

Framework Electronegativity: a Novel Concept in Solid State Chemistry

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Applying a recently developed formalism for calculating charges and the average electronegativity to the solid state, a marked influence of the structure type on the charge distribution and on the average electronegativity was discovered; for structures with SiO₂ composition (stishovite, coesite, quartz, tridymite, and cristobalite) the average electronegativity decreases with the density as well as with the refractive index.

The electronegativity (χ), *i.e.* the negative of the 'chemical potential' (μ) of the electrons [$\mu = -\chi = (\partial E/\partial N)_v$], in an atomic or molecular system (where E is the electronic energy, N the number of electrons, and the derivative is taken at constant external potential) is a fundamental quantity of a compound and its value is constant throughout.^{1,2} If the total energy of a molecule is considered as a function of the number of electrons on each atom (N_α, N_β, \dots), the nuclear charges (Z_α, Z_β, \dots) and of the internuclear distances ($R_{\alpha\beta}, \dots$), Politzer and Weinstein³ showed that in the ground state and at equilibrium, equation (1) applies, which expresses the equality of the electronegativity of all atoms in the molecule. For an explicit dependence of the total energy on the independent variables in equation (1), Mortier, Ghosh, and Shankar⁴ showed (using a spherical-atom approximation) that the electronegativity of an atom in a molecule can be written as in equation (2). For the isolated atom, the energy $E(N)$ roughly obeys a quadratic equation $E = E^\circ + \mu^\circ N + \eta^\circ N^2$ and it was proposed to apply a similar expansion for the atomic terms, but with expansion coefficients different from those of the isolated atom ($\mu^\circ + \Delta\mu$) and ($\eta^\circ + \Delta\eta$). This leads to equation (2) when it is considered that $\mu = -\chi$ and $N_\alpha - Z_\alpha = -q_\alpha$, denoting the charge on atom α .

$$\left(\frac{\partial E}{\partial N_\alpha}\right)_{N_\beta \dots} = \left(\frac{\partial E}{\partial N_\beta}\right)_{N_\alpha \dots} = \dots = \chi \quad (1)$$

$$\chi_\alpha = (\chi_\alpha^\circ + \Delta\chi_\alpha) + 2(\eta_\alpha^\circ + \Delta\eta_\alpha) q_\alpha + \sum_{\beta \neq \alpha} (q_\beta/R_{\alpha\beta}) \quad (2)$$

Knowing the variation of the electronegativity with charge, there remain, for an n -atom molecule, n charges and the value

of the average electronegativity $\bar{\chi}$ as unknowns. These can be obtained by solving a set of n equations of the type (2) (where for each atom the effective electronegativity is set equal to the common average), and one equation restricting the sum of charges to the total molecular charge. $\Delta\chi$ and $\Delta\eta$ can be calibrated to a set of known (*e.g. ab initio*) charges for some model molecules. There is an overwhelming evidence^{4,5} that: (i) $\Delta\chi$ and $\Delta\eta$ for any atom type can be transferred from molecule to molecule to a wide variety of environments, and (ii) if calibrated to *ab initio* charges, the charge distribution in the molecules is very accurately reproduced (to within a few hundredths of an electron).

For solid state applications the external potential is generated by a Madelung-type summation.⁶ Different atomic sites (differing because of the crystallographic position, structure, or because of the type of neighbours) will therefore carry different charges. The Hohenberg and Kohn theorems⁷ certify that the electron density distribution contains all information about the system. In the atomic regions $\rho(\vec{r})$ integrates to a certain number of electrons: N_α, N_β, \dots , hence the importance of the atomic charges as information carriers. Not only charges, but also the average electronegativity contain significant information. There is also a second characteristic of $\rho(\vec{r})$: the electron cloud may take on different shapes (in a spherical-atom approach we refer to compactness). This can be related to the average electronegativity, which for an isolated atom, is quite obvious. The 'size' can be measured by the value of the radius r_{\max} , giving the peak in the radial density distribution for the outermost atomic orbital, which is the most probable distance of the valence electrons from the nucleus; using Slater-type orbitals (STOs), this depends on the

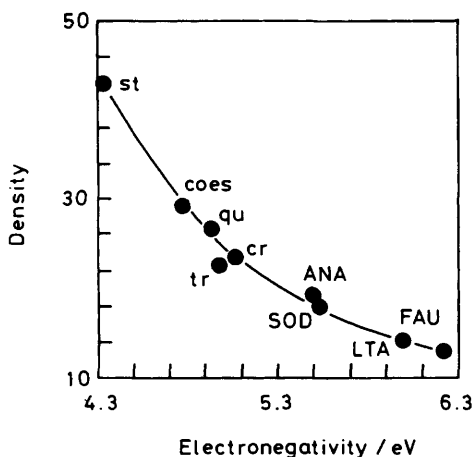


Figure 1. Relation between the average electronegativity (eV) and the framework density (number of Si atoms/1000 Å³) for stishovite, coesite, low-quartz, low-cristobalite, low-tridymite, and four-hypothetic SiO₂ polymorphs with the framework structure of analcime (ANA), sodalite (SOD), zeolite A (LTA), and faujasite (FAU). The average electronegativity contains an arbitrary constant.

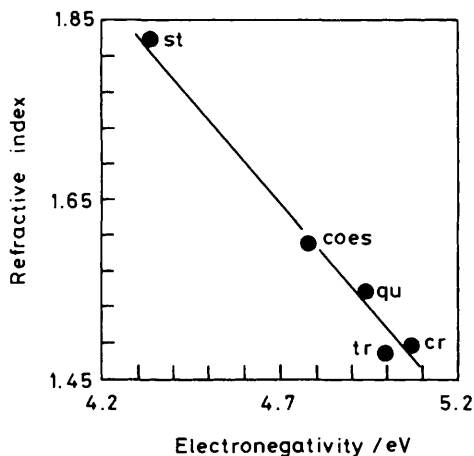


Figure 2. Relation between the average electronegativity (eV) and refractive index²⁵ at λ 589 nm for stishovite, coesite, low-quartz, low-cristobalite, and low-tridymite. The average electronegativity contains an arbitrary constant.

orbital exponent $\zeta = Z_e/n$, where Z_e is the effective nuclear charge and n the principal quantum number. Changing ζ or r_{\max} (as it occurs *e.g.* by placing an atom in a molecule) will change the orbital energy,⁸ and hence the electronegativity.

These concepts were then applied to the silica polymorphs stishovite,⁹ coesite,¹⁰ quartz,¹¹ tridymite,¹² and cristobalite¹³ and also to four zeolite structure types [ANA (analcime), SOD (sodalite), LTA (zeolite A), and FAU (faujasite), for which the Si–O distances and the unit cell parameters were converted to a SiO₂ composition with the DLS program¹⁴]. The Madelung potentials were calculated using a modified program by Fischer.¹⁵ The expansion parameters of the electronegativity (Si and O) as a function of the charge were calibrated using STO 3G¹⁶ *ab initio* charges (obtained by a Mulliken¹⁷ population analysis) from a series of simple molecules containing Si, O, and H.

It was found that the average electronegativity of these frameworks correlates with the framework density (with the lowest electronegativity for stishovite and the highest for the

zeolite-type framework of faujasite) (Figure 1). This explicitly relates a structure type with the electronic (and therefore also physico-chemical) properties. Especially for the zeolite-type frameworks, there exists a wide range of framework densities with consequently properties varying not only with the framework composition,^{18–21} but also with the framework type. This will be particularly important for the adsorptive and catalytic properties of these materials. The charge distribution (and bond ionicity), which contains another type of information than the average electronegativity, does not vary smoothly with the change in framework electronegativity. The charge distribution as well as the average electronegativity will have to be considered when discussing the physico-chemical properties.

As it is known that the index of refraction is connected with the electron distribution in the crystal,^{22–24} an investigation of the corresponding refractive index constitutes a test for the physical significance of the model. It was indeed found that the average electronegativity of the framework correlates linearly with the index of refraction for the silica polymorphs (Figure 2).

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