–V compounds, which crystallize in tetrahedral phases (ZB or wurtzite), the q_i values are listed in Table 1. There are three features to note from these data. First, apart from BN, the considered B-based compounds have very small ionicities. This can be easily understood, since as a first row element, B has a relatively large electronegativity – very close to those of P and As. The q_i values for BP and BAs lie between those of f_i and p_i , and closer to the former ones. In fact, the p_i values (of about 0.25) arise mainly from the N/M prefactor in Eq. 9, due to resonant bond concept (see above). As for the results of the other first-principles ionicity scales (shown in Fig. 5), the f_i^* values (of 0.001 and 0.002 for BP and BAs, respectively) are also very small as in the case of f_i , whereas the corresponding g_i values are in very good agreement with the present ones. Second, for a fixed anion, the ionicity does not monotonically increase by going down the group IIIB of the actions: q_i values of the Ga-based compounds are smaller than those of the corresponding Al-based systems. This is also consistent with the electronegativity values of group IIIB elements: $\chi(\text{Ga}) > \chi(\text{Al})$, see above. Third, the q_i values are, generally speaking, in good agreement with those of f_i and p_i – closer to the latter for the Al-based compounds, and closer to former for the Ga- and In-based compounds.

As for the considered II–VI compounds, one has to note that the group IIB elements are more electronegative than the group IIA ones, and, hence, the bonding in the IIA–VI compounds is more ionic than in the IIB–VI systems. For this reason, most of the IIB–VI compounds crystallize in a tetrahedral phase (except CdO), while the IIA–VI systems adopt the RS phase (except the Be-based compounds). Table 2 shows that the q_i values for the II–VI compounds with RS structure are very large (between 0.92 and 0.95), while for the others (with a tetrahedral phase) q_i ranges between 0.55 (in BeTe) and 0.77 (in ZnO). The q_i values are, generally speaking, in good agreement with both f_i and p_i . The exceptions are as follows. (i) The f_i values for the Be-based compounds are very small compared to those of q_i and p_i . It is worth noting that the obtained values of f_i^* for BeO, BeS, BeSe and BeTe are

respectively of 0.790, 0.537, 0.420 and 0.222 [8]. These results are much closer to the q_i values than those of f_i , especially for BeO and BeS. (ii) The noticeable discrepancies between q_i and p_i are mainly for the Te-based compounds, which can be due to an uncertainty in the used value of $\chi(\text{Te})$ [15]. (iii) Contrary to q_i and electronegativity arguments, f_i increases by going from ZnO to ZnS to ZnSe, and from CdS to CdSe to CdTe, and some oscillation in p_i occurs for the II–VI compounds because according to Allred–Rochow scale $\chi(\text{Se}) > \chi(\text{S})$ [3]. The ionicity in the CdS, CdSe and CdTe has been a subject for a recent study [18], in which f_i^* is obtained as in the Christensen et al. [8] approach, but with E_{sp^3} and h are extracted from Wannier function calculations. The obtained ionicity values (0.556, 0.551 and 0.475 for the ZB phase of CdS, CdSe and CdTe, respectively) decrease monotonically by going from CdS to CdSe to CdTe, in agreement with q_i .

The ionicity behavior of the alkaline-earth oxides is a controversial issue: [35,36] some arguments (mainly electronegativity) support the increase in the ionicity by going from MgO to BaO, while others (see Ref. [36]) indicates a reverse behavior. Pacchioni et al. [35,36] have carried out self-consistent Hartree–Fock calculations for isolated molecules and clusters that represent bulk materials. Analyses of the obtained wavefunctions have led them to conclude that the ionicity in the isolated molecules increases by going from MgO to BaO, while the reverse is observed for bulk materials. They argued thus that electronegativity arguments, which are perfectly applicable in the molecular case, may be less successful for ionic solids. Table 2 shows that β and hence q_i increase by going from MgO to BaO, in agreement with both p_i and f_i . It is interesting to note that the q_i values are in excellent agreement with those of p_i . Therefore, the present calculations not only provide a strong support to the behaviour of increasing ionicity by going from MgO to BaO, but also reflect the high predictive power of the electronegativity arguments.

The IB–VII compounds provide another border line between the fourfold and sixfold coordinated compounds: the Cu-based compounds crystallize in the ZB structure, while the Ag-based compounds exist in the RS phase – except AgI. As expected from electronegativity arguments, the ionicity in the tetrahedrally coordinated $A^N B^{8-N}$ compounds reaches a maximum value in this class of materials. The maximum obtained value of q_i is of about 0.9 (in CuF), see below for further discussion. Table 3 shows that the bonding in the Ag-based compounds crystallizing in the RS phase is highly ionic, with q_i ranging between 0.96 and 0.98. The q_i values for both the Cu- and Ag-based compounds are in good agreement with those of p_i , and are systematically larger than those of f_i by about 0.1.

The IA–VII compounds, which crystallize in the RS phase, are the most ionic ones as shown in Table 3. A very good agreement is achieved between the three considered ionicity scales, which is mainly due to the very narrow ionicity range of these compounds.

3.3. Critical ionicity value

As noted in Section 2.2, an interesting feature of the Phillips ionicity scale is the existence of a critical ionicity value (of about 0.8) separating between the tetrahedrally and octahedrally coordinated compounds. This feature is enforced further by the self-consistent calculations of Christensen et al. [8]. In Ref. [8], this is achieved by investigating the ionicity dependence of the transition pressure (P_t) at which the ZB to RS phase transformation occurs. They have shown that P_t approaches zero when the ionicity is about 0.8, in excellent agreement with the above value obtained by Phillips [6]. Following these arguments, Abu-Farsakh and Qteish [9] have obtained a critical value of q_i of about 0.7. It should be noted that the underlying assumption behind these analyses is

that the ZB and RS phases (of a certain compound) have comparable ionicity if P_t is very small, or if both phases do exist in nature – as in the case of MgS and MgSe. Table 2 shows that this is not a valid assumption: there is a big ionicity difference between the RS and ZB phases of MgS, MgSe and MgTe, even when they have almost identical ground state energy – as in the case of MgTe (see Section 3.1). Moreover, the ionicity is found (see Section 3.4) to decrease by reducing the lattice parameter, for most of the studied compounds, in contradiction with the above assumption. To determine a more accurate critical value of q_i it is worth noting (see Table 3) that there are tetrahedrally coordinated compounds with ionicity larger than the previously proposed critical value of 0.7 [9], with a maximum value of about 0.9 (in CuF). On the other hand, the minimum ionicity in the considered RS compounds is of 0.916 (in MgS). These two values can be considered as lower and upper limits for the critical value of q_i . Hence, a value of 0.91 would be highly reasonable.

ZB–CuF, which has the maximum value of q_i among the tetrahedrally coordinated $A^N B^{8-N}$ compounds, deserves some comments and further discussion. Very recently, the existence of the ZB phase of this system has been questioned, and its stable crystal structure is predicted to be the cinnabar phase. [37] Moreover, in Ref. [37], the ZB and RS phases of CuF are found to have same relative stability. In this work, only the relative stability and ionicity of the ZB and RS phases of CuF are investigated, at the LDA level. In good agreement with Ref. [37], these two phases of CuF are found to have comparable ground state energies, with the ZB phase being slightly more stable. The calculated lattice parameters of the ZB and RS phases of CuF are respectively of 4.685 and 4.445 Å. The difference between the calculated and experimental [38] (of 4.255 Å) lattice parameters of the ZB form is an order of magnitude larger than the usual error due to the use of LDA (of order of 1%). This finding provides a strong support to the conclusion of Ref. [37] that the observed structure [38], back in 1933, is definitely not the ZB phase of CuF. At the calculated equilibrium volumes, the obtained values of q_i are of 0.909 and 0.972 for the ZB and RS phases of CuF, respectively. As in the case of MgTe, the ionicity in these two phases of CuF are appreciably different in spite of their comparable relative stabilities. The q_i value of ZB phase is very close to, but still smaller than, the above suggested critical value that separates between the fourfold and sixfold coordinated compounds.

3.4. Volume dependence

The volume (V) dependence of q_i , defined as $dq_i/d \ln V$, for the considered $A^N B^{8-N}$ systems are listed in Tables 1,2 and 3. It is evident that $dq_i/d \ln V$ is positive for the majority of these systems, which means that q_i decreases with decreasing V . This trend is consistent with what has been observed for f_i^* [8]. The systems with negative $dq_i/d \ln V$ are SiC, SiGe, AlP, AlSb, InN and AgI, with values ranging between -0.327 and -0.007 . The positive $dq_i/d \ln V$ can be understood as follows. The reduction in the bond length leads to a stronger overlap between the valence wavefunctions of the atoms at the two ends of the bond, which increases the pile up of the valence charge density in the middle of the bond. This increases the covalency of the bond and reduces hence its ionicity. Thus, the negative $dq_i/d \ln V$ values are difficult to justify. It worth noting that there are appreciable differences in the calculated values of $dq_i/d \ln V$ and $df_i^*/d \ln V$ (see Ref. [8]). This is quite expected due to the different volume dependences of the physical quantities used to measure the ionicity. The values of $dq_i/d \ln V$ are smaller than $df_i^*/d \ln V$ for most of the studied systems, except for BP, BAs, CuBr and MgS.

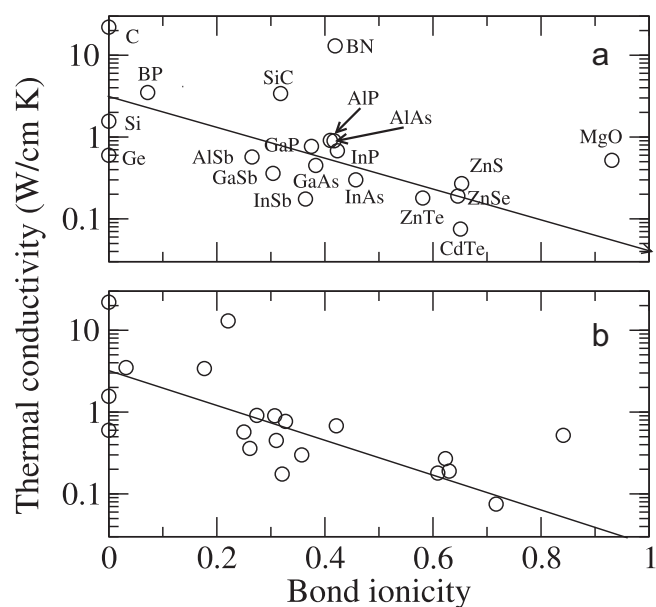


Fig. 7. Thermal conductivity (K) at 300 K of some group IV, III–V and II–VI semiconductors versus q_i (a) and f_i (b). The K values are taken from Ref. [30]. Solid lines are least-squares fit to $K = Ae^{Bx}$, with x is the ionicity.

3.5. Assessment of the q_i scale

We are now in a position to provide a good assessment of the Abu-Farsakh and Qteish ionicity scale [9]. From the above discussion one can conclude that q_i provides a superior account of the ionicity, in the considered $A^N B^{8-N}$ compounds, compared to the Phillips [6] and Pauling [1] ionicity measures. The main drawbacks of the Phillips ionicity scale can be summarized as follows. (i) Its tendency to underestimate the ionicity compared to f_i^* and q_i . This is most noticeable in the case of BeS, BeSe, BeTe and SiC. (ii) It fails to give the correct ionicity trend in the Zn- and Cd-based compounds. (iii) It does not account for the appreciable crystal structure effects on the ionicity. As for the Pauling ionicity scale, the main drawbacks are the following. (i) The lack of a precise definition of χ , and the empirical nature of the electronegativity–ionicity relationship. (ii) There is an ionicity overlap between the fourfold and sixfold coordinated compounds. (iii) It fails to give a reasonable account for the ionicity of BP and BAs, where the χ difference is very small. It is worth noting that the Abu-Farsakh and Qteish measure does not suffer from such shortcomings, which makes it a well established ionicity scale.

Finally, as an application, the thermal conductivity (K) of some group IV, III–V and II–VI compounds as a function of q_i is shown in Fig. 7. For comparison, K versus f_i is also shown in the same figure. It is evident that K decays exponentially as a function of ionicity. The decay is faster in the case of f_i , because (generally speaking) the q_i values are larger than those of f_i , see Fig. 4. The fitting is found to improve by going from f_i to q_i . For example, without considering the group IV elemental solids, the mean square difference reduces from 0.64 to 0.44 (W/cm K)². This demonstrates the usefulness of the latter measure.

4. Conclusions

The Abu-Farsakh and Qteish ionicity scale, based on the centers of the maximally localized Wannier functions (MLWFs), is used to calculate the ionicity (q_i) and its volume dependence ($dq_i/d \ln V$) for seventy two $A^N B^{8-N}$ compounds. The considered systems range from group-IV solids to I–VII compounds, which crystallize

in the tetrahedral [zincblende (ZB) or wurtzite] or octahedral [rocksalt (RS)] structures. Also investigated are the effects of the relaxation of the semicore electrons and the crystal structure on q_i . The obtained results are discussed among themselves and in comparison with mainly those of the Phillips (f_i) and Pauling (p_i) ionicity scales. The most important results and conclusions can be summarized as follows:

1. q_i is found to follow the expected trends, according to the period and group behaviors of the electronegativity. For example, q_i of the Zn- and Cd-based compounds is found to decrease by increasing the atomic number of the anion, contrary to f_i and p_i .
2. The ionicity of the alkaline-earth oxides, which is a controversial issue, is found to decrease by going from MgO to BaO.
3. A large difference in q_i between the tetrahedral and octahedral phases is observed, even for systems where such phases have very close relative stabilities, contrary to what has been previously assumed to determine the critical ionicity value that separates between them.
4. A new critical ionicity value that separates between the tetrahedrally and octahedrally coordinated compounds, of about 0.91, is directly inferred from the obtained values of q_i .
5. The relaxation of the semicore electrons is found to have negligible effects on q_i .
6. For the majority of the considered systems, $dq_i/d \ln V$ is found to be positive, in good agreement with previous calculations, but its magnitude (generally speaking) is found to be much smaller than previously thought.
7. The new bond ionicity scale of Abu-Farsakh and Qteish is proved to be a very strong competitor to most famous and widely accepted measures of Pauling and Phillips.

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