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A physical basis for Pauling's definition of bond strength

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Abstract The average strength, s, of the bonded interactions comprising a cation containing oxide anion coordination polyhedron and the value of the electron density, $\rho(\mathbf{r_c})$, at the bond-critical points are inversely correlated with bond length. In each case, the observed bond lengths, R, were modeled with power-law expressions defined in terms of s/r and $\rho(\mathbf{r_c})/r$, respectively, where r is the Periodic Table row number of the cation involved in the bonded interaction. On the basis of the close connection between bond strength and the value of the electron density at the bond-critical point, we conclude that bond strength is a direct measure of bond type; the greater its value, the greater the localization of electron density in the binding region and the greater the shared–electron covalent character of the bonded interaction.

Keywords Bond strength · Bond number

Introduction

In a highly cited paper in which Linus Pauling (1929) proposed a set of rules that bear his name, the average strength, s, of the v bonded interactions comprising a coordination MX_v polyhedron in a complex ionic crystal was defined to equal the ionic valence of the M cation, $+z$, divided equally among its coordinating anions such that $s = +z/v$. With this definition, he found the remarkable result that the sum of bond strengths, ζ, of the individual bonded interactions involving each anion in a variety of Earth materials like the SiO_2 polymorphs, olivine, garnet, the TiO_2 polymorphs, and topaz exactly equals the ionic valence of the anion with its sign changed. However, as observed later by Bragg (1937), there are notable exceptions, like diopside, where the ζ values for the constituent bonded interactions range between 1.75 and 2.50. Years later, Smith (1953) observed in a careful study of the interactions in the sheet silicate melilite that the ζ values for the SiO-bonded interactions correlate with the observed SiO bond lengths, with the longer bonds tending to involve larger ζ values. Subsequently, Baur (1961, 1970) discovered that the correlation is more general and holds for a relatively large number of MO-bonded interactions. Despite the relatively large departure of the ζ values in these materials from 2.0, he was careful to point out that the average ζ value for the oxide anions always equals 2.0, a necessary requirement for a material's global charge balance. In an important followup study, Brown and Shannon (1973) found that the bond lengths observed for a wide variety of oxide materials correlate with bond strength to the extent that the correlation can be modeled with the power-law expression $s = (R_0/R)^{-N}$, where s is the strength of a given bonded interaction with length R. The regression constants R_0 and N were generated for the individual bond lengths observed for a large number of materials with the side constraint that the sum of the strengths of the bonded interactions reaching each cation and anion in a structure is equal to its formal valence. Numerous applications of the power law expression have since revealed that the sum of the strengths of the individual bonded atoms of a structure satisfies the valences of both the cations and anions well within a few percent, despite a relatively wide range of

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coordination numbers, valences, and the irregularity of the coordination polyhedra. Although Pauling defined bond strength within the context of a purely ionic model, the power law expression was found to be capable of modeling the bonded interactions in terms of the observed bond lengths for a wide variety of oxide materials, ranging from predominately closed–shell ionic to shared–electron covalent bonded interactions. This observation suggests, as observed by Brown and Shannon (1973), that the Pauling bond strength is more universal in its application and holds for intermediate bonded interactions ranging from predominately ionic to predominantly covalent (see footnote 63, Pauling 1960 and note added in proof, Gibbs et al. 1972). Evidence also suggests that bond strength is related in some way to the value of the electron-density distribution associated with a bonded interaction; the greater the value of the bond strength, the greater the localization of the electron density in the binding region (Gibbs et al. 2001).

In this paper, the bond-critical point properties of the electron-density distributions (Bader 1990), calculated for 275 bonded interactions for more than 40 Earth materials (Gibbs et al. 2001; Table 1, Downs et al. 2002) will be examined with the goal of establishing whether a connection exists between the Pauling bond strength and value of the electron density at the bond critical point of the individual bonded interactions.

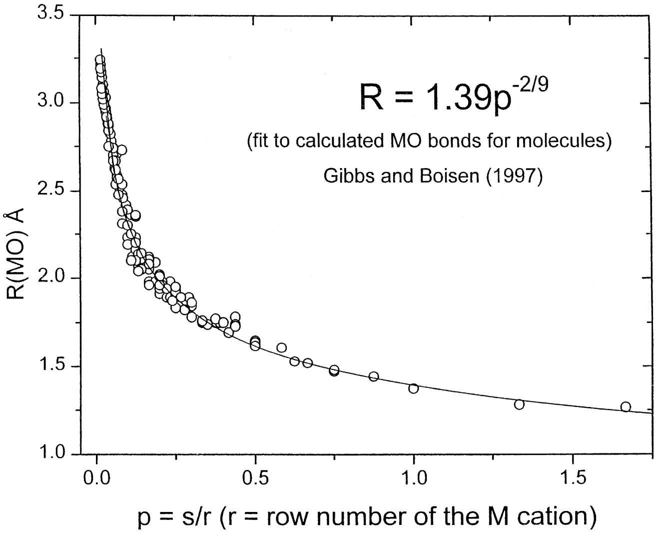

Fig. 1 Average bond-length data, ⟨R(MO)⟩ observed for the coordination polyhedra for a large number of oxide materials (Shannon 1976) plotted against the average bond strength $p = s/r$, where s is the Pauling bond strength of the MO bonds and r is the row number of the M cation (r = 1 for Li, Be, B, … and r = 2 for Na, Mg, Al, … (Gibbs et al. 2001). The *line* is a graph of the power-law expression $R = 1.39(s/r)^{-0.22}$ fit to the bond-length data generated for a variety of hydroxyacid molecules containing first- and second-row M cations. (Gibbs et al. 1987)

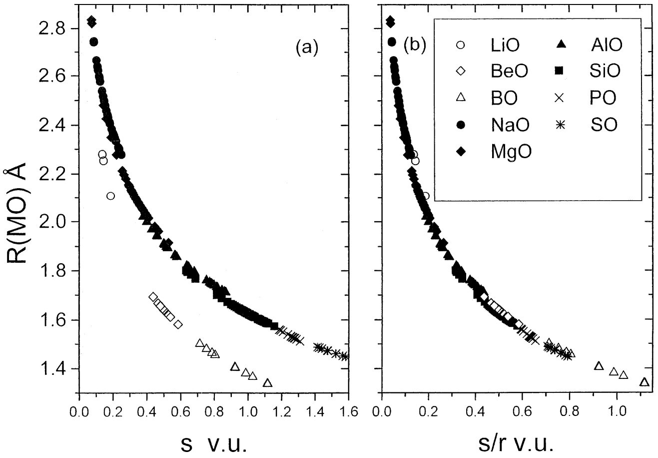

Fig. 2a, b Bond lengths observed for more than 40 oxide materials, R(MO), **a** plotted against Brown–Shannon (1973) bond strengths, s, and **b** the same bond lengths plotted against $p = s/r$. See text for the definition of r. The *open circles* in both **a** and **b** represent the LiO bonds; *open diamonds* BeO bonds; *open triangles* BO bonds; *open squares* CO bonds, *solid circles* NaO bonds; *solid diamonds* MgO bonds; *solid triangles* AlO bonds; *solid squares* SiO bonds; *crosses* PO bonds; *stars* SO bonds. (After Gibbs et al. 2001). The bond-length data used to prepare these plots are given by Downs et al. (2002) in Table 1 as determined by Gibbs et al. (2001)

The role of the M-cation periodic table row number on bond strength–bond length systematics

With the geometry optimization of a number of hydroxyacid molecules containing a variety of first- and second-row M cations, Gibbs et al. (1987) found that the resulting MO bond lengths, R(MO), scatter along two separate quasiparallel trends when plotted against the Pauling bond strengths, s, of the bonded interactions. For each trend, the calculated bond lengths correlate nonlinearly with increasing s; but, when s was divided by the Periodic Table row number r of the M cation, the bond-length data were found to be scattered roughly along a single trend when plotted against $p = s/r$. Moreover, they found that the resulting trend can be modeled with the power-law expression $R = 1.39p^{-0.22}$ where R is the geometry-optimized MO bond length. They also found that the bond lengths observed on average for the M cations from all six rows of the Periodic Table show a power-law trend that is statistically identical with that found for the molecules (Fig. 1). With the individual bond lengths observed for a large number of Earth materials (see above), Gibbs et al. (2001) used the Brown and Shannon (1973) expressions to generate the s values for each of the bonded interactions. The resulting s values are plotted against the observed bond lengths in Fig. 2a, where it is seen that the data define two roughly parallel trends, one for the bonded interactions involving first-row M cations and the other for second-row M cations. When the bond-strength values were each divided by the row number of the M cation and the observed bond lengths were plotted against s/r, the trend in Fig. 2b obtained. Moreover, when a power-law expression was fit to the dataset, the expression $R = 1.39(s/r)^{-0.22}$ emerged, exactly as observed for the molecules. It is noteworthy that Boisen et al. (1988)

undertook a graph–theoretic determination of the resonance bond numbers for the bonded interactions for representative moieties of ten silicate materials. When the observed bond lengths were examined in terms of n/r, the expression $R = 1.39(n/r)^{-0.22}$ was found, where n is the Lewis resonance bond number of the bonded interactions. Since the expression $R = 1.39(n/r)^{-0.22}$ is in a one-to-one correspondence with the expression $R = 1.39(s/r)^{-0.22}$ and since, in a classical sense, n can be viewed as the average number of electron pairs comprising a bond of length R, it appears that the Pauling bond strength is a direct measure of bond type; the greater the strength, the more covalent the bonded interaction and the greater the value of the electron density at the bond-critical point. It also suggests that bond strength can be equated with bond number defined as the number of valence electrons of a metal atom divided by its coordination number as done by Pauling (1947) in his study of bonded interactions in metals.

Connection between bond strength and value of the electron density at the bond critical point

As observed above, the electron-density distributions and the bond-critical point properties have been generated for the bonded interactions for a large number of Earth materials. With decreasing observed bond length, the value of the electron density at the bond critical point, $\rho(\mathbf{r}_c)$, increases nonlinearly along two nonlinear quasi-parallel trends, as observed when bond strength was plotted against the observed bond lengths, R(MO) (Fig. 3a). When $\rho(\mathbf{r}_c)$ is divided by the row number of the M cation, the data scatter roughly along a single trend with the shorter bonded interactions involving large values of $\rho(\mathbf{r}_c)$ (Fig. 3b). A modeling of the ρ/r data as a function of R yielded the expression $R = 1.42(\rho/r)^{-0.19}$. This expression (solid line) together with the expression $R = 1.39(\rho/r)^{-0.22}$ (dashed line) are both graphed in Fig. 3a. The graph for the expression $R = 1.42(\rho/r)^{-0.19}$ conforms with the trend of the data reasonably well. The curve of the expression $R = 1.39(\rho/r)^{-0.22}$ likewise conforms reasonably well with the data except with the exceptions of the BO- and CO-bond lengths which depart from the graph between 0.05 and 0.10Å. The similarity of the two expressions suggests that quotients s/r and $\rho(\mathbf{r}_c)/r$ are related, with large values of $\rho(\mathbf{r}_c)$ being associated with bonded interactions with large Pauling bond strengths. Given the correspondence between the two quotients, it is perhaps not surprising that the Brown and Shannon (1973) expression was found to be capable of modeling the bonded interaction for a wide range of materials, ranging from predominately ionic to predominately covalent (Brown and Skowron 1990). In other words, the greater the strength of a bonded interaction, the greater the electronegativity of the M cation, the greater the value of the electron density at the bond-critical point, and the more covalent the bonded interaction (Gibbs et al. 2001).

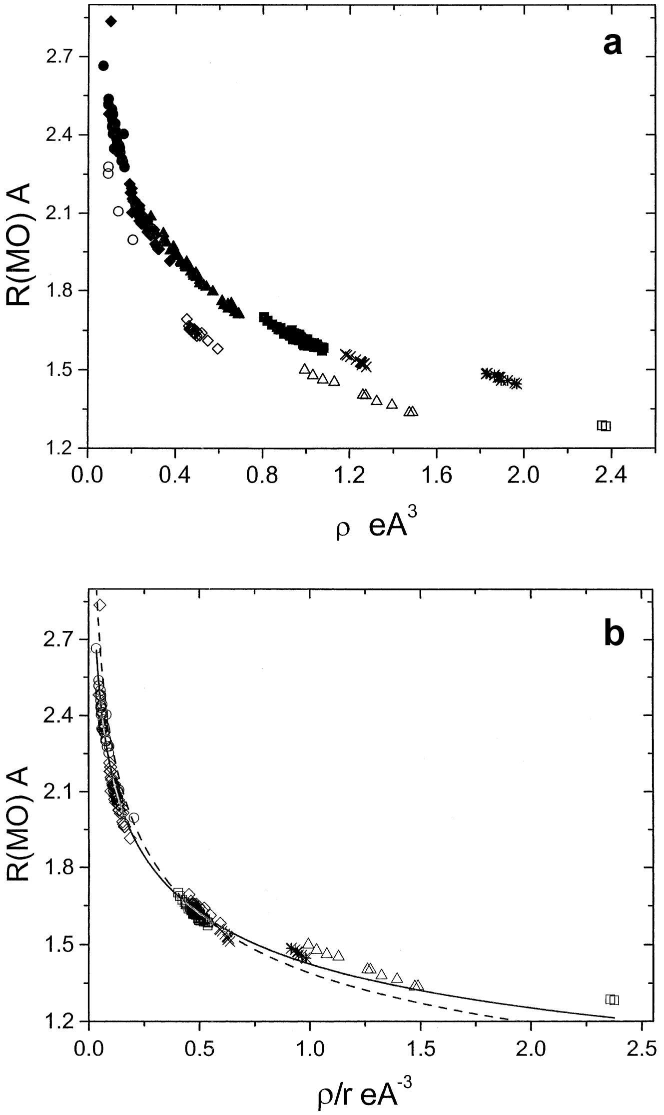

Fig. 3a, b Bond lengths, R(MO), observed for more than 40 oxide materials plotted against **a** the value of the electron density evaluated at the bond-critical points for each bonded interaction and **b** against the value of the bond-critical electron density, $\rho(\mathbf{r}_c)$, divided by the row number r of the M cation. The data symbols used in **a** are defined in the legend to Fig. 2. *Open symbols* are used for all of the bonds in **b** to avoid excessive overlap of the data points. The $\rho(\mathbf{r}_c)$ values used to prepare the plots were reported by Downs et al. (2002) as determined by Gibbs et al. (2001). The *solid line* in **b** is a graph of the expression $R = 1.42(\rho/r)^{-0.19}$ obtained in a regresssion analysis of the data and the *dashed line* is a graph of $R = 1.39(\rho/r)^{-0.22}$ where 1.39 and −0.22 are values obtained for the expression $R = 1.39(s/r)^{-0.22}$ (see legend Fig. 1)

Some closing comments

Regardless of whether the bonded interactions comprising a coordinated polyhedron in oxide materials involve predominately ionic or predominately covalent interactions, the average bond length for a polyhedron correlates with the average Pauling bond strength of its component bonded interactions. The structures of a few materials have been found to be inconsistent with bond strength–bond length considerations. But, to our knowledge, these structures are usually incorrect to one degree or another (cf. Baur 1970; Brown and Shannon 1973). Bond strength considerations have also been used to explain the absence of certain materials in nature despite the reasonable stoichiometric character of their chemical formulae. The fact that the bond strength is highly correlated with the value of the electron density at the bond-critical point is consistent with its universal application and measure of the strength of a bonded interaction; the greater its value, the greater the localization of the electron density in the binding region, the more covalent the interaction, and the shorter the bond. It also attests to Pauling 's genius in formulating a simple yet powerful definition of bond strength that is connected to the localization of the electron density in the binding region of a bonded interaction. Finally, the success of bond strength in providing a basis for the structures and bond length variations for a large number of inorganic materials closely parallels the success of resonance bond number in providing a basis for the structures and bond length variations for a large number of organic aromatic molecules. Despite the different bases upon which the definitions were made, this correspondence suggests that the bond strength and bond number are measuring similar properties of a bonded interaction and that bond strength in a universal measure of the localization of electron density in the binding region of a bonded interaction.

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