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A Classification of Covalent, Ionic, and Metallic Solids Based on the Electron Density

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Abstract: The electron density of crystals contains all of the information required to complete a classification of their bonding types. We propose here a set of three different indexes, flatness, charge transfer, and molecularity, easily obtained from the experimental or theoretical electron density, which give rise to a classification in close resemblance to the classical van Arkel−Ketelaar diagrams.

A detailed analysis of the electron density of many crystals is presented here to show that the classification of bonding properties, with resemblances to the classical van Arkel−Ketelaar diagram (VK), can be directly recovered from the electron density, with no explicit recourse to empirical or otherwise defined electronegativity scales.

The classification of compounds according to their chemical bonding type lies at the core of the chemistry language. About 50 years ago, van Arkel and Ketelaar[1,2] proposed an outstanding classification of binary crystals along an ionic−covalent−metallic triangular diagram. In a modern description, the triangle is based on the relative electronegativity of their atomic components: the covalency−ionicity of the AB compound is provided by the $|\chi_A - \chi_B|$ difference in electronegativity, whereas the average $(\chi_A + \chi_B)/2$ measures the metallicity−covalency character. The classical VK diagram has been revisited many times,[3−6] analyzing the role of different electronegativity scales, including nonbinary compounds, or even adding a fourth vertex to the triangle to represent van der Waals bonding and other forms of molecular interactions. Most remarkably, Sproul[5] has shown, on the basis of their statistical significance, that the many electronegativity scales proposed over the years provide different measurements of one and the same physical property.

Reliable total electron densities, $\rho(\vec{r})$, can now be obtained for many crystals,[7−9] as it is already routine in the case of small molecules, thanks to the recent advances on the experimental and computational techniques. The quantum theory of atoms in molecules (AIM), devised by Bader and others,[10] can be used to extract the chemically relevant information contained in the electron density,[11] that ranges from the chemical graph and bond properties to the atomic contributions to the multipolar moments or the crystalline pressure.[12−14]

Following VK's spirit, we have examined a collection of some 60 crystals in the search for a systematic classification of the features exhibited by their electron density. The crystalline electron densities have been determined by means of HF-LCAO calculations[15] at the experimental geometries using crystal optimized basis sets,[16] and their topological properties have been analyzed with the techniques described in, for instance, refs 12 and 17. As a general rule, we have used double- or triple-ζ valence plus polarization bases to prevent spurious basis set effects on the electron density.

First of all, among a large variety of electron density topological types, we find four limiting patterns that roughly correspond to the traditional classification of ionic, covalent, metallic, and molecular solids. The atomic basins of ionic crystals contain a substantial net charge, similar to the nominal oxidation state, and are linked to each other through closed-shell charge-depletion interactions, exhibiting a small electron density, ρ_b, and a positive laplacian, $\nabla^2\rho_b$, at the bond critical points (BCP). Whereas a positive laplacian value represents a

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region of depleted charge, a negative laplacian corresponds to regions where the electron density is locally accumulated. Accordingly, prototypical covalent crystals have a large electron density and a negative laplacian at the BCPs, and the charge concentration valence regions tend to form a three-dimensional network that spans the whole crystal. The most significant feature of metallic crystals is the great planarity and diffuse nature of the electron density in the valence region, producing very low values both for ρ_b and for $\nabla^2\rho_b$. Finally, molecular crystals can be identified because their electron densities exhibit well-defined molecular fragments surrounded by zero flux surfaces, and those fragments interact weakly through closed-shell BCPs.

Most crystals, however, do not belong to the extremal prototypes, and a quantitative scale is needed to account for the more complex intermediate situations. We were at first strongly tempted to classify the crystals by averaging in some way the properties of their BCPs. Such classification appears natural as ρ_b has been correlated with many classical bond concepts and even atomic electronegativity within families of related bonds.[18−20] However, after many fruitless attempts, we recognized that a general bonding classification demands not just looking at a particular BCP but instead at the electron density properties as a whole.

Keeping this idea in mind, we have searched for classifying indices with some desirable properties: (1) they should be simple to obtain from the theoretical or experimental electron density; (2) they should be adimensional; and (3) they should reflect the three-dimensional distribution of the electron density across the crystal.

We have designed a set of three indexes that distinguish qualitatively as well as quantitatively among the different topological varieties exhibited by the crystalline electron densities.

First, a flat electron density throughout the valence region has long been recognized as a characteristic feature of metallic systems, and, in fact, this has been used to justify the success of the crude Drude−Sommerfeld electron-gas model in accounting for the electrical and thermal conductivity of metals.[21] An appropriate measurement of the valence electron density flatness is provided by the ratio

$$f = \frac{\rho_c^{\min}}{\rho_b^{\max}} \tag{1}$$

where $\rho_c^{\min}$ is the absolute minimum of the electron density (necessarily a cage critical point of ρ), and $\rho_b^{\max}$ is the maximum electron density found among the BCPs. This index separates metals (with f approaching one) from nonmetals (f going to zero) by exploiting the idea that the relevant portion of the valence electron density starts at the highest density BCP and ends at the lowest density cage critical point. In a way, the interatomic space might be regarded as a foam such that inside each bubble is the high electron density region that surrounds and is dominated by a nucleus. Alkaline metals (Li−K) exhibit the highest value of f, 0.89−0.95, closely followed by the alkaline earth metals, 0.64−0.75, and most other metallic elements and alloys approach $f \approx 0.5$.

As a second independent coordinate, we define a charge-transfer scale by using the topological charges, that is, the integrated net charge within each atomic basin. It is well known that topological charges approach, in most ionic molecules and crystals, the values of the nominal oxidation state for each atom. Accordingly, the ratio between the topological charge, $\mathscr{Q}(\Omega)$, and the nominal oxidation state, $\mathrm{OS}(\Omega)$, provides a measurement of the separation from the ideal ionic model for a given basin Ω. The global charge-transfer index of the crystal can then be obtained as the average of those ratios for all atoms that form the unit cell of the crystal:

$$c = \frac{1}{N}\sum_{\Omega=1}^{N} \frac{\mathscr{Q}(\Omega)}{\mathrm{OS}(\Omega)} = \left\langle \frac{\mathscr{Q}(\Omega)}{\mathrm{OS}(\Omega)} \right\rangle \tag{2}$$

Most crystals made of a single element have $\mathrm{OS}(\Omega) = \mathscr{Q}(\Omega) = 0$ and are assigned $c = 0$ as a default. Typical ionic crystals showing $c \approx 0.9$ include alkali halides, simple oxides such as MgO, and even some nitrides such as AlN. Crystals such as zincite and rutile appear to be largely ionic too, with $c \approx 0.75$. Polar compounds with c ranging 0.3−0.6 include most III-V crystals and nitrides. Lower values are found in the covalent compounds, including the main elements crystals (diamond and graphite, for instance), and in the van der Waals molecular solids (N_2, CS_2, etc.).

It might appear particularly shocking that some of the most characteristic metals exhibit a nonzero charge-transfer index, in fact, a value that can approach $c \approx 1$ (0.88 in Be, 0.83 in Li) and shows a well-defined trend within the alkaline (0.83, 0.53, and 0.40 for Li, Na, and K, respectively) and alkaline-earth elements (0.88, 0.74, and 0.17 for Be, Mg, and Ca, respectively). This phenomenon is originated by the occurrence of nonnuclear maxima (NNM), that is, local maxima of the electron density that appear between two or more nuclei. These NNMs behave as pseudoatoms, trapping most of the valence electrons of the metallic atoms. The resulting structure is an electride in the classical sense, formed by nearly spherical metallic cores linked through asymmetric pseudoatoms that completely fill the interstitial space, making these metals appear as prototypical images of the Drude−Sommerfeld model. NNMs, however, are neither a necessary nor a ubiquitous feature of metals[22] and have, in fact, been identified in nonmetallic systems, most notably *F*-centers.[23−25] Although many concerns were initially raised on the potentially spurious character of these objects, they have now been proved beyond doubts,[23,24,26] and it has been shown that the occurrence of NNMs in homonuclear crystals or cluster arrangements can be regarded as a consequence of the atomic shell structure, with the internuclear distance the main controlling criterion.[26] Many prototypical metals such as Al, Cu, and Fe, for instance, lack NNMs at normal pressure because the interatomic distance largely exceeds the appropriate range.

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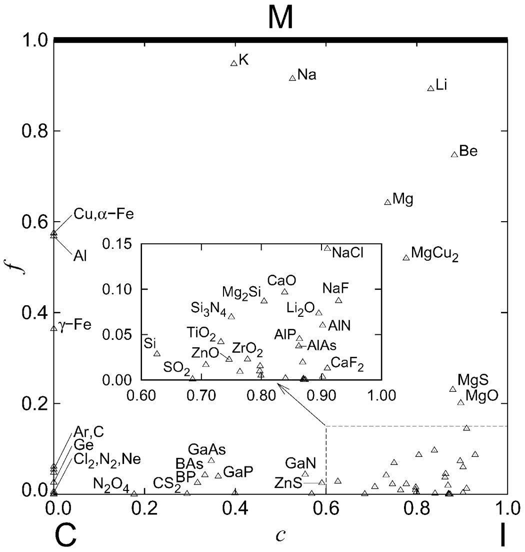

Figure 1. Flatness versus charge-transfer diagram for a collection of representative crystals. Unlabeled points in the inset include $AlBO_3$, $CaTiO_3$, $MgCO_3$, $NaNO_3$, $Mg(OH)_2$, and SiF_4.

The values found for c in many crystals, including metals, are evidence that the index here named charge transfer provides a measurement of the trend of some elements to lose electrons either to other elements such as in the ionic and polar compounds or to the interatomic space such as in the prototypical Drude−Sommerfeld metals.

As a consequence of the behavior discussed above, the f versus c plot in Figure 1 results in a square rather than a triangular diagram, and the metallic vertex of the VK triangle is here splitted into the corners of metals with and without NNMs. Otherwise, the new diagram shows the expected trends. Prototypical covalent, ionic, and metallic systems cluster around the corners labeled C, I, and the line M, respectively. On the way from the I to the C corner, we find a very intuitive gradation from ionic to covalent solids passing through intermediates that actually correspond to compounds with classical polarized bonds. Examples of polar crystals include ZnS, ZnO, or silicates, forming a fuzzy boundary between mainly ionic and covalent regimes. The trip from the I or C corners to the M line passes through the intermetallic alloys and the metalloids, as we are used to expecting. A look to particular families of compounds provides easily recognizable trends. In the III-V family, for instance, f generally increases, and c decreases as we go down on any of the III or V group elements. Accordingly, c varies from 0.80 to 0.33 and f from 0.00 to 0.04 in passing from BN to BAs. An effect easily recognizable in the I-VII, II-VI, and III-V families, well represented among the crystals chosen for our study, is that the elements in the second period (Li−Ne) differ significantly from their respective elements in the third and fourth periods, these being quite similar.

Clustered around the covalent corner, we find a large number of compounds that include true three-dimensional covalent crystals as well as molecular crystals formed by covalent molecules held together by weak intermolecular interactions. These two kinds of compounds can be differentiated by attending to a third classifying index: μ or molecularity, defined as

$$\mu = \begin{cases} (\rho_b^{\max} - \rho_b^{\min})/\rho_b^{\max} & \text{if} \quad \nabla^2 \rho_b^{\max} \times \nabla^2 \rho_b^{\min} < 0 \\ 0 & \text{otherwise} \end{cases} \tag{3}$$

such that $0 \leq \mu \leq 1$. The rationale behind this definition is related to the behavior of the electron density laplacian, $\nabla^2\rho(\vec{r})$. The laplacian is negative in regions where the charge is locally concentrated, whereas places of charge depletion are shown by positive laplacian values. Covalent solids exhibit a connected network of negative laplacian regions, which extends to the whole crystal and includes the BCPs inside. Diamond is a prototypical case of this behavior. Molecular crystals, on the contrary, present isolated islands of charge accumulation, containing $\nabla^2\rho_b < 0$ covalent bonds, which interact together by means of $\nabla^2\rho_b > 0$ closed-shell BCPs.

Compounds with a large value (0.8−1.0) of μ include the crystals of molecules such as N_2, Cl_2, and N_2O_4, but they also include ionic crystals such as $NaNO_3$, $Mg(OH)_2$, and $MgCO_3$, thanks to the occurrence of molecular ion entities such as NO_3^-, OH^-, and CO_3^{2-}. Graphite offers an interesting case: graphene sheets, tightly held together by covalent bonds, interact by means of weak $\nabla^2\rho_b > 0$ BCPs, and thus $\mu \approx 0.99$. Graphite appears then as a two-dimensional covalent crystal, being a molecular entity along the third direction.

It is easy to prove that $\mu + f \leq 1$. Accordingly, a three-dimensional f-c-μ diagram will have the shape of a triangular prism. However, the number of crystals in our sample is not large enough to fill densely the diagram, and we will skip it.

In conclusion, this work demonstrates that the classification of solids based on the properties directly contained in the experimental or theoretical electron density is certainly possible. The three indexes here proposed, charge transfer, flatness, and molecularity, provide a classification with clear resemblances to the long recognized VK-like diagrams, but they give rise to some surprises on their own.

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