Electronic structure effects in the vectorial bond-valence model

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ABSTRACT

The vectorial bond-valence model (VBVM) describes the spatial distribution of bonds to each atom in a system in terms of the vector sum of the incident bond valences. It has been applied in the past to cations not subject to electronic structure effects (e.g., lone-pair or Jahn-Teller effects) in which case the expectation is that the vector sum will be approximately zero. Here we analyze 178 simple-oxide crystal structures and show that the vectorial bond-valence sum is a predictable function of the atomic valence (oxidation state) of each atom and the valence of the strongest bond to atoms for which second-order Jahn-Teller and lone-pair effects play a role in determining molecular geometry. Outliers are uniformly metastable or unstable under ambient conditions, suggesting that deviation from ideal vectorial bond-valence sums might be used as a proxy for some aspect of structural potential energy. These results are all strictly in harmony with the VSEPR model of molecular geometry, but may allow for more quantitative prediction.

Keywords: Crystal structure, oxide, bond valence, vectorial bond-valence model, electronegativity, lone pair, second-order Jahn-Teller effect, spherical symmetry, minimum coordination number

INTRODUCTION

The bond-valence model (BVM) has become a standard in inorganic chemistry for predicting acceptable combinations of bonds, with their corresponding lengths, to ions in solid structures, as well as for assessing unknown oxidation states of ions in crystals (Brown 2002, 2009). It is now commonplace (e.g., Müller et al. 2003) to assess the plausibility of proposed crystal structures in terms of their adherence to the valence-sum rule, which states that in a stable crystal structure, the valence of bonds incident to an ion should ideally counterbalance the atomic valence of the ion (see the Theory section below for details). Bickmore et al. (2009) recently used ab initio molecular dynamics simulations to show that the valence-sum rule applies on a time-averaged basis to liquid structures, in addition to solids.

Simple structural models like the BVM, e.g., the Lewis model and the valence shell electron pair repulsion (VSEPR) model, have historically been very important for generating new ideas about, for example, reaction mechanisms (Brown 2003). And yet, the BVM stands apart from the others because of its ability to make quantitative predictions of bond lengths via the valence-sum rule. The BVM is conceptually and mathematically very simple, as it boils down complex, multi-body interactions into a single parameter, the bond-valence sum, which is predictive for many systems.

Even in cases where known structures deviate significantly from BVM predictions, the model can prove useful by identifying which aspects of the molecular structure cause the strain. If the valence-sum rule puts constraints on structures, it follows that deviation from the rule entails some energetic cost. Several quantitative structure-activity relationships (QSARs) have been formulated based partially on energy cost functions for deviation from the valence-sum rule (Salinas-Sanchez et al. 1992; Hiemstra et al. 1996; Adams 2001; Adams and Swenson 2002; Adams et al. 2004; Bickmore et al. 2004, 2006; Adams and Rao 2009; Perez-Mato et al. 2009). In fact, Rappe and coworkers have constructed a molecular mechanics force field based on such a cost function, along with several more standard potential energy terms (Grinberg et al. 2002, 2004; Cooper et al. 2003; Shin et al. 2005).

BVM-based energy cost functions are attractive because bond-valence calculations are empirically calibrated for different cation-anion pairs, so that the end product (bond valence) is a common currency, no matter what types of atoms are involved. This point is well illustrated by the work of Angel and colleagues, who showed that the rate of change of bond-valence sums with pressure is constant for cations in both the A and B sites in ABO3 perovskites (Zhao et al. 2004a, 2004b; Angel et al. 2005b, 2005a; Zhao et al. 2006). Such a relationship would be very unlikely if the bond valence-energy relationship were substantially different for A-O and B-O bonds.

QSARs based solely on the valence-sum rule necessarily have limited applicability, because they are an incomplete description of molecular structure. Since bond valences are only calculated between cations and anions, the model obviously neglects non-bonded forces such as would be needed to describe ligand-ligand interactions. And even if non-bonded interactions were addressed in the BVM, the valence-sum rule is non-directional, i.e., con-