

Theoretical Prediction of Bond-Valence Networks. II. Comparison of the Graph-Matrix and Resonance-Bond Approaches

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Abstract

This paper provides a common framework for the bond-valence and resonance-bond-number methods, both of which explain the principal variations in inorganic bond lengths from the sum of radii, as arising from the connectivity of the structure, and therefore may apply graph information in conjunction with the Valence-Sum Rule. Under these constraints, possible predictions are limited to specific ranges of $(M - N + 1)$ parameters, where M and N are the size and order of a multigraph describing the crystal motif. Further restrictions on these parameters may arise from non-crystallographic graph symmetries. Convenient graph-theoretical calculation schemes are described for both approaches. As it is possible to identify the best possible prediction within the limits described, which is that most closely corresponding to the experimental result, we have a means of making a direct comparison of the effectiveness of the various methods proposed, as well as being able to evaluate them against a statistically based prediction. The resonance-bond-number method proves to be the better predictor in most cases. Examples analysed in this way comprise KVO_3 (potassium metavanadate), $\alpha\text{-Ga}_2\text{O}_3$ (gallium oxide), TeI_4 [tellurium(IV) iodide], Li_2SiO_3 (lithium metasilicate), Li_2GeO_3 (lithium metagermanate) and CaCrF_5 (calcium chromium fluoride).

1. Introduction

The bond-valence approach to the description of inorganic crystal structures, originally due to Pauling (1929) and Zachariasen (1963), has gained popularity in recent years, with the bond-valence/bond-length relations of Brown & Shannon (1973) and subsequent improvements in the applicability of the approach to verifying structures (Brown, 1978, 1981; Brown & Altermatt, 1985). Recently there has been a great deal of interest shown in this bond-valence approach because of the correlations found with the experimental transition

temperatures of high-temperature ceramic superconductors (Brown, 1989, 1990). However, the possibility of using theoretically predicted bond-valence networks as a basis for the *a priori* calculation of probable bond lengths has not received much attention and, in fact, little progress was made on this problem until it was examined from a graph-theory viewpoint, starting with the observation of Mackay & Finney (1973) that the solution might have certain formal parallels to the use of Kirchhoff's Laws in the solution of electrical-network problems. This was followed by some work of Brown (1977) using iterative methods, which led in turn to the graph-theoretical analysis of the work of Mackay and Finney and of Brown given in the previous paper in this series (Rutherford, 1990). About the same time O'Keeffe (1989) reviewed the earlier work, and provided further insight and analysis of his own. O'Keeffe supported Brown's 'Equal-Valence Rule': subject to no other constraints, bonds from an atom strive to be as equal in valence as possible. Brown (1989) pointed out that his Equal-Valence Rule gave results equivalent to O'Keeffe's 'Ring-Sum Rule' and has since (Brown, 1992) shown formally that the two approaches are mathematically equivalent. Rutherford (1990) found that for examples not sufficiently symmetric to be trivial, there are an infinite number of solutions to the bond-valence network problem, including two special cases, one corresponding to the method of Mackay & Finney (1973) and the other to that of Brown (1977) and O'Keeffe (1989). Both special cases correspond to specific constraints on the bond valences in addition to the basic sum requirement; they operate in the network system in the same way as the Kirchhoff voltage law does in the electrical case, that is, in terms of the cycles present in the chemical graph of the structure.

2. The graph-theory approach

For a crystal the true chemical graph is very large. However, we can represent the crystal structure by a finite graph of N vertices (atoms) and m edges (bonds), corresponding to the motif of the structure, and then convert the graph thus formed to a weighted multi-

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Table 1. Observed and calculated bond valences for $K^{2,3}$ -based structures

Edge	Algebraic form	u	Obs	KVO ₃ Bond valences			u	Obs	β -Ga ₂ O ₃ Bond valences		
				EVR	RBN	Stat			EVR	RBN	Stat
a	$(f_1 - f_2 + 1)/3 + 2x$	2	0.99	1.12	0.93	0.89	1	0.72	0.68	0.71	0.85
b	$(f_1 + 1)/3 - x - y$	1	1.47	1.38	1.57	1.61	1	0.83	0.83	0.86	0.90
c	$(f_1 + 1)/3 - x + y$	1	1.50	1.38	1.57	1.61	2	0.76	0.75	0.71	0.62
d	$f_2 - 2x$	2	0.17	-0.12	0.07	0.11	3	0.41	0.44	0.43	0.38
e	$x + y$	4	0.11	0.15	0.11	0.10	2	0.51	0.59	0.57	0.55
f	$x - y$	4	0.08	0.15	0.11	0.10	1	0.57	0.51	0.57	0.75
σ			0.07	0.13	0.07	0.08		0.04	0.05	0.04	0.11

Abbreviations: Obs: observed value averaged over the u components; EVR: the graph-matrix method using the Equal-Valence Rule; RBN: resonance-bond-number method; Stat: the graph-matrix method using statistical weighting; σ : standard deviation of the calculated bond valences from the individual observed values; $\sigma(\text{Obs})$: standard deviation of the best-fit Valence-Sum Rule values of the bond valences from the individual observed values.

graph, in which each of the M multiple edges, with individual weights u_i , correspond to the u_i bonds from one atom to symmetry-equivalent versions of a second. This multigraph represents the limit of possible prediction of the bond-valence distribution, because we have no way of distinguishing individual bond components of each multigraph edge, but can only make a prediction regarding their sum, based on a knowledge of these weights. This limitation provides an important step in simplifying the overall solution. The multigraph is associated with a solution space of $(M - N + 1)$ dimensions, as described by Rutherford (1991).

Now, $(M - N + 1)$ is also the cyclomatic number of the multigraph, *i.e.* the number of cuts required to reduce it to a tree. This means that when we describe the solution space in terms of $(M - N + 1)$ variables, say x, y *etc.*, each of these variables can be associated with a specific basis vector in some representation of the cycle space of the directed multigraph. For example, the graph $K^{2,3}$ in Fig. 1 has six edges and so a cycle is represented by a vector with six elements, which may have the values $-1, 0$ or 1 . The fundamental cycle matrix \mathbf{C} for this graph, as given in Rutherford (1990), is (after reverting to alphabetic order for the edges): $[1\bar{1}0\bar{1}10/01\bar{1}0\bar{1}1]$. From this we can extract the two basis vectors $\mathbf{u}_1 = [1\bar{1}0\bar{1}10]$ and $\mathbf{u}_2 = [01\bar{1}0\bar{1}1]$, which correspond to cycles $1 \rightarrow 3 \rightarrow 2 \rightarrow 4 \rightarrow 1$ and $1 \rightarrow 4 \rightarrow 2 \rightarrow 5 \rightarrow 1$, respectively. However, to reflect the possible symmetry in the problem, we instead chose an orthogonal pair of basis vectors, one of which transforms symmetrically under a specific graph automorphism (permutation of vertices 4 and 5), and the other anti-symmetrically. These are

$$\mathbf{w}_1 = 2\mathbf{u}_1 + \mathbf{u}_2 = [2\bar{1}\bar{1}\bar{2}11]$$

and

$$\mathbf{w}_2 = -\mathbf{u}_2 = [0\bar{1}101\bar{1}].$$

Parameter x in Table 1 relates to \mathbf{w}_1 and y to \mathbf{w}_2 . This choice of basis ensures y is zero if vertices 4 and 5 are

equivalent. Most problems may be simplified by applying symmetry in a similar way.

Also, it should be noted that the fundamental constraints remain the same for any multigraph based on the same pattern of vertices and edges and, therefore, may be related for a number of structures with the same stoichiometry.

3. Resonance bond numbers

This approach, as developed by Boisen *et al.* (1988), effectively ignores the periodicity of the problem. The calculations for each atom are based on a 'pattern graph', a subgraph of the periodic chemical graph selected on the basis of a graph distance of 3, and

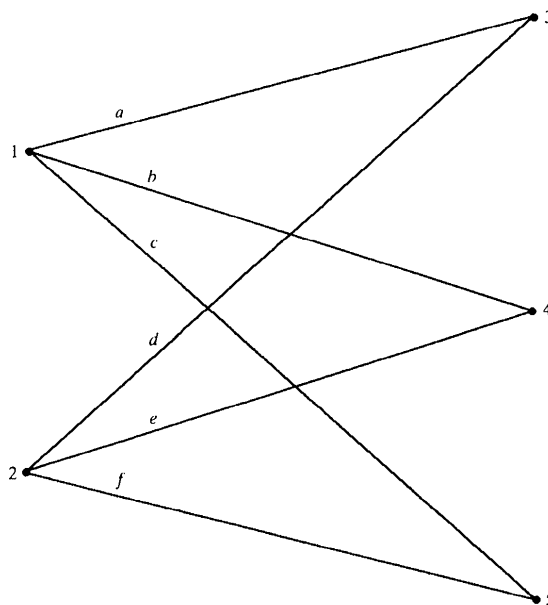


Fig. 1. The graph $K^{2,3}$ showing the labelling used in Table 1.

specifically omit any non-nearest-neighbour interactions, such as the type represented by the Dewar resonance structures for benzene. The totality of Lewis graphs (arrangements of electron-pair bonds) which are allowed by these restrictions is then derived and the (equally weighted) average resonance bond number is calculated. This method seems to be highly successful, but it is certainly cumbersome, involving perhaps 10^7 to 10^8 Lewis graphs per atom. It also lacks any obvious way of being programmed and contains certain inherent inconsistencies which arise from the localized nature of the model. These are that different values may be calculated for the same bond, depending on the central atom used for the pattern graph, and that a single pattern graph will normally contain bonds which are equivalent, either by crystallographic or graph symmetry, but for which different resonance bond numbers are calculated. However, the approach has the one strength that it would be equally applicable to glasses as to crystalline solids.

3.1. Simplified resonance bond number (RBN)

We can interpret the resonance bond number in terms of the configuration space introduced above. By their very construction individual Lewis graphs will satisfy the bond-valence constraints; that is, they will correspond to points within the solution space of the problem. An extreme point of this solution space will normally correspond to a periodic Lewis graph where the same arrangement of bonds is repeated in each unit, or to several such periodic graphs which are multigraph equivalent. The assumptions made in reducing the Lewis graphs on pattern graphs to their equivalents on the finite multigraph are discussed in Rutherford (1991). In this process the resonance bond number becomes an average over the distribution of such extremal Lewis graphs within the solution space of the multigraph.

The possible Lewis graphs can be enumerated through the generating function

$$F = \prod_{i=1}^M (1 - e_i v_{1i} v_{2i})^{-u_i},$$

where e_i is a dummy variable representing the edge i , and v_{1i} and v_{2i} are the vertices it joins. This is the Pólya figure-generating function (Pólya & Read, 1987) applied to a multigraph based on a labelled and, therefore, asymmetric pattern graph as the frame. However, in addition to the usual edge functions, we introduce associated vertex functions so that the edge property of figure content may be transformed into the vertex property of degree. The generating function may be expanded as a product of m formal infinite series, where m is the number of edges of the multigraph, to

give

$$F = \prod_{i=1}^M (1 + e_i v_{1i} v_{2i} + [e_i v_{1i} v_{2i}]^2 + \dots)^{u_i} \\ = \prod_{i=1}^M \left\{ 1 + \sum_{r=1}^{\infty} [(u_i + r - 1)! / (u_i - 1)! r! [e_i v_{1i} v_{2i}]^r] \right\}.$$

Valid Lewis graphs are enumerated by those terms which have the degree of each vertex, as measured by the power of the corresponding vertex function, equal to the appropriate valence. In addition, the arrangements of bonds on the edges of the graph, termed the figure content by Pólya & Read (1987), are represented by powers of the edge functions, with the effect that the combined coefficient of any individual term in the vertex-function powers forms a pattern inventory of Lewis graphs for that arrangement of atom valences.

As an example, the generating function for KVO_3 is (Rutherford, 1991)

$$F = (1 - e_a v_1 v_3)^{-1} (1 - e_b v_1 v_4)^{-1} (1 - e_c v_1 v_5)^{-2} \\ \times (1 - e_d v_2 v_3)^{-4} (1 - e_e v_2 v_4)^{-4} (1 - e_f v_2 v_5)^{-2},$$

where v_1 is V, v_2 is K and the remaining vertices are O.

The coefficient of the relevant term, namely that in $v_1^5 v_2 v_3^2 v_4^2 v_5^2$, is

$$[12e_a^2 e_b^2 e_c^2 e_d + 12e_a^2 e_b e_c^2 e_e + 4e_a^2 e_b^2 e_c e_f].$$

This inventory of Lewis graphs indicates that there are 28 possible arrangements in all, while the first term in the coefficient, for example, shows that 12 of them have edge a as a single bond, edge b as a double bond, edge c as some arrangement of either two single bonds or one double bond, and one component of edge d as a single bond.

No computer was used for the calculations by this method; however, a system capable of manipulating symbols could well be used to extract the required coefficient from the generating function.

4. Graph-matrix method

For the sake of clarity it is useful to establish the exact relationship of the electrical-network and bond-valence cases by stating them both in terms of a more general problem on a directed graph.

We have two properties a_i and σ_i of each edge i , such that they are proportional to each other with a known coefficient δ_i . That is, $\sigma_i = \delta_i a_i$ or, in matrix terms

$$\sigma = \Delta a, \quad (1)$$

where Δ is a diagonal matrix of the coefficients δ_i . We also consider two further sets of equations, one representing a constraint on the vertices of the graph

$$B a = \beta \quad (2)$$

and the other on its circuits or loops

$$\mathbf{C}^t \sigma = \gamma, \quad (3)$$

where \mathbf{B} is the incidence matrix of the graph and \mathbf{C} its fundamental cycle matrix. These terms and others below are explained in Bollobás (1979) and Rutherford (1990). We then seek values α_i and σ_i , which are solutions to this system of equations. We first combine (1) and (3) to give

$$\mathbf{C}^t \Delta \alpha = \gamma. \quad (4)$$

Then, applying the methods used previously, we find that the solution to this more general problem is

$$\alpha = [\mathbf{I} - \mathbf{C}(\mathbf{C}^t \Delta \mathbf{C})^{-1} \mathbf{C}^t \Delta] \mathbf{B}_T^{-1} \beta + \mathbf{C}(\mathbf{C}^t \Delta \mathbf{C})^{-1} \gamma, \quad (5)$$

where \mathbf{I} is the identity matrix and \mathbf{B}_T is the incidence matrix of a spanning tree of the graph. This result includes both real problems as special cases: for the electrical networks $\beta = 0$, while for the bond-valence networks $\gamma = 0$.†

We may now look at the practical application of the bond-valence result. Rutherford (1991) concluded that it was possible to generate a wide variety of bond-valence predictions for a particular graph (and hence crystal structure) based on differing values of the matrix elements corresponding to Δ . This is the matrix which represents the resistances in the electrical-network case and which arises not from Kirchhoff's laws, but from Ohm's law, (1) in our formulation. Through this law we can predict how the overall result is affected by linking two vertices by different numbers, n , of identical lengths of wire. The resistance R_{ii} varies as $1/n$ in such a case. In general, the matrix element δ_i behaves in this way if it represents a property of an edge component which is invariant to its position in the graph, which is the case for O'Keeffe's 'Ring-Sum Rule' and Brown's 'Equal-Valence Rule'.

In order to see that such 'ohmic' behaviour, however intuitive, is inappropriate in the bond-valence case, we must recognize that a further set of constraints operates in that system, namely the requirement that the value of each individual bond valence must be positive. This is different from the electrical-network case, where the current in a particular edge may have either sign (flow in either direction).

4.1. Equal-Valence Rule (EVR)

The calculations were carried out according to Rutherford (1990), except that the distance matrix was derived from successive powers of the adjacency matrix,

† In fact, O'Keeffe (1989) attempted to make the two problems equivalent by constructing a new graph which interchanges the role of vertices and cycles; however, he admits he is unable to describe a general procedure. An approach based on the familiar form of the chemical graph is clearly preferable.

a computationally more efficient method than by that used previously.

4.2. Statistical weighting (Stat)

The calculations are identical to EVR above, except for the input values of the weight matrix Δ . Rutherford (1991) suggested

$$\delta_i = \{2[(1 - f_i)/2]^{1/u_i} - f_i\} / \{1 - f_i\},$$

where δ_i is the appropriate element of the weight matrix and $f_i = v_{\min}/v_{\max}$, the ratio of extreme valence values possible for that bond. The intention was to represent that part of the bond-valence variation that may be predicted from the Valence-Sum Rule and graph connectivity alone, without recourse to any bonding model whatsoever. However, this weighting would be equivalent to the more general form of the resonance method, provided we could make the clearly unwarranted assumption that the distribution of Lewis graphs is uniform over the $(m - N + 1)$ -dimensional total configuration space, at least when measured on a sufficiently coarse scale.

5. Examples

The intention in this section is to apply the various calculation schemes to a number of known structures, in order to compare their effectiveness as predictors. For each example the best fit of the experimental results to an $(M - N + 1)$ -parameter model is included, as this represents the best possible prediction within the constraints.

In order to be a suitable example a crystal structure must be sufficiently simple to allow the algebraic analysis to be carried out and yet have the number of free parameters $(M - N + 1)$ non-zero, so that the various schemes will lead to different results. O'Keeffe (1989) and Rutherford (1990) have both noted that the fraction of structures with both these properties is small. In addition, such test examples should involve (if possible) large variations in atom valence, coordination number and the number u of multigraph equivalent bonds, as it is these factors which produce the difference in results between the different models.

All observed interatomic distances were converted to bond valences using the form

$$V = \exp\{-(R - R_o)/b\}$$

and the parameters of either Krebs & Paulat (1976), for TeI_4 only, or Brown & Altermatt (1985). For each example the methods were compared by calculation of the standard deviation of the predicted bond valence from their observed values; the equivalent standard deviation of an arbitrary 'best-fit' Valence-Sum Rule model was also calculated as a benchmark.

Table 2. Observed and calculated bond valences for Te_4I_{16}

Edge type	Algebraic form	u	Obs.	Bond valences		
				EVR	RBN	Stat
a	1	1	1.00	1.00	1.00	1.00
b	x	1	0.38	0.20	0.27	0.25
c	$(1+x)/2$	1	0.64	0.60	0.64	0.63
d	$(1-x)/2$	1	0.32	0.40	0.36	0.38
σ			0.02	0.05	0.03	0.03

Abbreviations: see Table 1.

5.1. KVO_3

This structure (Evans, 1960) was used as an example by Rutherford (1990). The bond valences calculated by the various schemes are indicated in Table 1.

5.2. $\beta\text{-Ga}_2\text{O}_3$

This structure (Geller, 1960) was used by O'Keeffe (1989) as one of his examples. It is very interesting in that, although there are only Ga—O bonds, the structure contains both four- and six-coordinated Ga, and distinct u_i values of 1, 2 and 3. As with KVO_3 , it is based on $K^{2,3}$, but the multigraph is now asymmetric, so that non-zero values of both parameters x and y are predicted, giving six distinct bond valences in all. Such is the character of this example that to simply predict the correct order of these six bond lengths is a stringent test of the model.

The solution space for the parameters x and y is shown in Fig. 2; it is subdivided by lines corresponding to the various possible equalities between pairs of these six bond valences. It shows that 54 different bond-length sequences are possible within the constraints of

the Valence-Sum Rule and that the resonance approach is best at predicting the correct sequence. Again, the numerical results are given in Table 1.

5.3. TeI_4

This structure (Krebs & Paulat, 1976) is included because it was used by Brown (1977) as one of his examples. Although it is a binary compound with a very unusual range of connectivities and iodine coordination numbers, it is perhaps out-of-place in being a molecular (Te_4I_{16}) rather than an infinite lattice complex. The connectivity of this molecule is shown Fig. 3 and the results given are in Table 2. Despite this problem being defined (after consideration of the graph symmetry) by one parameter only, none of the approaches are particularly close to the observed bond-valence arrangement, despite the Valence-Sum Rule being closely observed in this compound. In particular, this applies to the resonance-bond method, even though the counting of Lewis graphs can be performed exactly, rather than being a statistical process. These difficulties may arise either because the molecular nature of this compound introduces additional geometric constraints not present in infinite networks or from electronic distortions of Te^{IV} .

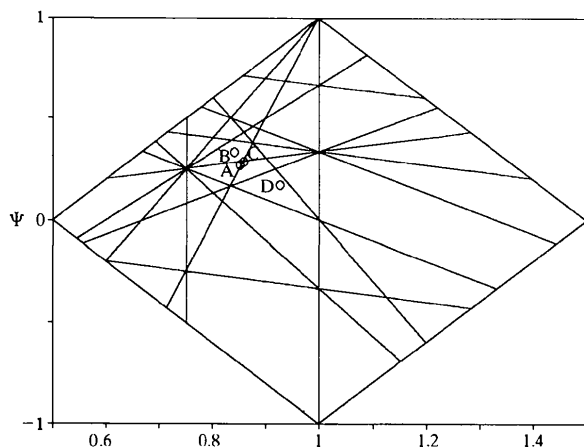


Fig. 2. The location of the various models within the solution space for $\beta\text{-Ga}_2\text{O}_3$. A Observed bond lengths; B Equal-Valence Rule; C resonance bond number; D statistical weighting.

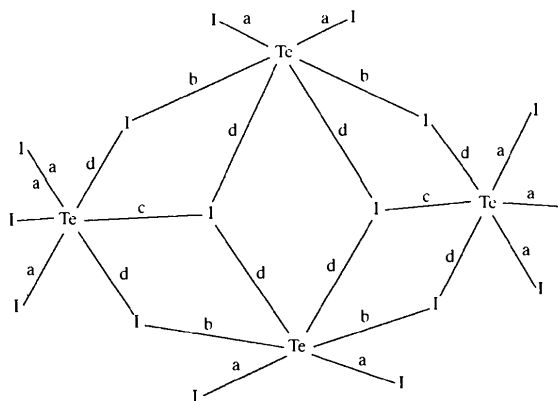


Fig. 3. The connectivity of the molecule Te_4I_{16} , showing the labelling used in Table 2.

Table 3. Observed and calculated bond valences for Li_2XO_3 compounds

Edge expression	Algebraic	u	Bond valences				
			$X = Si$	$X = Ge$	EVR	RBN	Stat
Li—O1	x	3	0.26	0.26	0.30	0.28	0.29
Li—O2	$2 - x$	1	0.16	0.16	0.10	0.18	0.14
X—O1	$4 - x$	1	1.12	1.13	1.10	1.18	1.14
X—O2	x	2	0.86	0.83	0.90	0.83	0.86
$\sigma(Si)$			0.02	—	0.04	0.03	0.03
$\sigma(Ge)$			—	0.02	0.05	0.03	0.03

Abbreviations: see Table 1.

5.4. Li_2SiO_3 and Li_2GeO_3 (Hesse, 1977; Vollenkle & Wittmann, 1968)

These compounds are isostructural and the experimental distributions of bond valence are very similar in the two cases. This example was used by O'Keeffe (1989). In this case the multigraph corresponding to the formula unit has inherent symmetry and may be simplified further for the purposes of the graph-matrix approach, in this case by folding the equivalent portions over on each other like the pages of a book. In order to give the correct result the merging of two equivalent vertices must double their valence, but keep the edge multiplicities the same. This is illustrated in Fig. 4. However, this simplification cannot be applied to the resonance method, because it is absolutely necessary to distinguish between the equivalent vertices in counting the Lewis graphs. The numerical results for this example are given in Table 3.

5.5. $CaCrF_5$ (Wu & Brown, 1976)

This is another case where the formula unit has inherent graph symmetry; if the multigraph shown in Fig. 5 is folded over on itself about the centre line, a multigraph based on $K^{2,3}$ again results. Table 4 gives the results for this compound; here, the correct trends in Cr—F and Ca—F bond lengths are reasonably predicted by all approaches.

6. Conclusions

In most cases the Valence-Sum Rule applies to the interatomic distances in a crystal structure and only a

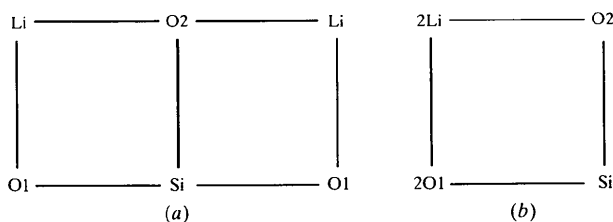


Fig. 4. The (a) 'open' and (b) 'closed' forms of the Li_2SiO_3 graph.

Table 4. Observed and calculated bond valences for $CaCrF_5$

Edge type	u	Obs	Bond valences		
			EVR	RBN	Stat
Cr—F1	2	0.47	0.41	0.43	0.38
Cr—F2	1	0.49	0.48	0.47	0.51
Cr—F3	1	0.60	0.61	0.60	0.61
Ca—F1	1	0.17	0.19	0.13	0.24
Ca—F2	2	0.26	0.26	0.27	0.25
Ca—F3	1	0.37	0.39	0.40	0.39
σ		0.03	0.03	0.03	0.05

Abbreviations: see Table 1.

small part of the observed variation arises from geometrical constraints. The rule fails, however, not only for ceramic superconductors (Brown, 1989, 1990), but also for other structures with highly coordinated cations such as K in its hydroxylamine-*N,N*-disulfonate salt (Rutherford *et al.*, 1988) and in many cases of hydrogen bonding (Brown, 1978). Such cases have been discussed by Brown (1992). Nevertheless, the major source of variation in bond lengths in most structures depends on the overall connectivity of the atoms in the structure and is, in principle, predictable in terms of the

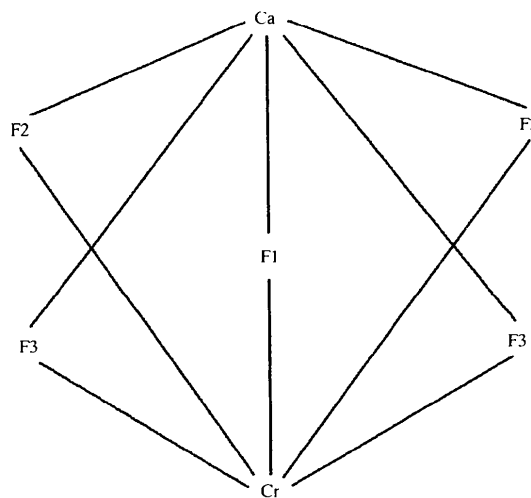


Fig. 5. The $CaCrF_5$ graph.

chemical graph. For this reason, those attempts at prediction which have met with any degree of success have so far all included some elements of graph theory.

However, no single approach has been entirely satisfactory. The Equal-Valence Rule does not represent the optimum solution in cases of large charge variation, where some sort of average over the permitted configurations is preferable. Overall, the resonance bond-number method appears best, with the standard deviation σ consistently within 0.01 valence units of the 'best-fit' value. This result suggests that the future direction in this area should be to improve the resonance approach so that it becomes as easy to apply as the graph-matrix formulation is at present.

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