First-principles ionicity scales. I. Charge asymmetry in the solid state

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Using a measure of the asymmetry of the valence charge distribution in $A^N B^{8-N}$ compounds, a mapping to Phillips's ionicity scale is achieved.

I. INTRODUCTION

Modern computational methods have made it possible to study the structural and electronic properties of a wide variety of molecules and solids in great detail. There are, however, instances where this level of detail either cannot be easily attained because of the complexity of the system or is not needed, as when studying broad trends in the behavior of a large set of systems. Empirical concepts such as valence, empirical radii, electronegativity, and ionicity are then useful.[1] These concepts are directly associated with the character of the chemical bond, and thus provide means for explaining and classifying many basic properties of molecules and solids.

It is instructive to consider the various methods by which empirical parameters have been defined over the years. Pauling[1] made use of thermochemical arguments to quantify the ionic character of molecular bonds and was able to develop an electronegativity (X) scale for the elements based on the relation

$$D(AB) = 1/2\{D(AA) + D(BB)\} + C(X_A - X_B)^2$$

$$(1)$$

between the formation energies (D) for the AA, BB, and AB bonds and the electronegativity difference of the A and B atoms (C is a constant with dimensions of energy). Pauling then proceeded to establish a quantitative ionicity scale for molecules based on the electronegativity difference

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

$$(2)$$

For crystals, a modified form is used,

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

$$(3)$$

where the N/M factor reflects the increased ionic character of resonant bonds, which appear when the classical valence N is smaller than the coordination number M.[2]

Coulson, Redei, and Stocker[3] used a molecular-orbital approach for the study of the tetrahedrally coordinated octet binary compounds $A^N B^{8-N}$ and wrote the bonding orbital in the form

$$\psi = \phi_A + \lambda\phi_B,$$

$$(4)$$

where ϕ_A and ϕ_B are sp^3 hybrid atomic orbitals centered on atoms A and B, respectively, and λ is to be determined variationally. Upon normalization, a bond ionicity can be written as

$$i_C = \frac{(\lambda^2 - 1)}{(\lambda^2 + 1)}$$

$$(5)$$

by considering the relative weights of the atomic orbitals in ψ. Net atomic charges can also be calculated in this approximation:

$$Q_A = \frac{N\lambda^2 - (8 - N)}{(1 + \lambda^2)} = -Q_B.$$

$$(6)$$

Phillips[4] introduced a dielectric model of the chemical bond in $A^N B^{8-N}$ crystals which is based on two band-gap parameters C and E_h. The homopolar gap E_h can be interpreted as produced by the symmetric part of the total potential $\frac{1}{2}(V_A + V_B)$, while the ionic or charge-transfer gap C results from the effect of the antisymmetric part $\frac{1}{2}(V_A - V_B)$. The average valence-conduction band gap is given by

$$E_g^2 = E_h^2 + C^2$$

$$(7)$$

and the ionicity is defined as

$$f_i = \frac{C^2}{E_g^2} = \frac{C^2}{E_h^2 + C^2}.$$

$$(8)$$

The homopolar gap E_h for a compound of lattice constant a is obtained by scaling the optical gaps of group-IV materials such as diamond and silicon:

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

$$(9)$$

E_g is determined from the dielectric constant ϵ_∞ for the crystal, and C then follows from Eq. (7). One of the most remarkable features of Phillips's ionicity scale is the existence of a critical value of f_i that separates fourfold-coordinated from sixfold-coordinated compounds. Both the Phillips and the Pauling scales[5] are in widespread use.

A critical review of the merits of the different ionicity scales can be found in Ref. 4. For the purposes of this work, we note that, although the Pauling and Phillips ionicity scales have different conceptual bases, both retain an empirical nature, since the determination of the

ionicity involves an experimental measurement such as the bond formation energy in a molecule or the dielectric constant of the solid.

Coulson, Redei, and Stocker[3] base their ionicity scale on the concept of net atomic charge. But the part of the total valence charge associated with a given atom is not an observable. Even if the total charge density were known at every point in the cell, there would be no unique way to decompose it into atomic contributions. This point was stressed by Christensen, Satpathy, and Pawlowska[6] who were able to present first-principles charge distributions for tetrahedrally coordinated compounds, but relied on a tight-binding parametrization of their linear-muffin-tin-orbital results to provide theoretical values for parameters such as E_h and C that enter Phillips's scale. They did not establish a direct connection between the calculated charge distribution and the ionicity of a compound.

Here we show that it is possible to construct a first-principles ionicity scale for $A^N B^{8-N}$ materials from the valence charge distribution. Rather than trying to assign net charges to the A and B atoms, we focus instead on the overall asymmetry of the charge density as a direct measure of the ionic character of a bond. We establish an unambiguous procedure to compute numerical values for the ionicity and compare its results to the Phillips scale.

II. CHARGE ASYMMETRY AND IONIC CHARACTER

First-principles calculations and analyses of the distribution of electronic charge in solids have been common since the work of Walter and Cohen.[7] Here we use ab initio norm-conserving pseudopotentials[8,9] and the local-density approximation[10] (LDA) to obtain self-consistent (pseudo) valence charge densities for $A^N B^{8-N}$ binary compounds. The relevant crystalline structures for this family of materials include diamond, zinc blende, wurtzite[11] and rocksalt. Figure 1 shows the valence charge density along the bond for Ge (N=4, diamond) and GaAs (N=3, zinc blende). As noted in Ref. 7, for GaAs there is a displacement of the bond charge toward the As atom. Also shown in Fig. 1 is the decomposition of the GaAs charge density (ρ) into symmetric (ρ_S) and antisymmetric (ρ_A) components, defined as follows:

$$\rho_S(\mathbf{r}) = \tfrac{1}{2} [\rho(\mathbf{r}) + \rho(-\mathbf{r})],$$

$$\rho_A(\mathbf{r}) = \tfrac{1}{2} [\rho(\mathbf{r}) - \rho(-\mathbf{r})]. \qquad (10)$$

The origin of coordinates is taken halfway between the Ga and As atoms along the [111] direction. We note that ρ_S for GaAs is remarkably similar to the total charge density of Ge, and that ρ_A represents a relatively small fraction of the total charge in GaAs.

As we move further away from the group-IV column and consider II-VI compounds, the relative contribution of ρ_A increases. This point is made clear by Fig. 2, which presents, on the same scale,[12] the (ρ_S, ρ_A) decomposition for GaAs and ZnSe ($N = 2$, zinc blende). The peak of the antisymmetric component of the valence charge is
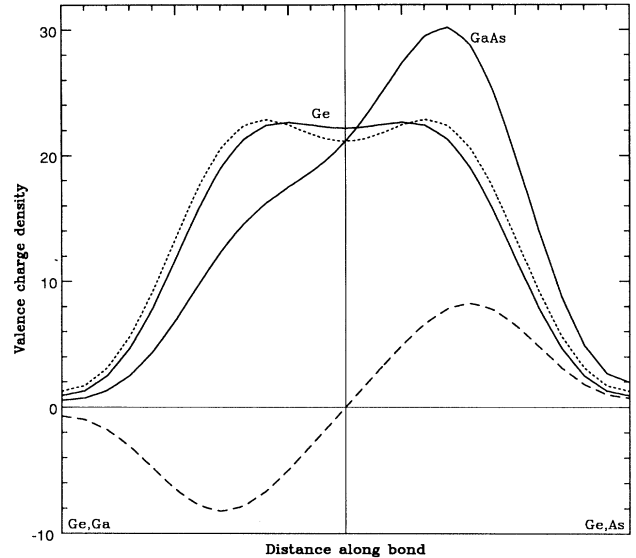

FIG. 1. Valence charge density along the bond for Ge and GaAs (solid lines). The dotted and dashed lines correspond to the symmetric and antisymmetric components of the GaAs charge, respectively (see text). The charge-density units are electrons/Ω, where Ω is the cell volume.

roughly twice as high in ZnSe as in GaAs, while the symmetric components are similar in magnitude. This feature illustrates the correlation between the ionic character of a bond and the relative magnitude of ρ_A. A simple procedure to obtain a quantitative measure of this correlation follows. We start with the Fourier decomposition
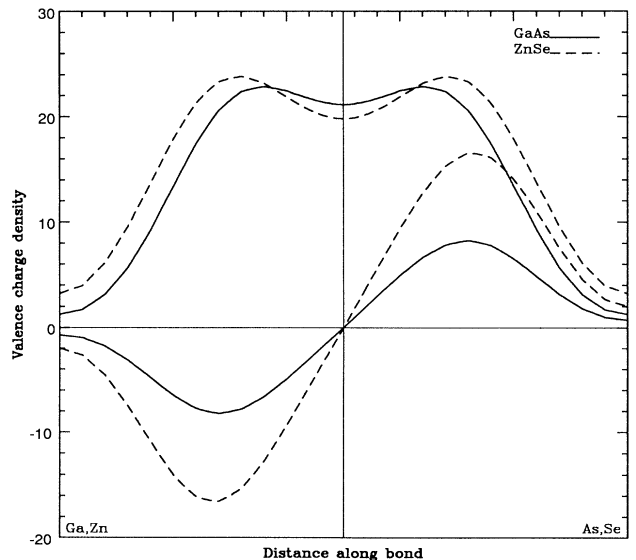

FIG. 2. Symmetric and antisymmetric components of the valence charge density along the bond for GaAs (solid lines) and ZnSe (dashed lines).

of the total valence charge density

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}, \tag{11}$$

and form the Fourier components of ρ_S and ρ_A:

$$\rho_S(\mathbf{G}) = \frac{1}{2}[\rho(\mathbf{G}) + \rho^*(\mathbf{G})],$$

$$\tag{12}$$

$$\rho_A(\mathbf{G}) = \frac{1}{2}[\rho(\mathbf{G}) - \rho^*(\mathbf{G})].$$

We now construct the integrated quantities

$$S_S = \sum_{\mathbf{G}} |\rho_S(\mathbf{G})|^2 = \frac{1}{\Omega}\int_\Omega \rho_S^2(\mathbf{r})d\mathbf{r},$$

$$\tag{13}$$

$$S_A = \sum_{\mathbf{G}} |\rho_A(\mathbf{G})|^2 = \frac{1}{\Omega}\int_\Omega \rho_A^2(\mathbf{r})d\mathbf{r},$$

which measure the strength of the symmetric and anti-symmetric components of ρ over the whole unit cell of volume Ω (and not only along the bond). We define the
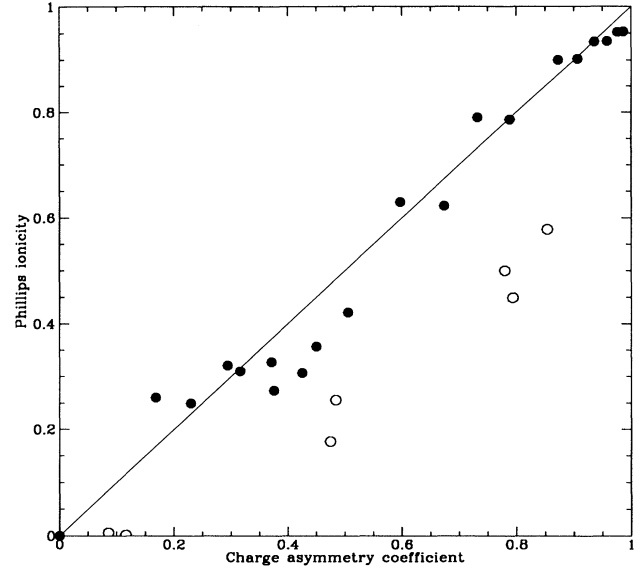

FIG. 3. Comparison of the Phillips ionicity to the charge asymmetry coefficient g defined by Eq. (14) for several octet binary compounds. The open circles represent compounds with first-row elements.

TABLE I. Calculated S_S, S_A, and g for a series of $A^N B^{8-N}$ compounds in the assumed structures shown [D, diamond; Z, zinc blende (Ref. 11); and R, rocksalt] together with the Phillips ionicity f_i. The compounds are ordered by increasing g.

Compound	Structure	S_S	S_A	g	f_i
Si	D	95.10	0.00	0.000	0.000
Ge	D	97.87	0.00	0.000	0.000
Sn	D	100.41	0.00	0.000	0.000
BP	Z	91.54	0.67	0.085	0.006
BAs	Z	91.81	1.23	0.116	0.002
GaSb	Z	98.57	2.80	0.169	0.261
AlSb	Z	96.79	5.13	0.230	0.250
InSb	Z	100.53	8.71	0.294	0.321
GaAs	Z	99.92	9.99	0.316	0.310
GaP	Z	99.39	13.69	0.371	0.327
AlAs	Z	97.94	13.81	0.375	0.274
AlP	Z	97.47	17.59	0.425	0.307
InAs	Z	102.23	20.72	0.450	0.357
SiC	Z	93.71	21.10	0.475	0.177
BN	Z	104.07	24.39	0.484	0.256
InP	Z	102.77	26.29	0.506	0.421
ZnSe	Z	107.28	38.19	0.597	0.630
ZnS	Z	111.94	50.75	0.673	0.623
MgSe	R	85.72	45.92	0.732	0.790
GaN	Z	126.80	77.09	0.780	0.500
MgS	R	90.88	56.47	0.788	0.786
AlN	Z	121.20	76.34	0.794	0.449
InN	Z	150.26	109.43	0.853	0.578
CaSe	R	96.32	73.20	0.872	0.900
CaS	R	106.66	87.52	0.906	0.902
NaBr	R	128.65	112.58	0.935	0.934
NaCl	R	150.96	138.47	0.958	0.935
KBr	R	166.39	158.52	0.976	0.952
KCl	R	204.62	199.09	0.986	0.953

charge asymmetry coefficient g as

$$g = \sqrt{\frac{S_A}{S_S}}. \qquad (14)$$

It is easy to see that the physical constraint $\rho(\mathbf{r}) \geq 0$ on the valence charge density implies that $|\rho_A(\mathbf{r})| \leq |\rho_S(\mathbf{r})|$, so $0 \leq g \leq 1$. A value of zero for g corresponds to homopolar compounds, and very ionic materials will exhibit asymmetry coefficients close to unity.

To gauge the usefulness of the charge asymmetry coefficient as a measure of ionic character of the chemical bond we compare (in Fig. 3 and Table I) the g values calculated using Eq. (14) for several $A^N B^{8-N}$ compounds to the ionicity values f_i assigned to them by Phillips.[4] We note that not only tetrahedrally coordinated compounds but also sixfold-coordinated materials (rocksalt structure) are included in the comparison. In all cases, the origin of the coordinates is chosen so that the A atom moves into the position of the B atom upon inversion. It is immediately apparent that the compounds studied fall into two classes: There is a clear correspondence between g and f_i for those compounds not containing first-row elements, whereas g is larger than f_i for BN, SiC, AlN, GaN, BP, BAs, and InN. The characteristic feature of B, C, and N is the lack of core p states. This translates into strongly attractive p pseudopotentials and large electronegativities and charge asymmetries. Compounds involving first-row elements also have comparatively small cell volumes. This implies that the homopolar gaps (E_h) computed using the scaling relation [Eq. (9)] are relatively large, and the f_i values are reduced accordingly. From the point of view of charge asymmetry the value ($f_i = 0.177$) for the Phillips ionicity for SiC appears to be too small when compared, for example, to GaAs ($f_i = 0.310$).[13] Christensen, Satpathy, and Pawlowska[6] have also reported consistently larger ionicities for the compounds containing first-row elements.

There is also some evidence that the values of f_i for small bond-length compounds fail to account for some structural trends. In particular, it has been shown[14] that there exists an approximate link between f_i and the type of structure (polar β-tin or rocksalt) to which a given tetrahedrally coordinated compound will transform under pressure. Higher values of f_i were found to reflect a preference for the rocksalt structure, with low f_i implying a transformation to the β-tin modification. Small bond-length compounds do not fit the trend. First-principles calculations for BN, BP, BAs,[15] SiC,[16] AlN,[17,18] and GaN (Refs. 19 and 20) suggest that these materials transform to the rocksalt structure upon compression, and not to the β-tin form as the low values of f_i would imply.[21] The trend is restored if the charge asymmetry coefficient g is used instead of f_i. Figure 4 shows a diagram analogous to Fig. 2 of Ref. 14 for III-V compounds and SiC. A horizontal line separates materials that favor the β-tin type as a high-pressure structure from those that transform to a rocksalt phase. There are two errors: BP and BAs are still classified as favoring the β-tin type.[22] The larger values of g result in the correct placement of the rest of the compounds containing first-row elements.[23]
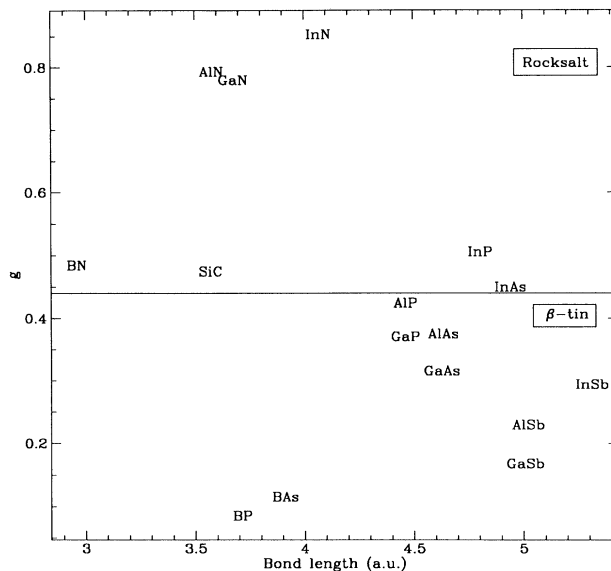

FIG. 4. Charge asymmetry coefficient g vs bond length for the III-V compounds and SiC. The horizontal line separates the materials that transform to the β-tin structure under pressure from those that prefer the rocksalt modification (see text).

The procedure followed to define the charge asymmetry coefficient is straightforward and unambiguous, and involves only the input of the total valence charge density, which can in principle be measured experimentally by x-ray diffraction or computed from first principles.[24] The latter option is attractive since it allows the consideration of hypothetical structures and the simulation of experimental conditions that are difficult to achieve in the laboratory, such as very high pressures.

In Table II we present values of $dg/d\ln V$ for BN, SiC, AlN, AlP, and GaAs. For all the compounds except SiC, the charge asymmetry decreases with pressure. This is in agreement with the results of Sanjurjo et al.,[25] who measured the frequency splitting of the zone-center TO and LO phonons as a function of pressure. This splitting can be related to the ionicity of the bond.[26] There is also semiquantitative agreement with the calculations of Christensen, Satpathy, and Pawlowska,[6] who computed the pressure dependence of the magnitudes associated in their tight-binding fit with Phillips's E_h and C to arrive at estimates of the volume dependence of the ionicity.

TABLE II. Volume derivatives of the charge asymmetry parameter.

Compound	$dg/d\ln V$
BN	0.155
SiC	-0.008
AlN	0.096
AlP	0.149
GaAs	0.134

We see that the charge asymmetry coefficient g calculated from S_S and S_A [Eq. (14)] has many of the attributes of an ionicity parameter. As stressed by Phillips,[4] a test of the "accuracy" of an ionicity scale can be based on its success in separating fourfold- from sixfold-coordinated compounds. In that sense (Fig. 5), the charge asymmetry criterion does not lead to a critical value g_c analogous to Phillips's f_c. (AlN, GaN, and InN would lie in the sixfold region for any reasonable choice of g_c.) It nevertheless provides a clear structural separation: fourfold and sixfold materials lie approximately on separate *lines* on the S_A versus S_S diagram. The compounds MgS and MgSe are special since they form both in a fourfold-coordinated structure (wurtzite) and in the rocksalt form. On our diagram they appear at one end of the "sixfold" line since we initially chose the rocksalt structure for them. We have also computed the values of S_S and S_A for their fourfold-coordinated forms at the experimental equilibrium volume (there is a small contraction in the bond length), and find that MgS and MgSe then move to the "fourfold" line, with very small changes in the computed charge asymmetry parameter g. This is consistent with their polymorphism. It could be argued at this point that the disposition of the AB octets in lines is just a geometrical effect. It is important to stress, however, that a given compound lies on a line only for a particular value of the bond length (precisely the experimental one). In this sense, the arrangement of structure types in lines rather than two-dimensional regions has physical content.

There is an *intrinsic* asymmetry in the charge distribution of an $A^N B^{8-N}$ compound. If we consider only the valence difference, we can define a simple "zeroth-order"

asymmetry coefficient

$$g_0 = \frac{(8 - N) - N}{8} = 1 - \frac{1}{4}N,$$

(15)

which equals 0 for IV-IV, 0.25 for III-V, 0.50 for II-VI, and 0.75 for I-VII compounds. These estimates neglect the details of the distribution of the valence charge. They fail, for example, to reflect the C-Si size difference that makes SiC significantly ionic. To consider in more detail the importance of the intrinsic charge asymmetry for our measure of ionicity we need then to focus on the charge density of the isolated atoms. A straightforward generalization of Eqs. (10)–(13) for the case of infinitely separated A and B atoms involves the construction of the symmetric and antisymmetric same-origin overlap integrals:

$$S_S^\infty = \int (\rho_A + \rho_B)^2 dV,$$

$$S_A^\infty = \int (\rho_A - \rho_B)^2 dV.$$

(16)

Here the valence charge density of the neutral atoms A and B is used.[27] The "atomic limit" asymmetry coefficient is now

$$g_\infty = \sqrt{S_A^\infty / S_S^\infty}.$$

(17)

There exists a definite correlation between g_∞ and the spectroscopically defined f_i, as shown in Fig. 6. We find then that a major part of the ionicity of a compound is directly related to the effects of valence and atomic size differences. In a companion paper[28] we will connect
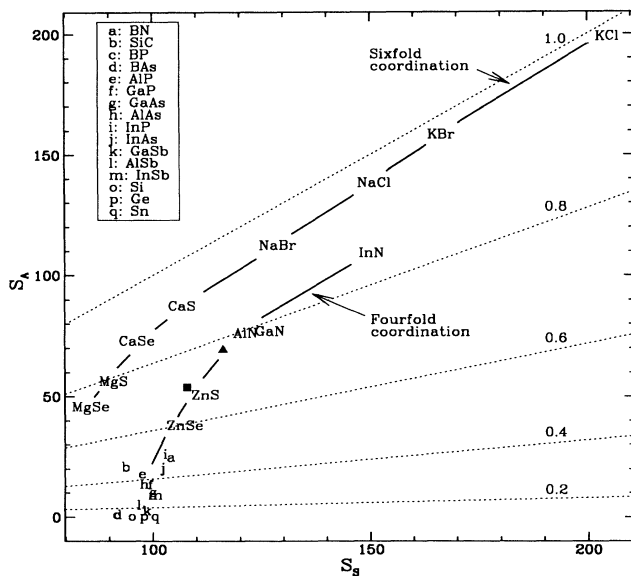

FIG. 5. S_A vs S_S for a group of AB octets. Also shown are lines of constant charge asymmetry coefficient g. The triangle and the square represent the fourfold-coordinated forms of MgS and MgSe, respectively.
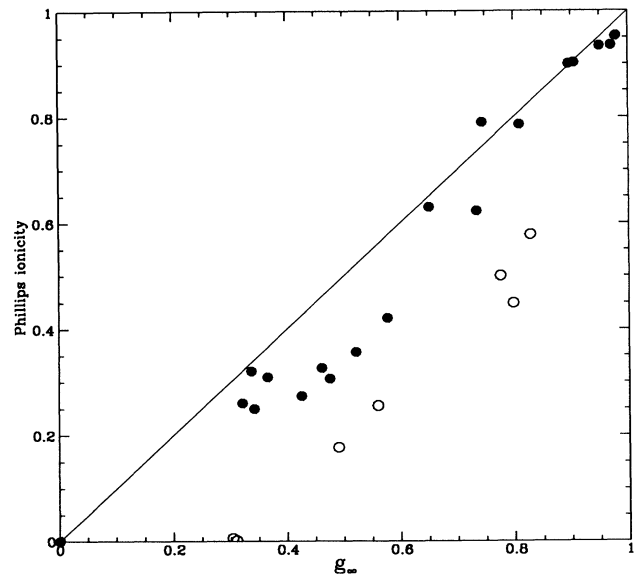

FIG. 6. The atomic-limit asymmetry coefficient g_∞ compared to the Phillips ionicity for several octet binary compounds. The open circles represent compounds with first-row elements.

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this qualitative statement with the traditional concept of atomic electronegativity.

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