

Hawthorne H&B.

ON UNDERSTANDING THE STRUCTURE AND COMPOSITION OF CRYSTALS

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Minerals come with complex chemical formulas and a variety of crystal structures, but although many different mineral are known, their number is far exceeded by the possible structures and compositions that apparently do not occur in nature. What is it that selects the particular combinations of compositions and structures that we observe? This is the question addressed in a recent paper in this journal by Frank Hawthorne (Hawthorne 2015). He answers this question using *bond valence theory* which he carefully distinguishes from what he calls *bond valence curves*, more usually known as the *bond valence sum (BVS)* model widely used for the validation of new structure determinations.

Based on the ionic model, the bond valence theory is a powerful tool for addressing questions such as the one posed above. In this theory, bonds are constructed in the ionic model by linking the cations to their neighboring anions by Faraday lines of electric field, the number of such lines being called the *electrostatic flux*. What makes this a powerful model is that the electrostatic flux has exactly the same properties as the traditional chemical bond: both describe a localized two-body interaction between neighboring atoms, both depend only on the amount of charge each atom contributes to the bond (known as the bond valence) and neither depends on where that charge is located. This last condition is important because it means that the ionic model can be used regardless of whether the bonding charge is physically located on the anion or whether it is concentrated at the center of the bond; in all cases the flux is the same. This description of bonding is complementary to the quantum picture which tells us where the charge is located but cannot say how much charge each atom contributes to individual bonds. By identifying a bond with its flux one can use electrostatic theory to derive the theorems of all the bonding models that are based on localized bonds, including the empirical rules of the traditional ball and stick model of organic chemistry (Brown 2014a), the rules of the VSEPR model of lone pairs (Gillespie and Hargattai 1991), and the rules of the ionic model as described by bond valences (Brown 2002). The flux theory shows that all localized bonds have the same physical origin and all obey the

same theorems which can, for example, be used to predict the bonding geometries of many compounds without the need to know their crystal structures (Brown 2014a).

Because the bond valence model treats a crystal or molecule as an array of atoms linked by chemical bonds, a chemical structure can be treated as a network of bonds whose properties depend both on its topology and on the valences and coordination numbers of its constituent atoms. For a given atom, dividing the valence by the coordination number gives the average flux (or valence) of the bonds it forms. If one uses a typical coordination number, one has an estimate of the typical valence of a bond, which can therefore be used to represent the bonding strength of that atom. Since the bonding strength of the cation and the anion are both estimates of the valence of the bond between them, the most stable bond should be formed between two atoms that have the same bonding strength. The greater the difference between the bonding strengths, the less stable the bond; if the bonding strengths differ by more than a factor of two, the bond is unlikely to form. Hawthorne calls this important theorem the ‘correspondence principle’, otherwise known as the ‘valence matching rule’.

This rule is remarkably powerful, because it identifies which atoms are most likely to form bonds. It can be used to generate the bond network from the chemical formula by matching strong cations with strong anions and weak cations with weak anions. The network can be displayed in the form of a molecular diagram or as an adjacency matrix whose elements describe whether or not a bond exists between each pair of atoms. In the Huckel approximation, the Schrodinger equation is expressed by a similar adjacency matrix whose topology can be characterized by a series which displays the numbers of loops in the network that contain exactly 2, 4, 6, etc. bonds. This is a series that approximates the various moments of the density of states, and Hawthorne shows how by analyzing the changes that occur in the topology during a chemical reaction one can obtain information about the changes in enthalpy.

In complex ions that have both Lewis acid and Lewis base functions, the bonding strength can be used as a measure of Lewis acid and base strength. To address the problem of mineral structure and composition, Hawthorne divides the structures of minerals into two parts. The strongly bonded complex ions (usually anions), which he calls *structural units*, are linked together by a weakly bonded *interstitial component* (usually cationic) to form a crystal. The boundary between the valence of the strong and the weak bonds is chosen as 0.30 valence units (vu), a number that ensures that any water molecules in the mineral reside in the interstitial component. If a crystal is to be formed, the Lewis base strength of the structural unit must match the Lewis acid strength of

the interstitial component, which places restrictions on the composition of both. Hawthorne argues that the form adopted by the structural unit is determined by the cations available in the interstitial component, and that the bonding strengths of the two parts of the mineral are equalized by inclusion of a predictable number of water molecules in the interstitial component.

Hawthorne's paper provides a very readable summary of the approach he has developed to analyzing and predicting mineral structure. It illustrates just one of the applications that elevates the bond valence model to the level of a theory of structural chemistry rather than just a technique for validating newly determined crystal structures. Other applications include the prediction of crystal structures (e.g., Lufaso and Woodward 2014), understanding how chemical structure affects the physical properties of solids (Brown 2009), extending the VSEPR model to include the secondary bonds formed around lone pair atoms in crystals (Bickmore et al. 2014), identifying diffusion paths in crystals and glasses (Adams and Swenson, 2000), and exploring surface structures and reactions (Bickmore et al. 2006). The flux theory that underlies the bond valence model has two special properties that particularly commend it. Firstly it provides a simplified but physically correct picture of chemical bonding which makes it more suitable for analysing the physical nature of the bond than any of the traditional bond models, such as covalent and ionic bonds, Lewis electron pairs, or hybridized orbitals. Secondly, since it involves only simple physical concepts, it is an ideal theory for introducing students to chemical bonding and structure (Brown 2014b). Not least, its implementation in the bond valence theory makes it a powerful tool for tackling complex problems in condensed matter research (Brown 2009).

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