A Step Closer to Predicting the Bonding Geometry of Crystals

I.D.Brown

Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1. idbrown@mcmaster.ca

Abstract

A recent paper in this journal by Bickmore et al. (2013, Amer. Min., 98, 340-349) describes an important extension of the bond valence model which allows us to predict the size of the distortions found in the environment of atoms with electronic anisotropies, paving the way for a quantitative prediction of bond lengths and angles around these atoms.

Text

X-ray diffraction provides a remarkably accurate picture of the way in which atoms arrange themselves to form the materials we see around us.   The discovery of this method exactly a hundred years ago served to confirm the structure predictions of the ball-and-stick model that chemists had developed to account for the many compounds formed by carbon; indeed for organic molecules the diffraction experiments could add nothing more to this model than lengths of the bonds. For minerals the situation was different. X-ray diffraction revealed more complex structures where the ball-and-stick model no longer worked. The ionic model provided a framework for describing mineral structures, but without computers quantitative predictions were impossible. Pauling (1929) attempted to bring order to the description of mineral structures with his electrostatic valence rule, but it was only when more accurate crystal structures became available that we realized that the distance between two atoms gives us a direct measure of the number of electrons each atom contributes the bond they form, a quantity now known as the bond valence. Since the valence of an atom is defined as the number of electrons it uses for bonding, and since we can use the bond length to determine how many electrons are used to form each bond, we can test a proposed structure by seeing whether the valences of the bonds add up to the valence of the atom that forms them. Checking bond valence sums is now a routine part of validating newly determined structures of minerals and inorganic crystals.

The success of the bond valence sum rule has led to further exploration of what bond valences

can tell us about complex structures (Brown, 2009). Within the ionic model, the bond valence can be identified with the electrostatic flux that links a cation to its neighboring anions, turning a bond network into a capacitive electrical circuit which can be solved using Kirchhoff's circuit equations. The bond valences predicted in this way give bond lengths that are as accurate as those predicted by other methods such as quantum mechanics.

This raises the question of whether we can also use bond valences to predict bond angles. In many structures atoms adopt the most symmetric possible arrangement: four bonds are arranged tetrahedrally and six bonds octahedrally. Atoms rarely form only five bonds because all five bonds can never be symmetrically equivalent. Harvey at al. (2006) recently showed how to determine when an atom is at the most symmetric point in its coordination sphere, even when all the ligands are different. They treated the bond valence as a vector directed from the cation to the anion and assumed that when an atom was in its most symmetric position, the sum of the bond valences vectors would be zero. This is the case when the atom's bonding electrons are uniformly distributed over the surface of the atom, so that the solid angle each bond subtends at the atom is proportional to its valence. It may not always be easy to convert the solid angles to interbond angles, but it does explain their observed variations.

There are cases where the bond valence vector sum is clearly not zero. This occurs around atoms subject to steric stresses or electronic anisotropy. Steric stress caused by the contact between the donor and acceptor atoms is responsible for the asymmetry of hydrogen bonds, and electronic anisotropy distorts the environment around atoms with lone pairs as well as around d^0 transition metals, the latter distortions being sometimes referred to as a second-order Jahn-Teller effect. In these cases the bond valence vector sum is not expected to be zero, but hitherto there has been no systematic study of how large we might expect it to be. This lack has now been remedied by the paper recently published in this journal by Bickmore et al. (2013)

Bickmore and his collaborators examined 178 simple oxide structures. They arranged the atoms into four groups: atoms that are expected to have valence vector sums of zero, oxygen atoms with lone pairs, cations with lone pairs, and d^0 transition metals. The most important factor they identified is the electronegativity, which is expressed in the bond valence model by the valence of the atom divided by its coordination number. This number is also the average valence of the bonds formed by the atom. Since the coordination number in distorted environments can be

difficult to define, Bickmore et al. used the valence of the strongest bond as a surrogate for the electronegativity and examined how this correlates with the bond valence vector sum. As expected, the valence vector sums around the first group are close to zero. The most impressive results are found for oxygen. If the strongest bond formed by oxygen has a valence of less than 0.5 valence units (vu) the valence vector sum is zero, meaning that the lone pair is inactive, but when the strongest bond has a valence greater than 0.5 vu, the valence vector sum increases linearly with the valence of the bond. They found similar correlations for the two groups of cations, though because the samples were smaller and each graph includes several different cations, the graphs tend to show more scatter.

This paper shows that bond valences can be used to predict bond angles at least qualitatively, even in cases where electronic effects influence the geometry. More work is needed to identify other relevant factors, particularly those related to the cation distortions. For example, we need to explore the role of the ligand environments; the authors suggest that ligand-ligand repulsion may be responsible for some of the outliers in their graphs. With this paper, Bickmore and his colleagues have moved the bond valence model another major step forward. If we follow up this work we should soon be able to use it to predict the bonding geometry of even the most complex of mineral structures.

References

Bickmore, B.R., Wander, M.F.C., Edwards, J., Maurer, J., Shepherd, K., Meyer, E., Johansen, W.J., Frank, R.A., Andros, C. and Davis, M. (2013) Electronic Structure Effects on the Vectorial Bond-valence Model. Americal Mineralogist, 98, 340-349.

Brown, I.D. (2009) Recent Developments in the Methods and Applications of the Bond Valence Model. Chemical Reviews, 109, 6858-6919.

Harvey, M.A., Baggio, S., and Baggio, R. (2006) A New Simplifying Approach to Molecular Geometry Description: the Vectorial Bond Valence Model. Acta Crystallographica, B62, 1038-1042.

Pauling, L. (1929) The Principles Determining the Structures of Complex Ionic Crystals. Journal of the American Chemical Society 51, 1010-1026.