Electronegativity and hardness as coordinates in structure stability diagrams

(crytal structure/density functional theory/chemical periodicity)

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ABSTRACT With electronegativity and hardness of an atom defined as $\frac{1}{2}(I + A)$ and $\frac{1}{2}(I - A)$, respectively, where $I$ and $A$ are the ionization potential and electron affinity, electronegativity difference and hardness sum are proposed as coordinates in structure stability diagrams. With these coordinates a successful topological classification of the crystal structures of octet and suboctet binary compounds is obtained, and a clear delineation of the structural classes portraying chemical periodicity is found.

For the past several decades a major goal of solid-state chemistry has been to identify simple structural coordinates to delineate and predict crystal structures. Though the problem of structure of solids can be formulated in precise quantum mechanical language, even approximate solutions that are consistently meaningful are not easy to obtain. Also, accurate solutions of the Schrödinger equation are of less interest than are descriptions derived from these that reveal correct periodic trends.

The earliest attempt, based on cation–anion radius ratios (1), was not particularly successful. The first breakthrough in the field was made by Mooser and Pearson (2) when, to classify binary octet compounds, they chose the electronegativity difference, $\Delta_\text{E}$ (identified by them as a measure of the ion potential energies), and the average principal quantum number, $\bar{n}$ (a measure of the kinetic energies), as structural coordinates. They were not only able to predict structures but explain their stability as well. With the advent of sophisticated quantum mechanical methods various sets of interesting structural coordinates that are artifacts of the particular methods have been identified (3). In the Phillips–Van Vecht model (4), the average band gap between occupied and empty states is separated into covalent and ionic components through a Hückel-like relation,

$$E^2_V = E^2_k + c^2.$$  \[1\]

The quantities $E_k$ and $E_v$ are obtained from the dielectric theory and the two parameters $E_k$ and $c$ are plotted against each other for various binary compounds. $c$ is similar to the electronegativity difference and $E_k$ is a more refined index for $\bar{n}$ that is a measure of the energy bandwidth. Many correlations have been drawn in this model (5, 6).

Pseudopotential theories also have been used to elucidate parameters that serve as useful structural indices. Simons and Bloch (7) obtained angular momentum-dependent orbital radii using the nonlocal Simons potential (8)

$$\nu(r) = -\frac{Z}{r} + \frac{B_1}{r^2} + \frac{l(l + 1)}{2r^2}.$$  \[2\]

where the first term on the right-hand side is the coulombic potential associated with a charged ion, the second is the Pauli term, and the last term is the $l$-dependent quantum centrifugal potential. Since the classical work required to remove an electron from $r_l$ to $\infty$ is

$$-\int_0^\infty \frac{d}{dr} \left[ -\frac{Z}{r} + \frac{l(l + 1)}{2r^2} \right] dr = \frac{1}{2} \frac{Z}{r_l},$$  \[3\]

The quantity $1/r_l$ is a pseudochemical potential or orbital electronegativity. St. John and Bloch (9) defined two structural parameters from these $l$-dependent radii and studied 34 non-transition elemental solids and 59 binary octet compounds. Linear combinations of these radii have also been used to define structural indices $R_\alpha$ and $R_\beta$ (see pp. 37 and 38 of ref. 6),

$$R_\alpha^{\alpha\beta} = (r_\alpha^\beta + r_\alpha^\beta) - (r_\alpha^\beta + r_\alpha^\beta),$$

$$R_\beta^{\alpha\beta} = (r_\beta^\alpha - r_\beta^\beta) + (r_\beta^\alpha - r_\beta^\beta).$$  \[4\]

These indices have been used to study structural distortions, elastic constants, bond charges, and relative stabilities of several binary compounds. Coordinates similar to $R_\alpha$ and $R_\beta$ have also been obtained from Fourier transforms of the wave vector (10). Zunger (11, 12) has used a density functional pseudopotential to obtain these radii and has studied 565 binary compounds. Recently, Villars (13) has given an exhaustive classification of 998 compounds using three structural parameters in a three-dimensional plot.

The success of these various structural coordinates is established, but it nevertheless remains desirable to find other parameters that are more simply representative of atoms bound in the crystal.

Since fundamental to all chemical interactions is the atomic electron density, and the change in it, ideal parameters should be those that portray this. Electronegativity, which indicates the propensity for change in electron density around the atom, and hardness, which is a measure of the resistance to this change, should be obvious possible choices for these parameters. Their use in describing chemical interactions is textbook knowledge (14).

Electronegativity and Hardness

The basis for a focus on electronegativity and hardness is provided by density functional theory (15), which guarantees that the ground-state energy of a many-electron system is a unique functional of its density (16). For the change from one ground state to another of an electronic system, the change of electronic energy $E[\rho]$ is given by the formula

$$dE[\rho] = \mu dN + \int \rho(r) d\nu(r) dr,$$  \[5\]
where \( \rho \) is the electron density, \( v(\nu) \) is the external potential, \( N \) is the number of electrons, and \( \mu \) is the chemical potential. Furthermore, \( E = E(N, \nu) \), and

\[
\mu = \left( \frac{\partial E}{\partial N} \right)_\nu.
\]  

[6]

It is clear from this formula that \( \mu \) is the negative of the electronegativity of chemistry (17); indeed, it follows rigorously (18) that

\[
\chi = -\mu = \frac{1}{2} (I + A),
\]  

[7]

where \( I \) and \( A \) are the ionization potential and electron affinity; \( \chi \) is the Mulliken electronegativity.

The chemical potential itself depends on \( N \) and \( \nu \)—i.e., \( \mu = \mu(N, \nu) \). Its derivative with respect to \( N \) has been defined as the hardness (19),

\[
\eta = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right)_\nu = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_\nu = \frac{1}{2} (I - A).
\]  

[8]

That this is the hardness of modern chemistry (20) has been discussed at length and applied to various chemical problems (ref. 19; R. G. Pearson, personal communication).

The quantities \( \chi \) and \( \eta \) are interesting possibilities as the base for structure stability coordinates because they are the simplest conceivable parameters describing the atomic ground state. This is even more clear from the simple formula for the amount of electron transfer accompanying bond formation obtained through the principle of electronegativity equalization—that is, if we ignore effects arising from concomitant changes in the external potential [which must be taken into account in a complete theory (21)], for atoms \( A \) and \( B \) in the species \( AB \), we find from

\[
\mu_A = \mu_0^A + 2\eta_\nu \Delta N, \quad \mu_B = \mu_0^B - 2\eta_\nu \Delta N,
\]  

[9]

that, for \( \mu_A = \mu_B \) at equilibrium,

\[
\Delta N = \frac{\mu_0^A - \mu_0^B}{2(\eta_A + \eta_B)} = \frac{\eta_A - \eta_B}{2(\eta_A + \eta_B)}.
\]  

[10]

where \( \Delta N \) is the charge transferred from \( B \) to \( A \). The charge transfer effects are the most important ones in ionic solids where electrostatic effects dominate. Large electronegativity difference leads to greater charge transfer, while larger hardness sum suppresses charge transfer. This is, of course, an old argument as far as electronegativity is concerned, but the equal emphasis on hardness as a defined quantity is new. We note in passing that \( I - A \) is a measure of the energy band gap in solids, so that hardness is a parameter that in effect has been used in the past as a structural coordinate (4, 22).

Structure Classification

In Fig. 1, \( \chi \) is given as a function of \( \eta \) for the 34 non-transition elements. All values of \( \chi \) and \( \eta \) are obtained from Eqs. 8 and 9, respectively; the \( I \) and \( A \) values are ground-state values obtained from the literature (23–26). The plot is seen to satisfactorily separate the elements according to their most stable metallic structures. Following St. John and Bloch (9), we classify all elements that form directional bonds as covalent.

Figs. 2 and 3 show \( \Sigma \eta \) vs. \( \Delta \chi \) diagrams for 86 binary octet

![Fig. 1. Hardness vs. electronegativity plot for non-transition elements.](image1)

![Fig. 2. \( \Sigma \eta \) vs. \( \Delta \chi \) plot for binary octet compounds of group A cations.](image2)

![Fig. 3. \( \Sigma \eta \) vs. \( \Delta \chi \) plot for binary octet compounds of group B cations.](image3)
Fig. 4. $\Sigma \eta$ vs. $\Delta \chi$ plot for binary octet compounds displaying periodic trends in chemical behavior.

Compounds ($A^N B^{8-N}$) of group A and group B cations, respectively. The nature of coordination around an atom should be measured by the atomic charge and size (which in turn is determined by the charge). As expected, the highest coordination occurs with the largest difference in electronegativity and the smallest values of hardness. It is apparent that Figs. 2 and 3 make a clear distinction between the tetrahedrally coordinated zinc blend and wurtzite structures as well, indicating that atomic parameters are sensitive enough to portray third neighbor effects on bonding. An extremely interesting feature that emerges from the plots is the display of periodic trends in chemical behavior. For example, the respective alkali halides all lie on smooth curves, as do the oxides and sulfides (Fig. 4).

The appropriateness and versatility of these structural coordinates is demonstrated further in the delineation of members of the family of suboctet non-transition metal compounds ($A^N B^{8-N}$; with $3 \leq P \leq 6$) in Fig. 5. We consider the 45 compounds studied by Machlin et al. (27); 23 of these are derived from bcc structures and 22 are anion valence coordination structures (open and solid symbols, respectively). The respective classes are indicated. Near-perfect separation of the structural classes is obtained.

Discussion

We may conclude that the simple ground-state atomic parameters, electronegativity and hardness, suffice to describe the nature of bonding in solids. In a solid where coulomb effects dominate, perhaps it is not surprising that the two parameters, the electronegativity difference and the sum of hardness, which completely determine the charge transfer, $\Delta N$, characterize the structure. What is surprising, however, is the transparent manner in which chemical periodicity is portrayed.

Many research problems are suggested by the success of this work—for example, the delineation of structures of intermetallic phases or other bonding situations. Also, related structural coordinates like $x A \eta + y A + \eta A$ and $x B \eta + y B + \eta B$; or $x A \eta = (x A \eta + y A \eta A)/(x + y A)$ and $y B \eta = (y B \eta + y B \eta B)/(x + y B)$, which would be the final electronegativity and the molecular hardness, could be used to study stability diagrams.

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