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Theoretical Prediction of Bond-Valence Networks

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Abstract

By representing a bond-valence network to which the valence-sum rule applies as an oriented bipartite multigraph, it is possible to use matrix methods to obtain an exact solution without making successive approximations. For this solution to be unique requires some equivalent of the Kirchhoff voltage law be applied to the system; the methods of Mackay & Finney [*J. Appl. Cryst.* (1973), **6**, 284–289] and Brown [*Acta Cryst.* (1977), **B33**, 1305–1310] involve two distinct special cases of such a rule. In general, the bond valences **s** can be calculated from the formal charges **f** as $\mathbf{s} = [\mathbf{I} - \mathbf{C}(\mathbf{C}'\mathbf{U}^{-1}\mathbf{C})^{-1}\mathbf{C}'\mathbf{U}^{-1}]\mathbf{B}_T^{-1}\mathbf{f}$, where $\mathbf{B}_T$ is the incidence matrix of a spanning tree of the graph, matrix **C** represents the corresponding fundamental cycles, and U_i is some function of the weight of edge *i*.

Introduction

Any successful attempt to make an *a priori* prediction of inorganic crystal structures will necessarily include predictions of individual bond lengths. Brown (1977) has suggested that these bond lengths may be derived, in turn, from estimates of the bond valence, which obey the 'valence-sum rule', or electroneutrality principle, a set of concepts originated by Pauling (1929). Empirical relationships between bond length and bond valence are now well established (Brown & Shannon, 1973; Brown, 1981), and methods such as that of Meier & Villiger (1969) may predict the structure once the ideal bond lengths are known. The problems remaining are to predict the connectivity of the structure, and to estimate the individual bond valences from the connectivity.

An advance on this last-mentioned problem was the realization by Mackay & Finney (1973) that it was in some ways analogous to an electrical network problem to which Kirchhoff's laws apply; in particular the valence-sum rule is equivalent to Kirchhoff's current law.

However, the matrix method they introduced appears to become unwieldy in all but simple cases. Brown (1977) increased the scope of the method by introducing an 'equal-valence rule', not obviously linked to Kirchhoff's laws, which allowed him to solve the network problem for a number of fairly complex structures. However, Brown's method is again an iterative one, for which computing time increases rapidly as the network increases in size.

Since the chief difficulty with both approaches seemed to be the exact form of restriction to play the role of the voltage law in this system, it seemed worthwhile to re-examine the whole problem, using simple graph theory.

Method

The analysis follows the terminology and methods in Bollobás (1979) in dealing with electrical networks by matrix methods. The symbols *n* and *m* are used for the size and order of the graph, respectively. For clarity, we first consider the case where there are no atoms which form bonds with two or more other atoms, which are themselves symmetry-related images of each other. This restriction is very unlikely in practice, but would be true, for example, for a structure in space group $P1$, provided the axis lengths are sufficiently large. It is always possible, however, to ignore the inherent symmetry to achieve this situation. We can then take the contents of the unit cell as the vertices of the graph, and the bonds, including bonds to vertex images in neighbouring unit cells, as the edges of the graph.

If the structure consists of alternating cations (Lewis acids) and anions (Lewis bases), the graph formed is 'bipartite', and if each edge is defined as beginning at the base and ending at the acid, it is also 'oriented'.

The electrical network problem can be expressed in matrix form as the current law (1), the voltage law (2), and Ohm's law (3).

$$\mathbf{Bw} = 0 \tag{1}$$

$$\mathbf{C}'\mathbf{p} = 0 \tag{2}$$

$$\mathbf{p} = \mathbf{Rw} + \mathbf{g}. \tag{3}$$

The vectors **w**, **p** and **g** are the current, voltage and voltage generator, and **R** is a diagonal matrix of the

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resistances. The graph-theoretical concepts introduced are the incidence matrix $\mathbf{B}$, and $\mathbf{C}$, a matrix of the fundamental cycle vectors. Using $\mathbf{f}$ for the atomic valences and $\mathbf{s}$ for the bond valences, the valence-sum rule can be written:

$$\mathbf{Bs} = \mathbf{f}. \tag{4}$$

This is superficially similar to (1). However, unlike (1), for which a change in the direction of an edge merely changes the sign of one component of $\mathbf{w}$, (4) holds for one specific orientation of the graph only.

Equation (4) alone does not produce a unique solution to the network, because, given one solution, there exist other solutions related to it by the alternate addition and subtraction of a constant around any circuit of the graph. We can prevent this effect by applying a rule that there must be no net bond-valence alternation of this sort around any cycle of the graph, and, in fact, we need only apply it to the fundamental cycles. In that case, we have

$$\mathbf{C}'\mathbf{s} = 0. \tag{5}$$

This is obviously similar to (2). However, equations (4) and (5) involve the same vector $\mathbf{s}$, while (1) and (2) involve $\mathbf{w}$ and $\mathbf{p}$, requiring a third equation (3) to link the two.

Given this formulation, we may follow Bollobás in splitting the graph into a spanning tree T and chords N, constructing $\mathbf{B}_T$, $\mathbf{B}_N$, $\mathbf{C}_T$, $\mathbf{s}_T$ and $\mathbf{s}_N$. However, Bollobás introduces an additional vertex into the graph, which is subsequently ignored in order to produce a square matrix $\mathbf{B}_T$. This is unnecessary, as it is possible to construct $\mathbf{B}_T^{-1}$, the left inverse of B_T, by other means. The dimensions of $\mathbf{B}_T$ and $\mathbf{B}_T^{-1}$ are $(n, n-1)$ and $(n-1, n)$, respectively, as the spanning tree has n vertices and $n-1$ edges. Otherwise a parallel derivation to that in Bollobás may be followed, using the relation $\mathbf{C}_T = -\mathbf{B}_T^{-1}\mathbf{B}_N$ to give

$$\mathbf{s} = [\mathbf{I}_m - \mathbf{C}(\mathbf{C}'\mathbf{C})^{-1}\mathbf{C}']\mathbf{B}_T^{-1}\mathbf{f} \tag{6}$$

where $\mathbf{I}_m$ is the mth-order identity matrix, and '$\mathbf{B}_T^{-1}$' is a matrix of dimension (m, n), being the concatenation of B_T^{-1} with the $(m-n+1,\ n)$ null matrix, *i.e.*

$$\left[\frac{B_T^{-1}}{0}\right].$$

In other words we have an answer in the form

$$\mathbf{s} = \mathbf{Mf} \tag{6a}$$

where $\mathbf{M}$ is derived from properties of the graph.

This is comparable to the electrical network solution

$$\mathbf{w} = -\mathbf{C}(\mathbf{C}'\mathbf{RC})^{-1}\mathbf{C}'\mathbf{g}. \tag{7}$$

The information regarding the cycles in the graph is included in the matrix $\mathbf{C}$ of dimensions $(m, m-n+1)$. A convenience in this method is that $\mathbf{C}$ may be constructed by matrix operations without explicit searching, for

$$\begin{aligned}\mathbf{C} &= [\mathbf{C}_T|\mathbf{C}_N]\\ &= [-\mathbf{B}_T^{-1}\mathbf{B}_N|I_{m-n+1}].\end{aligned}$$

An example of $\mathbf{C}$ is given in Table 1.

Table 1. *Matrices for $K^{2,3}$*

(*a*) $\mathbf{M}'$ (×6), (*b*) $\mathbf{M}''$ for the KVO_3 structure (×65), (*c*) $\mathbf{B}_T$, (*d*) $(\mathbf{B}_T^{-1})'$ (×2), (*e*) $\mathbf{C}$.

$$\begin{array}{c} \text{Atom} \\ 1\\2\\3\\4\\5 \end{array}
\begin{array}{c} \text{Edge} \\ \begin{array}{cccccc} a & b & c & d & e & f \end{array} \\ \left[\begin{array}{rrrrrr} 1 & 1 & 1 & -1 & -1 & -1\\ -1 & -1 & -1 & 1 & 1 & 1\\ -3 & 0 & 0 & -3 & 0 & 0\\ 0 & -3 & 0 & 0 & -3 & 0\\ 0 & 0 & -3 & 0 & 0 & -3 \end{array}\right] \\ (a) \end{array}
\begin{array}{c} \\ \begin{array}{cccccc} a & b & c & d & e & f \end{array} \\ \left[\begin{array}{rrrrrr} 20 & 10 & 10 & -20 & -10 & -10\\ -5 & -10 & -10 & 5 & 10 & 10\\ -25 & 0 & 0 & -40 & 0 & 0\\ 0 & -19 & -6 & 0 & -46 & 6\\ 0 & -6 & -19 & 0 & 6 & -46 \end{array}\right] \\ (b) \end{array}$$

$$\begin{array}{c} 1\\2\\3\\4\\5 \end{array}
\begin{array}{c} \left[\begin{array}{rrrr} 1 & 1 & 0 & 0\\ 0 & 0 & 1 & 1\\ 0 & 0 & -1 & 0\\ -1 & 0 & 0 & -1\\ 0 & -1 & 0 & 0 \end{array}\right] \\ (c) \end{array}
\qquad
\begin{array}{c} \left[\begin{array}{rrrr} 1 & 1 & 1 & 1\\ -1 & 1 & 1 & 1\\ -1 & 1 & -1 & -1\\ -1 & 1 & 1 & -1\\ 1 & -1 & 1 & 1 \end{array}\right] \\ (d) \end{array}$$

$$\begin{array}{c} \text{Cycle} \\ a \\ f \end{array}
\begin{array}{c} \text{Edge} \\ \begin{array}{cccc|cc} b & c & d & e & a & f \end{array} \\ \left[\begin{array}{rrrr|rr} -1 & 0 & -1 & 1 & 1 & 0\\ 1 & -1 & 0 & -1 & 0 & 1 \end{array}\right] \\ (e) \end{array}$$

Equation (6) involves two matrix inversions. The matrix $\mathbf{C}'\mathbf{C}$ is symmetric and standard methods can be used. The matrix $\mathbf{B}_T$, however, is not square, and a special method for its inversion is outlined in the *Appendix*. The overall method has been implemented as a Basic language computer program.

As an illustration, the method can be applied to a complete bipartite graph of order 5, that designated $K^{2,3}$. This graph has two vertices in one class and three in the other, and is shown in Fig. 1. It is also the graph used by Mackay & Finney for their example of $BaTiO_3$. Table 1 shows the corresponding $\mathbf{M}$ matrix. It is not in its original form, but has been made to show the symmetry of the problem by the addition of a constant to the elements in each row. This alteration is valid, since the elements of $\mathbf{f}$ must sum to zero by definition. If we now allow for the case where an atom may be bonded to two or more equivalent atoms, the complexity of the graph is reduced by associating a weight with each edge of a collapsed form, which is a directed multigraph. In this way we reduce the order of the graph to correspond to the asymmetric unit or the formula unit of the crystal, whichever is larger. Multigraphs based on $K^{2,3}$ represent the structures of most M_2X_3 compounds, the various alkali-metal nitrates and halates, the perovskite, ilmenite, calcite and aragonite structure types, but not the pyroxenes, and not the majority of the alkali-metal metapnictates. However, potassium metavanadate (Evans, 1960), is one useful exception to which $K^{2,3}$ does apply.

In the case of a multigraph, each edge has an associated weight w_i. Although it is formally correct to build these weights into **B** and **C**, again for clarity we use the alternative of creating a diagonal matrix **W**, and treating **s** as the total bond valence for that edge. Then the individual bond valences are given by $\mathbf{W}^{-1}\mathbf{s}$, and (4) remains unaltered.

However, if we examine the voltage law, we find not one, but two, possibilities have been suggested. Although presented without a physical explanation, Mackay & Finney's matrix elements correspond to (5), which now requires no alternation of bond valences around a cycle of the multigraph, which lumps equivalent bonds together. On the other hand, Brown's equal-valence rule applies the same criterion to a cycle of individual bonds, and therefore takes the matrix form

$$\mathbf{C}'\mathbf{W}^{-1}\mathbf{s} = 0. \tag{8}$$

The same manipulations as before now give

$$\mathbf{s} = [\mathbf{I}_m - \mathbf{C}(\mathbf{C}'\mathbf{W}^{-1}\mathbf{C})^{-1}\mathbf{C}'\mathbf{W}^{-1}]\mathbf{B}_T^{-1}\mathbf{f} \tag{9}$$

$$\mathbf{s} = \mathbf{M}'\mathbf{f}. \tag{9a}$$

Table 1 gives the resulting matrix for the KVO_3 structure, which is one of the few based on this graph for which the bond valences cannot be allocated by inspection, as they can for $BaTiO_3$, for example. KVO_3 gives a good opportunity to compare the two approaches, since it must involve a very large range of bond valences. The two very different answers given by (6) and (9) are shown in Table 2.

Discussion

The results derived above have several interesting features. Firstly the matrix **M** or **M′** contains only information about the network, and therefore a particular network need be solved only once, even though there may be several isostructural compounds with distinct atomic valences, or distinct structures reducible to the same graph, as with the zinc blende and wurtzite, and calcite and aragonite pairs. Also the matrix elements are necessarily rational, and therefore rational values of the bond valences are predicted, provided integer values of the atomic valences are used.

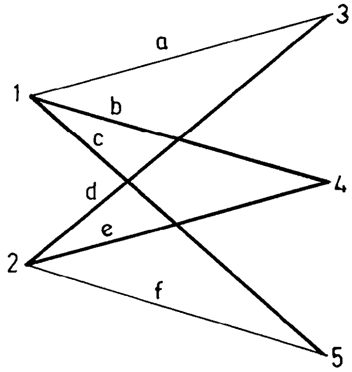

Fig. 1. The graph $K^{2,3}$ showing the numbering used in the tables. The spanning tree is shown as heavy lines, and the light lines are the chords.

Table 2. *Calculated and observed bond valences for* KVO_3

	V—O(1)	V—O(2)	V—O(3)	K—O(1)	K—O(2)	K—O(3)
Edge	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
Calculated by equation						
(6)	5/6	5/3	5/3	1/6	1/12	1/12
(9)	29/26	18/13	18/13	− 3/26	2/13	2/13
Observed	0·95	1·47	1·52	0·15	0·16	0·17
					0·11	0·05
					0·06(× 2)	0·02(× 2)
			Average		0·10	0·07

The method improves on earlier approaches in not being iterative, and in dealing with structure types independent of chemical formulae. It also specifies the minimum $m - n$ cycles required to define a solution, an aspect not considered by Mackay & Finney.

The question remains as to whether equation (6) or equation (9) is the better criterion to predict bond valence. For many structures their effects are either identical or very similar, and it is necessary to find examples, such as KVO_3, for which they differ markedly. It appears from the KVO_3 results that (9) places too much emphasis on equalizing valences at vertices of low degree (here V), at the expense of higher-degree vertices in the same class (here K). In the same way, for example, Brown predicts for $K_2S_5O_{16}$ (De Vreis & Mijlhoff, 1969), variations which are too small for S, and too large for K. Equation (6) also seems somewhat unsatisfactory, but in the opposite sense.

This suggests it may be possible to improve the agreement of the network method by formulating the 'voltage law' as

$$\mathbf{C}'\mathbf{U}^{-1}\mathbf{s} = 0$$

analogous to combining (2) and (3) for the electrical network, where **U**, like the resistance, is an empirical property of the edges, possibly of the form $\mathbf{I} + \lambda\mathbf{W}$ or $\mathbf{W}^{\lambda}$.

I wish to thank Professor I. D. Brown for suggesting the problem, and for helpful comments.

APPENDIX

The approach adopted to finding an inverse to the rectangular matrix is an alternative to the much more general Moore–Penrose method, and is specific to the particular problem discussed here. This is because it relies on certain properties of a tree graph, as can be seen from what follows.

$\mathbf{B}_T$ is a matrix in which each column contains one element of value 1, one -1, and the rest zero. The corresponding row of its inverse has only values $\pm\frac{1}{2}$, the sign depending on whether that vertex lies in the same component of the graph as the positive or negative end of the corresponding edge used as cut. Table 1 gives the $K^{2,3}$ case. For programming purposes the components are best determined from a matrix of distances within the spanning tree T, for then each vertex takes the sign of the nearer end of the edge which is cut. The distance matrix is constructed by first forming the adjacency matrix of the tree, $\mathbf{A}_T$, using $\mathbf{A}_T = \mathbf{B}\mathbf{B}' - \mathbf{V}$ where $\mathbf{V}$ is a diagonal matrix of the vertex degrees.

Then the zero elements A_{Tik} are found for which A_{Tij} and A_{Tjk} are both non-zero, and are filled in with the distance of the path ijk, namely $A_{Tij} + A_{Tjk}$. Repetition of this procedure will find all distances up to and including 2, 4, 8 ... and so on, until the distance matrix is complete.

It is now possible to determine each element of $\mathbf{B}_T^{-1}$ by comparing two elements of this distance matrix, which we may call $\mathbf{P}$. However, the programming may be made even simpler by noting

$$\mathbf{B}_T^{-1\prime} = -\tfrac{1}{2}\mathbf{P}\mathbf{B}_T.$$

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On the Crystal Structure of Staurolite. The X-ray Crystal Structure of Staurolite from the Pyrenees and Brittany

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Abstract

The crystal structures of two natural crystals of staurolite, from Heas, the Pyrenees (*H*), and Scaer, Brittany (*S*), France, have been refined from X-ray Mo $K\alpha$ data at 293 K. Monoclinic, $C2/m$, $Z = 1$. (*H*): $\mathrm{Fe_{3\cdot59}Ti_{0\cdot09}Mn_{0\cdot01}Zn_{0\cdot01}Mg_{0\cdot83}Al_{17\cdot90}Si_{7\cdot50}O_{45}(OH)_3}$, $M_r = 1690{\cdot}8$, $D_x = 3{\cdot}79$ g cm^{-3}, $\mu = 28{\cdot}01$ cm^{-1}, $a = 7{\cdot}8700$ (9), $b = 16{\cdot}6228$ (18), $c = 5{\cdot}6613$ (4) Å, $\beta = 90{\cdot}124$ (5)°, $V = 740{\cdot}6$ (2) Å^3, $R(F) = 0{\cdot}018$ for 2494 unique reflections. (*S*): $\mathrm{Fe_{3\cdot38}Ti_{0\cdot11}Mn_{0\cdot06}Zn_{0\cdot47}Mg_{0\cdot75}Al_{17\cdot81}Si_{7\cdot66}O_{45}(OH)_3}$, $M_r = 1684{\cdot}9$, $D_x = 3{\cdot}777$ g cm^{-3}, $\mu = 27{\cdot}52$ cm^{-1}, $a = 7{\cdot}8713$ (2), $b = 16{\cdot}6235$ (7), $c = 5{\cdot}6608$ (2) Å, $\beta = 90{\cdot}016$ (2)°, $V = 740{\cdot}71$ (8) Å^3, $R(F) = 0{\cdot}026$ for 2997 unique reflections. It is demonstrated that the crystal structure of staurolite can be derived from that of spinel through crystallographic shear. The geometric differences between the (*H*) and (*S*) varieties and previously studied staurolites are confined to the partially occupied cation sites. The disorder in the tetrahedral Fe site can be effectively modelled using third- and fourth-order coefficients of a Gram–Charlier expansion of the Fe temperature factor or by a threefold-split Fe(*A*/*B*/*C*) site. Model calculations demonstrated that neither the difference electron density ($\Delta\rho$) peak separation, nor the $\Delta\rho$ peak heights, are directly interpretable, while the increase in temperature-factor coefficients owing to disorder is reliably related to the site splitting. The separation between the Fe(*A*/*B*/*C*) positions is estimated to be 0·25 Å. The large variation between previously reported Fe-site $\Delta\rho$ peak separations can be related to different experimental resolutions. The present study suggests that the Fe-site splitting is in the range 0·20–0·25 Å for all staurolites.

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