Electronegativities of Elements in Covalent Crystals

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A new electronegativity table of elements in covalent crystals with different bonding electrons and the most common coordination numbers is suggested on the basis of covalent potentials of atoms in crystals. For a given element, the electronegativity increases with increasing number of bonding electrons and decreases with increasing coordination number. Particularly, the ionicity of a covalent bond in different environments can be well-reflected by current electronegativity values; that is, the ionicity of chemical bonds increases as the coordination number of the bonded atoms increases. We show that this electronegativity scale can be successfully applied to predict the hardness of covalent and polar covalent crystals, which will be very useful for studying various chemical and physical properties of covalent materials.

1. Introduction

The concept of electronegativity (EN) was originally defined by Pauling as "the power of an atom in a molecule to attract electrons to itself".[1] Pauling first established a quantitative EN scale using thermochemical data that is predominantly used in chemistry. For more than 70 years, many definitions and interpretations of EN have been introduced.[2] EN provides a simple and efficient way to predict the nature of chemical bonding and to rationalize a large variety of chemical phenomena. More importantly, it can be applied to explain and predict various properties of materials and to further explore new materials.[3,4] Recently, perovskite-based inorganic yellow-red pigments were successfully synthesized by simple composition adjustments according to the EN values of constituent elements.[5]

Because the EN of an element in any particular compound depends in detail on its environment, we more recently proposed an EN model based on effective ionic potential, by which we quantitatively calculated EN values for 82 elements with different oxidation states, spin states, and coordination numbers (CNs).[6] These EN values were satisfactorily applied to estimate some useful physicochemical parameters of ions and to predict the structure and property of ionic materials, such as to estimate the Lewis acid strength for main-group elements, the hydration free energy of transition-metal cations and the charge-transfer energies of trivalent lanthanides in inorganic compounds.[6,7] However, for covalent materials, the environment of their constituent atoms is quite different from that in ionic materials because of the different bonding characters; therefore, an EN scale for covalently bonded elements is needed.

Indeed, in the present work, we propose a new EN scale for 58 elements in covalent crystals by including the number of bonding electrons of an atom and its coordination polyhedron. Applying this EN scale to hard and superhard materials, most of which are covalent or polar covalent crystals, we quantitatively calculated the hardness values of these materials, and the results obtained agree well with the experimental values. The current EN scale will thus be very helpful for predicting various properties of covalent solids.

2. Calculation Model

Among various scales of EN, Luo and Benson proposed a quite simple and useful EN scale called the "covalent potential", which is defined as the ratio of the number of valence electrons n_x of an atom x to its single-bond covalent radius r_x.[8] This scale can be used satisfactorily for estimating group parameters, heats of formation of alkyl derivatives, bond dissociation energies, and other properties for molecules. However, because the chemical environment of an atom in a crystal, including the hybridization state of the bond orbital, the number of bonding electrons, and the coordination number, differs greatly from that in a molecule, the covalent potential of an atom in a crystal can be particularly defined as[9]

$$\phi_j = \frac{n_j}{R_j} \quad (1)$$

where n_j is the number of bonding electrons of an atom j and R_j is its crystalline covalent radius in a given coordination polyhedron. The current covalent potential φ_j reflects the energy of attraction between the atomic nucleus, which is shielded by the core electrons, and the valence electron at the crystalline covalent radius. To obtain more commonly acceptable values, an EN value of 2.500 (Pauling scale) is assigned to tetrahedral carbon, the most typical covalently bonded element, and therefore, the ENs of other elements can be determined by the equation

$$\chi_j = \frac{2.500}{5.195}\phi_j = 0.481\frac{n_j}{R_j} \quad (2)$$

where the value of 5.195 is the covalent potential of tetrahedrally coordinated carbon. Herein, this new definition of EN is generalized to 58 elements of the periodic table.

3. Results and Discussion

By using eq 1, the covalent potentials of elements in crystals with different numbers of bonding electrons and different CNs were calculated (data are taken from refs 1 and 10). As illustrated in Figure 1, there is an excellent linear correlation (R = 0.997) between the current covalent potentials φ_j and

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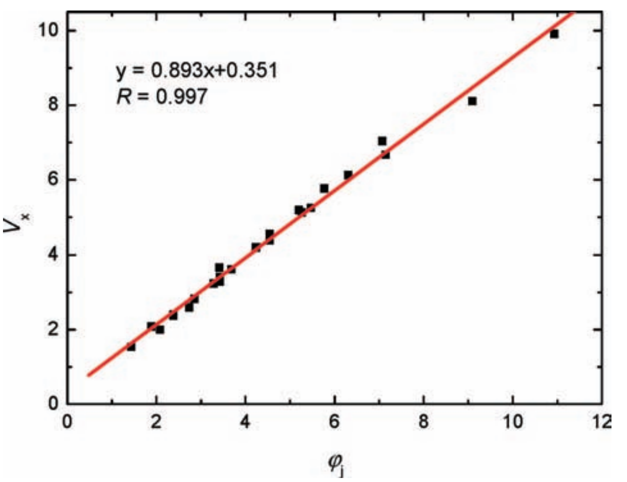

Figure 1. Comparison between current covalent potentials φ_j and Luo−Benson's V_x for main-group elements with numbers of bonding electrons equal to their group numbers.

TABLE 1: Data on φ_j and V_x for Main-Group Elements with the Numbers of Bonding Electrons Equal to Their Group Numbers

element	φ_j	V_x	$\varphi_j - V_x$
Be	1.887	2.08	−0.193
Mg	1.429	1.54	−0.111
B	3.409	3.66	−0.251
Al	2.381	2.40	−0.019
Ga	2.381	2.38	0.001
In	2.083	2.00	0.083
C	5.195	5.19	0.005
Si	3.419	3.41	0.009
Ge	3.279	3.24	0.039
Sn	2.857	2.83	0.027
Pb	2.740	2.60	0.140
N	7.143	6.67	0.473
P	4.545	4.55	−0.005
As	4.237	4.20	0.037
Sb	3.676	3.62	0.056
Bi	3.425	3.29	0.135
O	9.091	8.11	0.981
S	5.769	5.77	−0.001
Se	5.263	5.13	0.133
Te	4.545	4.38	0.165
F	10.938	9.915	1.023
Cl	7.071	7.04	0.031
Br	6.306	6.13	0.176
I	5.469	5.25	0.219

Luo−Benson's values V_x for main-group elements with numbers of bonding electrons equal to their group numbers, providing strong support for the reasonableness of the new EN definition. (Because the most characteristic CN for covalent solids is four, tetrahedrally coordinated φ_j is selected herein.) It can be seen that, for most elements, φ_j is larger than V_x (Table 1), which can be attributed to their larger covalent radii in molecules due to the inter- and intra-atomic interactions between the lone pairs in the valence shells of the elements.[11] The largest deviations are for nitrogen, oxygen, and fluorine owing to their relatively strong lone-pair effects.

The EN values of elements in various chemical environments were calculated according to eq 2, and an EN table for covalently bonded elements in crystals is provided in Table 2. This new scale is reasonable because it follows the general rules of EN. For main-group elements, the EN values show a systematic increase from left to right across periods and a general decrease down groups. For a given element, the EN increases with increasing number of bonding electrons. Moreover, the EN of an element decreases with increasing CN, which can be attributed to the fact that the higher the CN of an atom in a crystal, the larger its covalent radius, which, in turn, leads to a lower covalent potential at the covalent boundary. The elements nitrogen, oxygen, and fluorine have the highest ENs among the main-group elements, and the EN of nitrogen is higher than that of chlorine, which well satisfies the criteria for an acceptable EN scale.[12] The seven considered metalloid elements (B, Si, Ge, As, Sb, Te, Bi), that separate the metals from the nonmetals, have a very narrow range of EN values, and most metals have EN values less than that of silicon (for example, Al < Si, Ga < Si, Ge < Si), which follows the so-called silicon rule.[12] In addition, the EN values of the chalcogens (O, 4.375; S, 2.776; Se, 2.533; Te, 2.187) reveal distinct properties between oxides and the corresponding compounds of other chalcogen elements.[13] For transition-metal atoms, the obtained ENs fall in a narrower range of values than do those of the main-group atoms. EN values of the third transition series are comparable to those of the second transition series, which might be due to the larger relativistic effects in the third-row transition metals.

4. Application

The current EN scale of covalently bonded elements was used to predict the hardness values of hard and superhard materials, most of which are covalent or polar covalent crystals. It was found that bond density, bond strength, and degree of covalent bonding are three determinative factors for the hardness of a covalent material.[14] Higher bond density, greater bond strength, and higher degree of covalency result in greater hardness. Recently, we found that EN can be used to characterize the hardness of materials.[9] Herein, for an A−B covalent bond the strength can be characterized by $\sqrt{x_A x_B}$, where χ_A and χ_B are EN values of atoms A and B, respectively. $\sqrt{x_A x_B}$ reflects the binding power of a covalent bond to an electron pair. Two bonded atoms that have larger ENs bind electron pairs more tightly, making the covalent bond harder to break. Therefore, the hardness of a covalent material can be expressed as

$$H = a\frac{N}{\Omega}\sqrt{\chi_A \chi_B} f_c^{\ \delta} + b \tag{3}$$

Here, N/Ω is the bond density, where N is the number of covalent bonds per unit cell and Ω is the volume of unit cell. f_c is a covalency indicator, given by $f_c = 1 - f_i$, where f_i is an ionicity indicator defined as $f_i = 0.25|\chi_A - \chi_B|/\sqrt{x_A x_B}$, and a, b, and δ are constants. For good agreement with experimental Knoop hardness values, H_k, of purely covalent crystals, viz., diamond and silicon, a and b were determined to be 106 and −3.4, respectively. The constant δ should be 2.4, which was chosen to fit the experimental Knoop hardness values for InSb and ZnTe crystals having relatively low covalency and low hardness among the typical polar covalent crystals. For the crystals A_mB_n with average CN ($\overline{CN}$) ≤ 4, the hardness can be calculated by eq 3, where $\overline{CN} = (m\mathrm{CN}_A + n\mathrm{CN}_B)/(m + n)$. For crystals with $\overline{CN} > 4$, a correction factor of $\kappa = 4/\overline{CN}$ is introduced into the first term of eq 3 considering the combined effects of the three factors of hardness that are all closely related to CN. In the case of a complex crystal, the hardness can be calculated as the geometrical sum of all binary systems in the crystal.[9] For spinel nitrides γ-M_3N_4, M occupies both the tetrahedral and octahedral sites of the cubic lattice, which thus contain two types of bonds, namely, 32 M_t−N and 96 M_o−N bonds. The hardness of γ-M_3N_4 materials can be expressed as

TABLE 2: EN Values (χ_j) of Elements in Covalent Crystals[a]

IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			1B	IIB	IIIA	IVA	VA	VIA	VIIA
							Period II								
Be											B	C	N	O	F
(2,te) 0.908											(3,te) 1.641 (3,oc) 1.415	(4,tr) 2.619 (4,te) 2.500 (4,oc) 2.347	(5,tr) 3.565 (5,te) 3.437 (5,oc) 3.085	(6,tr) 4.561 (6,te) 4.375 (6,oc) 3.750	(7,te) 5.264 (7,oc) 4.552 (7,cu) 4.433
							Period III								
Mg											Al	Si	P	S	Cl
(2,te) 0.688 (2,oc) 0.638 (2,cu) 0.602											(3,te) 1.146 (3,oc) 1.111	(4,te) 1.645 (4,oc) 1.565	(5,te) 2.187 (5,oc) 2.074	(6,te) 2.776 (6,oc) 2.533 (6,cu) 2.468	(7,te) 3.403 (7,oc) 3.008 (7,cu) 2.929
							Period IV								
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
(2,oc) 0.544 (2,cu) 0.520	(3,oc) 0.962	(2,oc) 0.646 (4,te) 1.481 (4,oc) 1.415 (4,cu) 1.346	(3,te) 1.155 (3,oc) 1.046	(2,te) 0.703 (2,oc) 0.659 (3,te) 1.183 (3,oc) 1.086	(2,te) 0.741 (2,oc) 0.697 (3,te) 1.183 (3,oc) 1.137	(2,oc) 0.782 (4,oc) 1.604	(2,te) 0.804 (2,oc) 0.729 (2,cu) 0.625 (3,oc) 1.183	(2,sq) 0.692 (2,oc) 0.692 (3,oc) 1.111 (4,oc) 1.591	(1,li) 0.408 (1,te) 0.357 (1,oc) 0.344 (2,te) 0.782	(2,te) 0.735 (2,oc) 0.697	(3,te) 1.146 (3,oc) 1.077	(4,te) 1.578 (4,oc) 1.540	(5,te) 2.039 (5,oc) 1.925	(4,oc) 1.375 (6,te) 2.533 (6,oc) 2.292 (6,cu) 2.221	(7,te) 3.035 (7,oc) 2.653 (7,cu) 2.591
							Period V								
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
(2,oc) 0.491 (2,cu) 0.484	(3,oc) 0.859	(4,te) 1.328 (4,oc) 1.301 (4,cu) 1.234	(3,te) 1.077 (3,oc) 1.031	(4,oc) 1.328 (6,oc) 2.171	(4,te) 1.504 (4,oc) 1.365	(2,oc) 0.724 (3,oc) 1.111 (4,oc) 1.540	(2,oc) 0.683 (3,oc) 1.094 (4,oc) 1.578	(2,sq) 0.735 (2,te) 0.708 (2,oc) 0.678 (4,oc) 1.469	(1,li) 0.346 (1,te) 0.317 (1,oc) 0.283	(2,te) 0.650 (2,oc) 0.587 (2,cu) 0.538	(3,te) 1.002 (3,oc) 0.962	(2,oc) 0.547 (4,te) 1.375 (4,oc) 1.328	(5,te) 1.769 (5,oc) 1.683	(4,oc) 1.267 (6,te) 2.187 (6,oc) 1.991 (6,cu) 1.925	(7,te) 2.632 (7,oc) 2.292 (7,cu) 2.216
							Period VI								
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
(2,oc) 0.448 (2,cu) 0.446	(3,oc) 0.772	(2,oc) 0.587 (4,te) 1.319 (4,oc) 1.292 (4,cu) 1.242	(3,te) 1.069 (3,oc) 1.031	(4,oc) 1.309 (6,oc) 2.171	(4,te) 1.481 (4,oc) 1.356	(2,oc) 0.724 (3,oc) 1.094 (4,oc) 1.504	(2,oc) 0.678 (3,oc) 1.094 (4,oc) 1.528	(2,sq) 0.735 (2,te) 0.703 (2,oc) 0.673 (4,oc) 1.469	(1,te) 0.321 (3,sq) 1.031 (4,oc) 1.375	(2,li) 0.746 (2,te) 0.650 (2,oc) 0.587 (2,cu) 0.538	(1,oc) 0.229 (1,cu) 0.213 (3,te) 0.982 (3,oc) 0.908	(2,oc) 0.523 (2,cu) 0.488 (4,te) 1.318 (4,oc) 1.283	(5,te) 1.648 (5,oc) 1.533		

[a] χ_j calculated from eq 2. Values in parentheses are numbers of bonding electron. li (linear) denotes CN = 2; tr (trigonal), CN = 3; te (tetrahedral) and sq (square), CN = 4; oc (octahedral), CN = 6; and cu (cubic), CN = 8.

$$H_k = 106\frac{2}{\Omega} \times \left[32{\sqrt{\chi_{\mathrm{M_t}}\chi_{\mathrm{N}}}f_{\mathrm{c(M_t-N)}}}^{2.4} \times 96{\sqrt{\chi_{\mathrm{M_o}}\chi_{\mathrm{N}}}f_{\mathrm{c(M_o-N)}}}^{2.4}\frac{4}{4.8}\right]^{1/2} - 3.4 \quad (4)$$

where 4.8 is the average CN of the octahedral units in γ-M_3N_4 crystals. By using eq 3, we quantitatively calculated the Knoop hardness values of typical covalent and polar covalent crystals. We also calculated the hardness values of γ-C_3N_4 and γ-Si_3N_4 using eq 4. The related parameters and the calculated results are listed in Table 3. (Unit cell volumes were taken from the Inorganic Crystal Structure Database.[15]) It can be seen that the calculated ionicity indicators of M_o—N bonds are larger than those of M_t—N bonds, in agreement with the general viewpoint on solid-state materials that the ionicity of chemical bonds is enhanced as the CNs of the bonded atoms increase. For comparison, the experimental Knoop hardness values are also given. (Data were taken from refs 14 and 16−18.) We found that there is a good agreement between calculated and experimental hardness values, and the accuracy of this model is expected because of the incorporation of the actual environment of atoms in covalent crystals.

TABLE 3: Hardness and Parameters Related to Hardness Calculations for Typical Covalent and Polar Covalent Crystals

crystal	f_i	Ω (Å^3)	$H_{k,\mathrm{calc}}$ (GPa)	$H_{k,\mathrm{expt}}$ (GPa)
diamond	0	45.37	90.1	90
Si	0	160.17	14.0	14
Ge	0	181.09	11.4	11.3
Sn	0	273.26	5.1	4.5
SiC	0.105	82.77	28.4	29
c-BN	0.189	47.28	48.1	48
BP	0.072	93.45	25.3	32
BAs	0.054	108.94	21.5	19
AlN	0.289	43.2	13.8	12.25
AlP	0.164	159.22	7.6	9.4
AlAs	0.146	179.31	6.5	5.0
AlSb	0.109	231.47	4.5	4.0
GaN	0.289	45.73	12.9	10.8
GaP	0.164	151.25	8.1	9.5
GaAs	0.146	167.1	7.2	7.5
GaSb	0.109	226.53	4.7	4.5
InN	0.328	119.97	6.7	9.0
InP	0.200	199.89	3.9	5.4
InAs	0.181	221.23	3.4	3.8
InSb	0.144	272.02	2.3	2.2
ZnS	0.357	160.46	1.8	1.8
ZnSe	0.329	183.93	1.4	1.4
ZnTe	0.286	230.46	0.8	1.0
OsB	0.064	20.65	18.4	18.5[a]
TiC	0.128	80.23	24.3	24.7
WC	0.148	20.75	21.0	18.8
hex-OsC	0.112	20.17	26.3	24.3[a]
NbN	0.288	84.84	12.4	17
c-Zr_3N_4	0.237	306.18	16.4	17.5[a]
c-Hf_3N_4	0.235	300.9	16.9	18.7[a]
Stishovite	0.280	44.5	31.3	32
BeO	0.435	28.2	11.8	13
Al_2O_3	0.370	232.35	16.5	19
ZrO_2	0.338	69.83	12.3	12
Y_2O_3	0.453	1184.89	3.1	7.5
SnO_2	0.328	71.47	13.4	13.8[a]
MgO	0.503	76.8	3.0	3.7
β-Si_3N_4	0.198	147.47	21.2	21
γ-C_3N_4	0.080^{t,b} 0.096^{o}	324.3	73.1	73.5[a]
γ-Si_3N_4	0.188^{t,b} 0.202^{o}	452.37	29.7	30

[a] Because there are no experimental values, other calculated values are given as a comparison.[14,19,20] [b] t and o, respectively, denote that M is tetrahedrally and octahedrally coordinated by N in γ-M_3N_4 (M = C, Si) crystals.

5. Conclusions

A comprehensive EN scale for covalently bonded elements in crystals is presented that includes the number of bonding electrons and the actual coordination of the bonded atoms. Because the bonding environment of the atoms is fully considered, the bond strength and bond ionicity of a covalent bond can be reasonably reflected by the current EN values. Combined with crystal structure data, these EN values can be employed to quantitatively calculate the hardness values of covalent and polar covalent materials. The calculated values for these materials compared favorably with the available experimental data. This EN scale provides important insights into the structure−property relationships of covalent solids and thus offers a simple and powerful way to both predict the properties of various covalent materials and design new materials with desired properties. In addition, it should be noted that each EN scale has its own theoretical basis and is more accurate in its own area of use; therefore, EN values of different scales should not be mixed in real cases.

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