MSA Review

Pauling's rules for oxide-based minerals: A re-examination based on quantum mechanical constraints and modern applications of bond-valence theory to Earth materials

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Abstract

Since their introduction in 1929, Pauling's five rules have been used by scientists from many disciplines to rationalize and predict stable arrangements of atoms and coordination polyhedra in crystalline solids; amorphous materials such as silicate glasses and melts; nanomaterials, poorly crystalline solids; aqueous cation and anion complexes; and sorption complexes at mineral-aqueous solution interfaces. The predictive power of these simple yet powerful rules was challenged recently by George et al. (2020), who performed a statistical analysis of the performance of Pauling's five rules for about 5000 oxide crystal structures. They concluded that only 13% of the oxides satisfy the last four rules simultaneously and that the second rule has the most exceptions. They also found that Pauling's first rule is satisfied for only 66% of the coordination environments tested and concluded that no simple rule linking ionic radius to coordination environment will be predictive due to the variable quality of univalent radii.

We address these concerns and discuss quantum mechanical calculations that complement Pauling's rules, particularly his first (radius sum and radius ratio rule) and second (electrostatic valence rule) rules. We also present a more realistic view of the bonded radii of atoms, derived by determining the local minimum in the electron density distribution measured along trajectories between bonded atoms known as bond paths, i.e., the bond critical point ($\mathbf{r}_c$). Electron density at the bond critical point is a quantum mechanical observable that correlates well with Pauling bond strength. Moreover, a metal atom in a polyhedron has as many bonded radii as it has bonded interactions, resulting in metal and O atoms that may not be spherical. O atoms, for example, are not spherical in many oxide-based crystal structures. Instead, the electron density of a bonded oxygen is often highly distorted or polarized, with its bonded radius decreasing systematically from ~1.38 Å when bonded to highly electropositive atoms like sodium to 0.64 Å when bonded to highly electronegative atoms like nitrogen. Bonded radii determined for metal atoms match the Shannon (1976) radii for more electropositive atoms, but the match decreases systematically as the electronegativities of the M atoms increase. As a result, significant departures from the radius ratio rule in the analysis by George et al. (2020) is not surprising. We offer a modified, more fundamental version of Pauling's first rule and demonstrate that the second rule has a one-to-one connection between the electron density accumulated between the bonded atoms at the bond critical point and the Pauling bond strength of the bonded interaction.

Pauling's second rule implicitly assumes that bond strength is invariant with bond length for a given pair of bonded atoms. Many studies have since shown that this is not the case, and Brown and Shannon (1973) developed an equation and a set of parameters to describe the relation between bond length and bond strength, now redefined as bond valence to avoid confusion with Pauling bond-strength. Brown (1980) used the valence-sum rule, together with the path rule and the valence-matching principle, as the three axioms of bond-valence theory (BVT), a powerful method for understanding many otherwise elusive aspects of crystals and also their participation in dynamic processes. We show how a priori bond-valence calculations can predict unstrained bond-lengths and how bond-valence mapping can locate low-Z atoms in a crystal structure (e.g., Li) or examine possible diffusion pathways for atoms through crystal structures.

In addition, we briefly discuss Pauling's third, fourth, and fifth rules, the first two of which concern the sharing of polyhedron elements (edges and faces) and the common instability associated with structures in which a polyhedron shares an edge or face with another polyhedron and contains high-valence cations. The olivine [α-$(Mg_xFe_{1-x})_2SiO_4$] crystal structure is used to illustrate the distortions from hexagonal close-packing of O atoms caused by metal-metal repulsion across shared polyhedron edges.

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