*American Mineralogist, Volume 98, pages 340–349, 2013*

# 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