

A Cation–Anion Distance-Dependent Method for Evaluating Valence-Bond Distributions in Ionic Structures and Results for Some Olivines and Pyroxenes

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A method is described for evaluating the bond strengths in known ionic structures according to the Pauling electroneutrality principle with formal charges assumed for the ions and with allowance being made for different cation–anion distances within a cation–anion polyhedron by distributing the bonds in amounts that are inversely proportional to the cation–anion distances. Where the CN of a cation by anions is in doubt, evaluations may be made for different reasonable CN's, and the one(s) that yields closest to ideal results may be taken as the most probable. The relationships are derived both for summing the bond strengths to each anion from its surrounding cations, and for calculating the standard deviations of the total bond strengths to each anion from the experimental errors in the cation–anion distances. Computer program *VLBDDDB* capable of carrying out such calculations for a wide variety of ionic structures is described. The bond strengths computed in this way for eight refined olivine structures show that for conventional coordination numbers (CN's) for Si, M1 and M2 of 4, 6 and 6 respectively, the three oxygens in each of the eight olivines receive within ~ 0.01 v.u. or 11σ of the ideal of 2 v.u., but in all eight olivines the values for oxygens O(1) and O(2) are within 2σ of 2.010 and for O(3) within 2σ of 1.990 v.u. (where $1\sigma \leq \sim 0.003$ v.u.). For eight ordered clinopyroxenes and three orthopyroxenes, the results show that nearly ideal bond strengths are received by each of the three oxygens only for the unconventional CN's for M1 and M2 of 4 and 4, that is when each is regarded as bonded to its two closest pairs of non-bridging oxygens O(1) and O(2). Under this assumption, each of the three oxygens in all 11 of these pyroxenes receives within 0.05 v.u. or $\sim 11\sigma$ of the ideal of 2 v.u. However, as with the olivines, the results show some striking consistencies in that certain groups of corresponding oxygens receive within $\sim 3\sigma$ of the same value. The bond strengths for several different assumed CN's of M1 and M2 are, for corresponding oxygens, very close in the two Li and the four Na clinopyroxenes, but markedly different from this in the two ordered Ca clinopyroxenes examined. The consistencies of certain of the results suggest that, for a number of crystals within one closely related isostructural group, comparable anions are required to receive the same total bond strengths, and the relative cation–anion distances within the different structures are constrained to assure that this is so.

Introduction

The work described here is based on an application of Pauling's well-known electroneutrality principle which has been widely used to interpret ionic structures, and which may be expressed in the following way (Evans, 1964, p. 180): 'The total strength of the valency bonds which reach an anion from all the neighbouring cations is equal to the charge on the anion'. The evaluation of the valence bonds contributed by the cations to the anions, when done by the original simple Pauling method or by the modification of that method described here, has meaning only for those structures that have more than one structural anion: if a structure has only one anion, that anion must inevitably receive from the cations a total bond strength equal to its negative charge. Only when the evaluation is done by some other methods, for example that of Brown & Shannon (1973), is this not strictly so. Thus Pauling's original electroneutrality principle and its modification described here

have no meaning for many of the simpler high-symmetry structures including such important silicate minerals as quartz (SiO_2) and garnet [for example, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$] which have only one structural anion. In general, this principle is applicable to the more complex, lower-symmetry ionic structures such as those of the olivines, pyroxenes, amphiboles, micas, feldspars *etc.*

The authors of numerous recent papers in this journal and others, describing structure analyses of natural and synthetic silicates, phosphates, sulphates, borates, *etc.*, have interpreted their structures in terms of bond distributions according to the Pauling electroneutrality principle, either in its simplest form where no account is taken of different cation–anion distances within a given cation–anion polyhedron, or in some modification of the Pauling principle that attempts to make allowance for such different cation–anion distances. The most widely used modifications are probably those of Zachariasen (1963), Evans (1960), Donnay & Allmann (1970), and Brown & Shannon (1973). Closely related to these is the procedure of Baur (1970, 1972) for predicting cation–anion bond distances. Some other theoretical approaches that are relevant to the interpretation

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of inorganic structures are the bonding theories of Cruickshank (1961) and the calculations of Madelung energies to determine cation site preferences in amphiboles by Whittaker (1971), but the procedure I describe below is most closely related to the cation-anion distance-dependent methods of those authors listed above.

In relation to the method described here we ask, in essence, some pertinent questions: if for a given structure for which there is reasonable doubt about the coordination number (CN)* of the cations, for example the M2 site in a clinopyroxene (the Ca site in $\text{CaMgSi}_2\text{O}_6$), does one assumed CN for that cation (and reasonable assumed CN's for the other cations) result in ideal bond strengths to each of the anions? If not, does one assumed coordination result in bond strengths to the anions that, although not ideal within the limit of error, are distinctly closer to the ideal than for a different assumed coordination for that site? And further, if in a structure group such as the pyroxenes, the 'best' (closest to the ideal) bond strengths to the anions for particular coordinations of the cations are, although the best, still not ideal within the limit of error, is there any pattern or consistency within the structure group to the bond strengths that do result? The method for evaluating valence-bond distributions in ionic structures that I describe in this paper has as its purpose the answering of questions such as these. It should be noted that, like the authors of the related papers quoted above, I use the terms 'ionic' crystal or structure, 'cation', 'anion', *etc.*, as a convenience and without necessarily implying anything about the proportion of ionic and covalent character in a given 'cation-anion' bond.

The general method

The purpose of the method described here is to evaluate, for an ionic crystal whose interatomic distances are known accurately, the total bond strengths contributed to each anion by the cations when the latter are assumed to have their formal positive charges or oxidation states and when *the valence bonds are distributed to the surrounding anions in amounts that are inversely proportional to the cation-anion distances*. Having carried out a given calculation, we are able to assess how closely the total bond strength to each anion comes to its formal negative charge or valence, that is, how closely the structure fulfils the Pauling electroneutrality principle when allowance is made for differing cation-anion distances within one polyhedron in this way. An essential part of such an assessment is the standard deviation of the total bond strength to each anion, the error in each of these totals being a function of the error in the experimentally determined cation-anion distan-

ces in the structure; the derivation of the standard deviation of the total bond strengths to each anion constitutes an essential part of the procedure described here.

Another important aspect of this method is the manner of dealing with cations of uncertain CN such as, for example, (as given above) the CN with respect to oxygens of the M2 site in a pyroxene (the Ca site in $\text{CaMgSi}_2\text{O}_6$, for example). In this procedure, one simply computes the bond strengths to all the anions for different, reasonable, assumed CN's of the cation(s) in question, assesses which CN('s) lead(s) to the ideal, or closest to the ideal, total bond strength to each anion, and concludes that this (or these) particular CN('s) may be the most likely effective CN('s) of that (those) cation(s).

In two important ways, therefore, this method differs from other similar ones: first, the manner of distributing the valence bonds from each cation is 'internal' and does not depend upon arbitrarily derived bond-length bond-strength relationships; and second, the CN derived for a given cation of uncertain CN neither is simply adopted arbitrarily nor depends upon assumed ionic radii, but rather is deduced from the results themselves. In fact, the results described below suggest that it may provide an empirically sound criterion for determining the effective CN of a cation.

To my knowledge, the only case where bond strengths ('charge distributions') have been calculated using the principles described here is that of the feldspar low albite ($\text{NaAlSi}_3\text{O}_8$) by Gait & Ferguson (1970). In this case, the authors distributed the bond strengths from the cations to the anions in amounts that are inversely proportional to the squares of the cation-anion distances, and they computed the bond strengths in this way for different CN's of the irregularly coordinated Na atom and for different effective charges on (Si^{4+} , Al^{3+} distributions in) the four tetrahedral sites. They found that only a CN of 6 for Na and a 'largely' but not 'fully' ordered distribution of Si and Al among the tetrahedral sites gave 'ideal' bond strengths to all the oxygen anions when the structure was interpreted in this way. In the present paper the bond strengths are distributed inversely as the cation-anion distances rather than those distances squared, for reasons given below. Following that work on low albite, I felt it would be valuable to generalize the method and to apply it to some structures like the olivines and the end-member pyroxenes where no uncertainty exists about the effective formal charges on the cations. The present paper is the result.

Regarding the question of whether the valence bonds should be distributed inversely as the cation-anion distances or as those distances squared, no sound theoretical criterion can be used to make this choice because this method, like the other similar ones, is empirical. To help resolve this question, mathematical expressions have been derived for the total bond strengths to an anion when the valence bonds are

* In this paper, 'coordination number (CN)' of a cation implies the number of anions to which valence bonds are contributed by the cation.

distributed on the one hand, inversely as the distances only, and on the other hand, inversely as the distances squared. These expressions are derived in an Appendix to this paper, and from this derivation one can see, as one might expect, that a simple relationship exists in the total bond strengths to an anion when calculated in these two different ways: when the valence bonds are distributed inversely as the distances squared, the departure of the total bond strength to an anion from what it would be were the bonds distributed equally, is simply twice the departure relative to the case when the bonds are distributed inversely as the distances only. This being the case, I adopted for the final form of this method distributions inversely as the distances only.

Derivation of the valence-bond distribution relationships

Let there then be in a given structure m structurally different cations c_i and p structurally different anions a_k and let a given cation c_i be coordinated by n anions a_j . If we let d_{ij} be the observed distance (in Å) from the i th cation c_i to its j th anion a_j in the i th cation-anion polyhedron, and if we let z_i be the formal positive charge of this cation c_i , then if the valence bonds are distributed in amounts that are inversely proportional to the cation-anion distances, the expression for the bond strength contributed by cation c_i to its j th anion a_j , $i z_j$, involves a weighting factor for this i th cation-anion polyhedron,

$$w_i = \sum_{j=1}^n 1/d_{ij} \quad (1)$$

and the bond strength contributed by c_i to a_j is

$$i z_j = z_i / d_{ij} \cdot w_i \quad (2)$$

or, substituting for w_i ,

$$i z_j = \frac{z_i}{d_{ij} \sum_{j=1}^n 1/d_{ij}} \quad (2a)$$

[Expressions comparable to (1) and (2) but for distances squared are given in the unpublished thesis of Gait (1967) quoted by Gait & Ferguson (1970).]

Now, one of the p structural anions a_k will in general receive valence bonds from q different cations c_i (where a_k is one anion in each of q cation-anion polyhedra). Thus the total bond strength received by anion a_k , t_k , will be

$$t_k = \sum_{i=1}^q i z_k \quad (3)$$

in which all the contributing cations need not be structurally independent.

The total bond strengths t_k contributed to each of the anions given by (3) are the fundamental values that we wish to derive, but as indicated above, it may also be useful in some cases to evaluate the bond unbalance

for each anion, Δ_k : for anion a_k the bond unbalance will be simply

$$\Delta_k = ||Z_k| - t_k| \quad (4)$$

when Z_k is the formal negative charge of anion a_k ; the total bond unbalance for the structure, $\sum \Delta$, will be the sum of the bond unbalances for the p anions:

$$\sum \Delta = \sum_{k=1}^p \Delta_k \quad (5)$$

and the mean bond unbalance for all the p anions, $\bar{\Delta}$, will be simply

$$\bar{\Delta} = \sum \Delta / p \quad (6)$$

with allowance being made, if necessary, in equations (5) and (6) for differences in valence and/or in multiplicities of different anions.

Derivation of the relationships for the standard deviations of the valence-bond distributions

The bond strengths calculated for any given structure will involve errors that are functions of the experimental errors in the measured cation-anion distances. Given for an actual structure the interatomic distances utilized in the previous section, and in addition the errors or standard deviations (σ) in those interatomic distances, one can derive relationships for the standard deviation of the bond strengths using applications of the following fundamental statistical relationship given in, for example, Baird (1962, pp. 62-63):

$$\bar{z} = f(\bar{x}, \bar{y})$$

then

$$\sigma_{\bar{z}} = \left[\left(\frac{\partial \bar{z}}{\partial \bar{x}} \right)^2 \sigma_x^2 + \left(\frac{\partial \bar{z}}{\partial \bar{y}} \right)^2 \sigma_y^2 \right]^{1/2}$$

To do this, we use the same terminology as in the previous section but introduce additional terms involving the standard deviation σ . Then, where the mean cation-anion distance within the i th polyhedron is

$$\bar{d}_i = \sum_{j=1}^n d_{ij} / n$$

and where the experimentally determined σ of a given cation-anion distance is $\sigma_{d_{ij}}$, then

$$\sigma_{\bar{d}_i} = \left[\sum_{j=1}^n \sigma_{d_{ij}}^2 / n \right]^{1/2} \quad (7)$$

From this relationship it can be shown that the mean of the bond strength contributed by cation c_j to each of its n anions a_j is given by

$$\bar{\sigma}_{iz} = \sum_{j=1}^n \sigma_{izj} / n \simeq z_i \sigma_{\bar{x}_i} / \bar{x}_i^2 \quad (8)$$

where

$$\bar{x}_i = \bar{d}_i \cdot w_i$$

The σ of our fundamental value, the total bond strength to each structural anion a_k , σ_{tk} , will then be, from equation (8),

$$\sigma_{tk} = \left[\sum_{i=1}^q \sigma_{i^2k}^2 \right]^{1/2}. \quad (9)$$

The σ of the bond unbalance for anion a_k , $\sigma_{\Delta k}$, will be, from (4) and because Z_k will have a fixed value in a given case, simply

$$\sigma_{\Delta k} = \sigma_{tk}. \quad (10)$$

For all the p anions in the structure, the σ of the total bond unbalance, $\sigma_{\Sigma \Delta}$, will be, from (5),

$$\sigma_{\Sigma \Delta} = \left[\sum_{k=1}^p \sigma_{\Delta k}^2 \right]^{1/2} \quad (11)$$

and the σ of the mean bond unbalance, $\sigma_{\bar{\Delta}}$, will be, from (6) and (11),

$$\sigma_{\bar{\Delta}} = \sigma_{\Sigma \Delta} / p^{1/2} \quad (12)$$

where, as with expressions (5) and (6), allowance is made, if necessary, in (11) and (12) for differences in valence and/or in multiplicities of different anions.

Computer program

A computer program *VLBDDDB* ('valence-bond distribution') has been written in Fortran IV by the author to evaluate the valence-bond distributions and their

standard deviations for known ionic structures according to the principles described in the preceding two sections of this paper. This program is written in a fairly general form that permits one to evaluate the valence-bond distributions for any structures that can be regarded as an assemblage of any number of 'tetrahedra' (*i.e.* four-coordinated polyhedra), and/or 'octahedra' (*i.e.* six-coordinated polyhedra), and/or polyhedra of one chosen CN, and/or polyhedra of another chosen CN.

The input data required for this program are, for the structure in question: the numbers of anions, and of 'tetrahedral', 'octahedral', *etc.* cations; the formal charge of each cation and each anion; all relevant cation-anion distances; the error (taken to be the standard deviation) of these distances; and the coordinations of both cations by anions, and anions by cations. Many published descriptions of ionic structures include all these data, but some are not complete: in particular, the coordinations of anions by cations are sometimes not given and for this reason it is desirable to have access to a crystallographic bond-distance bond-angle program that calculates the distances (and angles although these are not used here) of all atoms around a given atom out to some desired distance. Such programs are widely available in crystal structure analysis laboratories.

Copies of the program *VLBDDDB* either as a print-out or as punched cards, and of a description of the program, may be obtained from the author.

Table 1. *Specimen identifications and valence-bond distributions for olivines and monticellite*

(a) Identification of specimens

	Atomic proportions and formal charges of large cations	Designation in this paper
(i) Olivines of Birle, Gibbs, Moore & Smith (1968) (designation <i>B</i>)	Mg _{0.90} ²⁺ Fe _{0.10} ²⁺ Mg _{0.535} ²⁺ Fe _{0.465} ²⁺ Mn _{0.006} ²⁺ Ca _{0.002} ²⁺ Mg _{0.49} ²⁺ Fe _{0.49} ²⁺ Mn _{0.01} ²⁺ Ca _{0.01} ²⁺ Mg _{0.04} ²⁺ Fe _{0.92} ²⁺ Mn _{0.04} ²⁺	Mg90(<i>B</i>) Mg54(<i>B</i>) Mg49(<i>B</i>) Mg04(<i>B</i>)
(ii) Olivines of Wenk & Raymond (1973) (designation <i>W</i>)	Mg _{0.985} ²⁺ Fe _{0.012} ²⁺ Mn _{0.003} ²⁺ Mg _{0.893} ²⁺ Fe _{0.099} ²⁺ Ni _{0.008} ²⁺ Mg _{0.672} ²⁺ Fe _{0.319} ²⁺ Ni _{0.004} ²⁺ Mg _{0.637} ²⁺ Fe _{0.358} ²⁺ Ca _{0.005} ²⁺	Mg99(<i>W</i>) Mg89(<i>W</i>) Mg67(<i>W</i>) Mg64(<i>W</i>)
(iii) Monticellite of Onken (1965)*	Mg ₂ ²⁺ Ca ₂ ²⁺	MTCL

(b) Total bond strengths t_k , bond unbalances Δ_k , total bond unbalances $\Sigma \Delta$, and mean bond unbalances $\bar{\Delta}$, (all in v.u.)
Standard deviations (σ) in the last place(s) are given in parentheses.

Specimen	O(1)		O(2)		O(3)		$\Sigma \Delta$	$\bar{\Delta}$
	t_1	Δ_1	t_2	Δ_2	t_3	Δ_3		
Mg99(<i>W</i>)	2.0090 (6)	0.0090 (6)	2.0098 (6)	0.0098 (6)	1.9906 (6)	0.0094 (6)	0.0376 (12)	0.0094 (6)
Mg90(<i>B</i>)	2.009 (3)	0.009 (3)	2.009 (3)	0.009 (3)	1.991 (3)	0.009 (3)	0.036 (6)	0.009 (3)
Mg89(<i>W</i>)	2.0100 (6)	0.0100 (6)	2.0089 (6)	0.0089 (6)	1.9906 (6)	0.0094 (6)	0.0377 (12)	0.0094 (6)
Mg67(<i>W</i>)	2.0098 (6)	0.0098 (6)	2.0078 (6)	0.0078 (6)	1.9912 (6)	0.0088 (6)	0.0352 (12)	0.0088 (6)
Mg64(<i>W</i>)	2.0103 (4)	0.0103 (4)	2.0090 (4)	0.0090 (4)	1.9903 (4)	0.0097 (4)	0.0387 (8)	0.0097 (4)
Mg54(<i>B</i>)	2.011 (3)	0.011 (3)	2.010 (3)	0.010 (3)	1.989 (3)	0.011 (3)	0.043 (6)	0.011 (3)
Mg49(<i>B</i>)	2.009 (4)	0.009 (4)	2.009 (4)	0.009 (4)	1.991 (4)	0.009 (4)	0.036 (8)	0.009 (4)
Mg04(<i>B</i>)	2.013 (1)	0.013 (1)	2.009 (1)	0.009 (1)	1.989 (1)	0.011 (1)	0.044 (2)	0.011 (1)
Mean	2.010 ₁	—	2.009 ₁	—	1.990 ₃	—	—	—
MTCL*	1.973	0.027	2.009	0.009	2.009	0.009	0.054	0.014

* Because Onken (1965) gives no standard deviations for the interatomic distances in monticellite, none have been computed for the bond strengths.

Results for some olivine and some pyroxene structures

The olivines

I have evaluated the valence-bond distributions using the method described here for eight olivines that represent well the complete Mg-Fe series: four are terrestrial olivines refined by Birle, Gibbs, Moore & Smith (1968), and four are recent highly refined structures of Wenk & Raymond (1973), two of which are terrestrial and two lunar. I have also evaluated the

valence-bond distributions for the isostructural mineral monticellite, CaMgSiO₄, using the structural data of Onken (1965) for a natural specimen with close to the ideal composition. The specimens are identified in Table 1(a) but the interatomic distances and standard errors from the original authors are not given in table form; rather they are shown graphically in Fig. 1(a) which emphasizes the striking differences in cation-anion distances in all polyhedra. The results of the present investigation, the bond strengths to the anions

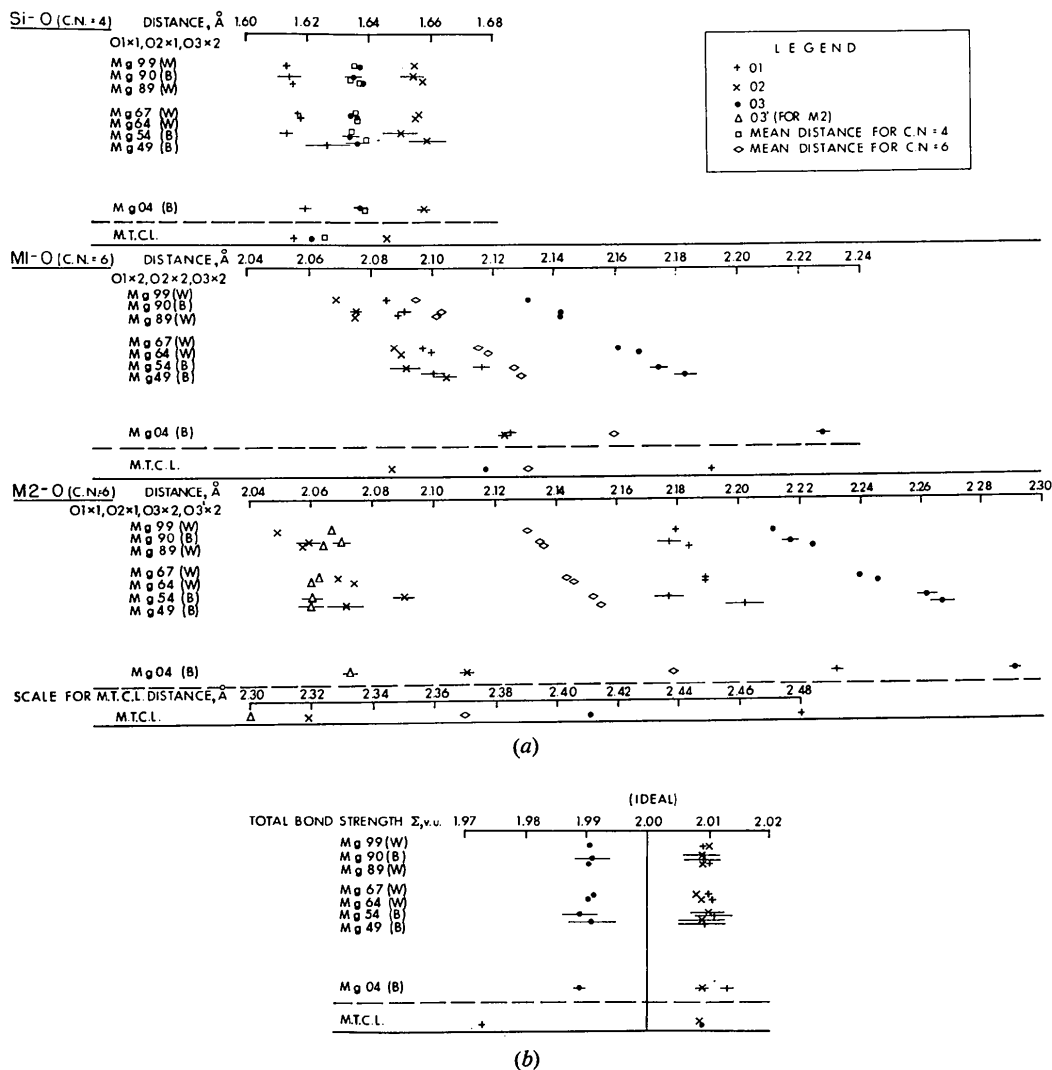


Fig. 1. Cation-anion distances d_{ij} in Å (a) and total bond strengths t_k in v.u. to the three oxygen anions O(1), O(2) and O(3) (b) for olivines and monticellite. Sources of the cation-anion distances, the meaning of the specimen identification symbols [Mg99(W), etc.] and the bond strengths, are given in Table 1. The exact values of the cation-anion distances may be obtained from the original papers. Plotted positions with respect to the ordinate for the forsterite-fayalite specimens correspond approximately to their atomic proportions of Mg and Fe. The bars through the plotted distance points for the (B) (= Birle *et al.*, 1968) olivines in (a) show those authors' standard errors, and the corresponding bars in (b) show the σ values of the bond strengths; the standard errors of the very accurate cation-anion distances for the (W) (= Wenk & Raymond, 1973) olivines are too small (0.0005-0.0011 Å) to be shown in (a) as are the resulting σ values (0.0004 to 0.0006 v.u.) of the total bond strengths in (b). For monticellite, Onken (1965) gives no errors for his cation-anion distances and so none are shown for this specimen in (a) or (b) although from the experimental method the errors are probably about the same as for specimen Mg49(B).

and their standard deviations computed by the present method, are given in Table 1(b) and plotted in Fig. 1(b) where they may be easily assessed and interpreted in relation to the cation-anion distances. These results are considered below under *Observations, discussion and conclusions*.

The pyroxenes and the possible CN's of the M1 and M2 cation sites

The well-known pyroxenes have the general formula $ABSi_2O_6$ in which AB is either $A^{2+}B^{2+}$ where A^{2+} and B^{2+} may be Ca^{2+} , Mg^{2+} , Fe^{2+} , etc., or A^+B^{3+} where A^+ may be Na^+ or Li^+ and B^{3+} may be Al^{3+} , Fe^{3+} , Cr^{3+} , etc. The pyroxenes fall into two major groups, one monoclinic (clinopyroxenes) and the other orthorhombic (orthopyroxenes). In general, the orthopyroxenes are those with A and B consisting of Mg^{2+} and/or Fe^{2+} , and the clinopyroxenes embrace most other compositions. Of recent papers describing refinements of pyroxene structures, the most valuable for the present purpose is that of Clark, Appleman & Papike (1969) who give detailed descriptions of eleven clinopyroxenes, eight having ordered (end-member)

compositions and three disordered (intermediate) compositions; of these eleven pyroxene structure refinements, five were carried out by Clark *et al.* (1969) themselves, and six by others as given in Table 2. I have evaluated the valence-bond distributions according to the method described here in these eleven clinopyroxenes and in three refined orthopyroxene structures, one Mg-rich, one intermediate, and one Fe-rich, by the authors given in Table 2. As with the olivine structures, the cation-anion distances and their standard deviations are not given in table form but they are shown graphically in Fig. 2 which, as in the case of the olivines, emphasizes the striking differences in cation-anion distances within most polyhedra.

The simpler clinopyroxene structure is characterized by one (pseudo-) tetrahedral four-coordinated cation which is Si^{4+} in the ordered members, and by two large-cation sites M1 and M2 corresponding respectively to B^{2+} and A^{2+} or to B^{3+} and A^+ . The CN's assumed for the two cation sites M1 and M2 are of paramount importance in any assessment of bond strengths in the pyroxenes because they determine how close the bond strengths to each oxygen will, in general, approach the ideal 2 v.u.; allowance for different cation-anion

Table 2. *Pyroxene specimen identifications*

	Idealized composition and formal charges*	Author(s) of structure refinement	Designation in this paper
Clinopyroxenes			
Ordered A^+B^{3+}			
Spodumene	$Li^+Al^{3+}Si_6^{4+}O_6^{2-}$	Clark <i>et al.</i> (1969)	LiAl
—	$Li^+Fe^{3+}Si_6^{4+}O_6^{2-}$	Clark <i>et al.</i> (1969)	LiFe
Jadeite	$Na^+Al^{3+}Si_6^{4+}O_6^{2-}$	Prewitt & Burnham (1966) in Clark <i>et al.</i> (1969)	NaAl
Ureyite	$Na^+Cr^{3+}Si_6^{4+}O_6^{2-}$	Clark <i>et al.</i> (1969)	NaCr
Acmite	$Na^+Fe^{3+}Si_6^{4+}O_6^{2-}$	Clark <i>et al.</i> (1969)	NaFe
—	$Na^+In^{3+}Si_6^{4+}O_6^{2-}$	Christensen & Hazell (1967)	NaIn
$A^{2+}B^{2+}$			
Diopside	$Ca^{2+}Mg^{2+}Si_6^{4+}O_6^{2-}$	Clark <i>et al.</i> (1969)	CaMg
Johannsenite	$Ca^{2+}Mn^{2+}Si_6^{4+}O_6^{2-}$	Freed & Peacor (1967) in Clark <i>et al.</i> (1969)	CaMn
Disordered			
Omphacite	$(Ca_{.59}^{2+}Na_{.32}^{+}Mg_{.06}^{2+}Fe_{.03}^{2+})^{-}$	Clark <i>et al.</i> (1969)	OMPH
Augite	$(Mg_{.54}^{2+}Al_{.24}^{3+}Fe_{.12}^{3+}Fe_{.10}^{2+})Si_6^{4+}O_6^{2-}$		
Augite	$(Ca_{.62}^{2+}Mg_{.19}^{2+}Fe_{.11}^{2+}Na_{.09}^{+})^{-}$	Clark <i>et al.</i> (1969)	AUGT
Augite	$(Mg_{.71}^{2+}Al_{.13}^{3+}Fe_{.09}^{2+}Fe_{.01}^{3+})^{-}$		
Fassaite	$(Si_{1.82}^{4+}Al_{1.16}^{3+}Ti_{1.02}^{4+})O_6^{2-}$	Peacor (1967) in Clark <i>et al.</i> (1969)	FASS
Fassaite	$Ca_{.99}^{2+}(Mg_{.27}^{2+}Al_{.17}^{3+}Fe_{.16}^{2+}Fe_{.06}^{2+})^{-}$		
Orthopyroxenes			
Orthoenstatite	$Mg_2^{2+}Si_2^{4+}O_6^{2-}$	Morimoto & Koto (1969)	MgMg
Intermediate orthopyroxene	$Mg_{.93}^{2+}Fe_{1.07}^{2+}Si_2^{4+}O_6^{2-}$	Ghose (1965)	MgFe
Iron-rich orthopyroxene	$Mg_{.26}^{2+}Fe_{1.70}^{2+}Ca_{.04}^{2+}Si_2^{4+}O_6^{2-}$	Burnham <i>et al.</i> (1971)	FeFe

* For the ordered clinopyroxenes, the exact compositions (which are little different from the ideal) are given by Clark *et al.* (1969). For all ordered clinopyroxenes, formal charges corresponding to the ideal compositions were used for the valence bond evaluations, and for the three orthopyroxenes the two cation sites M1 and M2 were assumed to have formal charges of 2+; for the three disordered clinopyroxenes, effective formal ('positive') charges for the cation sites used for the valence bond evaluations were deduced from the compositions as follows: for the A(=M2), B(=M1), and Si sites respectively, for OMPH, 1.68, 2.37, 4.00; for AUGT, 1.93, 2.20, 3.94; and for FASS, 2.00, 2.31, 3.84.

distances within polyhedra simply modifies these bond strengths slightly. In view of this, the following consideration of the possible CN's for these two cations appears to be in order. The M1 site, which in most members is smaller than the M2, is generally considered to be (pseudo-) octahedrally coordinated by six oxygens whereas the larger M2 site is most commonly regarded as eight-coordinated except in the case of Li pyroxenes such as spodumene $\text{LiAlSi}_2\text{O}_6$ where the small Li^+ in M2 is regarded as six-coordinated [see such authoritative works as Zussman (1968) and Clark *et al.* (1969)]. It is well known that the six oxygens around cation site M1 are all non-bridging [two pairs of O(1) and one pair of O(2)], and so it is reasonable to postulate bonding from the cation in M1 to all six of these oxygen anions. However, what is also well known is that in the case of cation site M2 only the closest four oxygens are non-bridging [one pair of each of O(1) and O(2)] whereas the fifth–sixth and seventh–eighth pairs of oxygens are bridging [O(3)]; for ordered clinopyroxenes with only Si^{4+} in the tetrahedral sites, the bridging O(3) anions would be saturated by their two linked Si^{4+} cations if the bond-strength distribution is non-distance-dependent. This consideration suggests that an assumed four-coordination for cation M2 (and six for M1) would result in bond strengths to the oxygens that are much closer to the ideal than would the higher six or eight coordination for M2. It can be readily shown that this is so if one distributes the valence bonds from the cations to the anions in simple fractional amounts

taking no account of different cation–anion distances. It can be further shown in the same simple way that only an assumed four-coordination for cation M1 (to its four closest non-bridging oxygens) as well as for M2 will result in each of the three oxygens receiving total bond strengths of the ideal +2 v.u. In contrast, assumed coordinates of, for example, six and eight for M1 and M2 respectively in a clinopyroxene result in departures from the ideal to the oxygens of as much as $\frac{1}{2}$ v.u. [for O(3)]. This argument suggests that, on the basis of simple bond-strength distributions, cations M1 and M2 in the pyroxenes should both be regarded as four-coordinated to their closest two pairs of non-bridging oxygens O(1) and O(2) in the clinopyroxenes or O(1A), O(1B) and O(2A), O(2B) in the orthopyroxenes, rather than, as is generally accepted six- or eight-coordinated when the M2 cation is large or six- and six-coordinated when M2 is small.

Because of the unorthodox CN's for M1 and M2 that are suggested by the above reasoning, it is appropriate to ask at this point whether, in view of the large differences that exist in the different cation–anion distances within the M1 and M2 polyhedra in the pyroxene structures (Fig. 2), such differences can be used to support or refute the possibility of four-coordination for M1 and M2 in a pyroxene structure. One could argue, for example, that the greater distances from the M2 cation of the two pairs of oxygens O(3) in the Ca clinopyroxenes and of O(3A) and O(3B) in the orthopyroxenes are evidence for four-coordination of M2 in

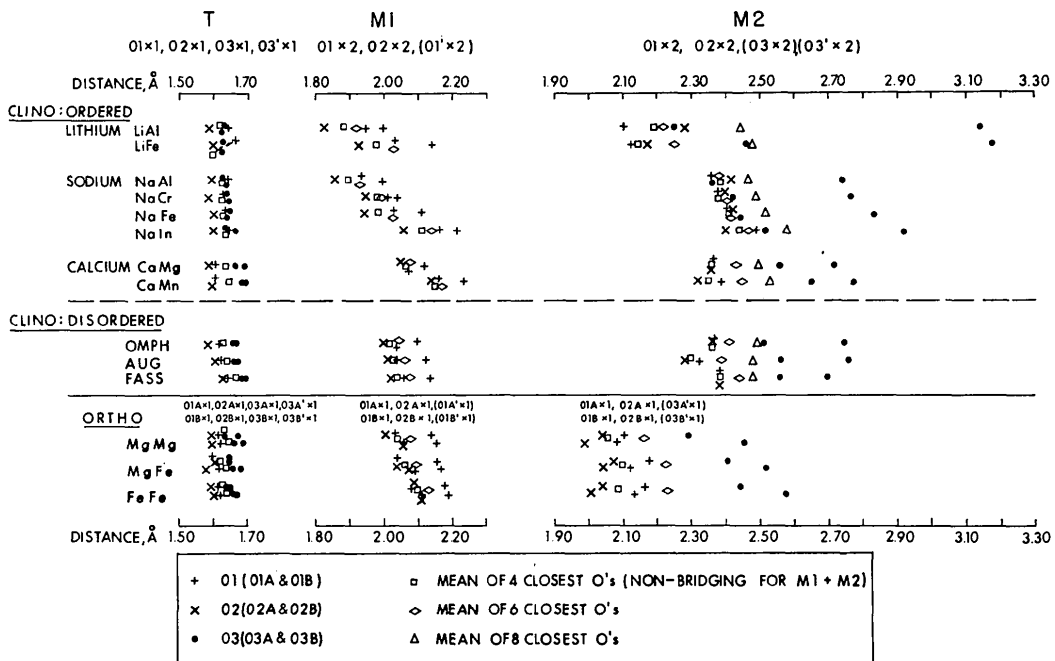


Fig. 2. Cation–anion distances d_{1j} in Å for pyroxene structures. Sources of the structural data from which the distances are taken, and the meaning of the specimen identification symbols (LiAl, OMPH, *etc.*) are given in Table 2. The exact cation–anion distances may be obtained from the original sources as may the σ values which are not shown here because of the closeness of many of the plotted points.

these structures. On the other hand, in the Na clinopyroxenes only one pair of O(3) oxygens around M2 is distinctly beyond the closer ones (suggesting six-coordination). Furthermore, the M1 and M2 sites in the olivine structures show differences in cation-oxygen distances (Fig. 1) that could also be used to argue for four-coordinations of those sites whereas bond strengths suggest the conventional six-coordinations (Table 1, Fig. 1). Considerations like these suggest that, despite the importance that greater cation-anion distances play in determining the effective CN of a cation in such bond-strength evaluation methods as those of Donnay & Allmann (1974) and Brown & Shannon (1973), in the method described here the cation-anion distances cannot in general be used as evidence for any given reasonable CN for M1 or M2, and in particular they cannot be used to substantiate or refute four-coordination for these two cations.

I am aware that experimental approaches other than the results of crystal structure refinements, for example the interpretation of Mössbauer effects, have provided evidence for apparent six-coordination of M1 and M2 in orthopyroxenes [see for example Burns (1970)], but one of my objectives in the part of this investigation that relates to the pyroxenes has been to try to assess the likely coordination of M1 and M2 on the basis of valence-bond distributions.

The considerations about the possible CN's of M1 and M2 just given are relevant to the distance-dependent valence-bond evaluations carried out for the pyroxene structures during this study. Total bond strengths (t_k) in v.u. to the three oxygens in the eight ordered clinopyroxenes of Clark *et al.* (1969) were computed for a number of possible CN's of M1 and M2, initially of 6 and 8, 6 and 6, and 6 and 4 respectively, and the results are given in Table 3(a) and Fig. 3. From

Table 3. Total bond strengths t_k (in v.u.) to the oxygen anions in pyroxenes

(a) For ordered clinopyroxenes for different CN's of M1 and M2

No σ values were computed for these bond strengths, but they will be in general slightly greater than the σ values given in part (b) of this table.

Structure type	Individual designation (Table 4)	CN of M1 CN of M2 Oxygen anions	6 8				6 6				6 4			
			O(1)	O(2)	O(3)	$\Sigma\Delta$	O(1)	O(2)	O(3)	$\Sigma\Delta$	O(1)	O(2)	O(3)	$\Sigma\Delta$
A ⁺ B ³⁺	LiAl		2.102	1.678	2.220	0.644	2.135	1.709	2.156	0.583	2.220	1.787	1.992	0.451
	LiFe		2.109	1.682	2.209	0.636	2.142	1.715	2.143	0.571	2.219	1.790	1.991	0.438
	NaAl		2.103	1.667	2.231	0.666	2.140	1.704	2.156	0.593	2.225	1.787	1.988	0.450
	NaCr		2.116	1.667	2.217	0.667	2.154	1.704	2.142	0.592	2.236	1.786	1.977	0.473
	NaFe		2.107	1.670	2.222	0.659	2.144	1.707	2.148	0.586	2.228	1.790	1.983	0.455
	NaIn		2.104	1.678	2.218	0.644	2.140	1.716	2.144	0.569	2.220	1.799	1.981	0.440
A ²⁺ B ²⁺	CaMg		1.946	1.633	2.422	0.844	2.024	1.711	2.265	0.578	2.181	1.869	1.950	0.362
	CaMn		1.948	1.641	2.410	0.821	2.026	1.721	2.253	0.558	2.177	1.877	1.946	0.354

(b) For all pyroxenes for CN of M1=4 and of M2=4 (closest to ideal results)

(i) Clinopyroxenes

		O(1)		O(2)		O(3)		$\Sigma\Delta$	$\bar{\Delta}$
		t_1	Δ_1	t_2	Δ_2	t_3	Δ_3		
A ⁺ B ³⁺	LiAl	1.973 (2)	0.027 (2)	2.035 (2)	0.035 (2)	1.992 (2)	0.008 (2)	0.070 (3)	0.023 (1)
	LiFe	1.975 (2)	0.025 (2)	2.033 (2)	0.033 (2)	1.991 (2)	0.009 (2)	0.067 (3)	0.022 (1)
	NaAl	1.979 (2)	0.021 (2)	2.033 (2)	0.033 (2)	1.988 (2)	0.012 (2)	0.066 (3)	0.022 (1)
	NaCr	1.988 (3)	0.012 (3)	2.035 (3)	0.035 (3)	1.977 (4)	0.023 (4)	0.070 (6)	0.023 (4)
	NaFe	1.982 (2)	0.018 (2)	2.035 (2)	0.035 (2)	1.983 (2)	0.017 (2)	0.070 (3)	0.023 (1)
	NaIn	1.972 (6)	0.028 (6)	2.047 (6)	0.047 (6)	1.981 (7)	0.019 (2)	0.093 (11)	0.031 (13)
	Mean	1.981	—	2.036	—	1.985	—	—	—
A ²⁺ B ²⁺	CaMg	2.017 (1)	0.017 (1)	2.033 (1)	0.033 (1)	1.950 (2)	0.050 (2)	0.100 (2)	0.033 (1)
	CaMn	2.014 (5)	0.014 (5)	2.040 (5)	0.040 (5)	1.946 (6)	0.054 (6)	0.108 (9)	0.036 (9)
	Mean	2.016	—	2.034*	—	1.948	—	—	—
Disordered	OMPH	2.016 (3)	0.016 (3)	2.046 (3)	0.046 (3)	1.961 (3)	0.039 (3)	0.102 (5)	0.034 (3)
	AUGT	2.021 (2)	0.021 (2)	2.047 (2)	0.047 (2)	1.937 (2)	0.063 (2)	0.131 (3)	0.044 (2)
	FASS	2.046 (4)	0.046 (4)	2.064 (4)	0.064 (4)	1.889 (4)	0.111 (4)	0.221 (7)	0.074 (4)

(ii) Orthopyroxenes

	MgMg		MgFe		FeFe		Mean t_k
	t_k	Δ_k	t_k	Δ_k	t_k	Δ_k	
O(1A)	1.998 (7)	0.002 (7)	2.004 (11)	0.004 (11)	1.991 (2)	0.009 (2)	1.998
O(1B)	2.001 (7)	0.001 (7)	1.999 (11)	0.001 (11)	1.995 (2)	0.005 (2)	
O(2A)	2.031 (7)	0.031 (7)	2.026 (11)	0.026 (11)	2.031 (2)	0.031 (2)	2.029
O(2B)	2.040 (7)	0.040 (7)	2.046 (11)	0.046 (11)	2.040 (2)	0.040 (2)	
O(3A)	1.971 (9)	0.029 (9)	1.970 (14)	0.030 (14)	1.975 (2)	0.025 (2)	1.972
O(3B)	1.959 (9)	0.041 (9)	1.954 (14)	0.046 (14)	1.967 (2)	0.033 (2)	
	$\Sigma\Delta$	0.144 (19)		0.153 (29)		0.142 (5)	1.966
	$\bar{\Delta}$	0.024 (10)		0.025 (24)		0.024 (2)	

* This 'mean' has been arbitrarily chosen such that it differs by no more than $\sim 1\sigma$ from the two values.

Fig. 3 and from the total bond unbalance ($\Sigma\Delta$) values in Table 3(a) one can see that, as one would expect from the above considerations, the CN's of 6,8 yield the least satisfactory results and CN's of 4,6 the most satisfactory of these three combinations of CN's although the latter are still, again as one would expect

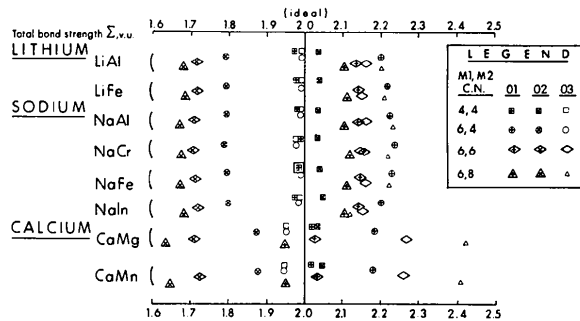


Fig. 3. Total bond strengths t_k in v.u. to the three oxygen anions O(1), O(2), O(3) in ordered clinopyroxenes for different CN's of M1 and M2 taken from Table 3(a). Sources of the cation-anion distances used in the calculations are given along with the meaning of the specimen identification symbols (LiAl, etc.) in Table 2, and the cation-anion distances are plotted in Fig. 2. The σ values of the bond strengths were computed only for CN's of M1 and M2 of 4 and 4 and these are given in Table 3(b) and plotted in Fig. 4; for other CN's the σ values would be nearly the same (most are close to 0.003 v.u.).

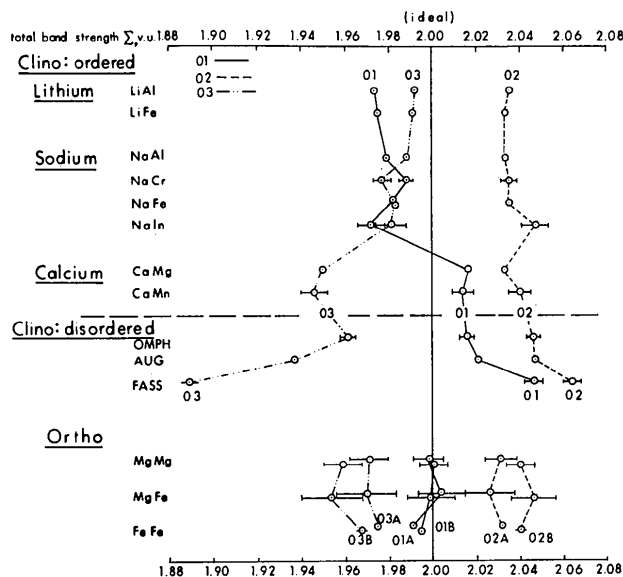


Fig. 4. Total bond strengths t_k in v.u. to the three oxygens O(1), O(2), O(3) in the clinopyroxenes and to the three oxygen pairs O(1A), O(1B), O(2A), O(2B), O(3A), O(3B) in the orthopyroxenes for M1 and M2 both four-coordinated to the four closest non-bridging oxygens O(1) or O(1A), O(1B) and O(2) or O(2A), O(2B). The bond strengths are taken from Table 3(b). Sources of the cation-anion distances used in the calculations are given along with the meaning of the specimen identification symbols (LiAl, OMPH, etc.) in Table 2, and the cation-anion distances are plotted in Fig. 2. The σ values of the bond strengths are shown as bars.

from the above discussion, appreciably different from the ideal. The results for these CN's and the considerations given above indicated that the closest to the ideal bond strengths to the oxygens would likely occur, even when account is taken of the different cation-anion distances, for four-coordinations of both M1 and M2 by the two closest pairs of O(1) and O(2) despite the unorthodoxy of these CN's, and the bond strengths for these were accordingly computed. The detailed results including standard deviations are given in Table 3(b) for the eight ordered clinopyroxenes and, because these CN's do indeed give the 'best' results, for the three disordered clinopyroxenes and the three orthopyroxenes as well. Fig. 3 shows the results for CN's of 4 for both M1 and M2 along with those for the higher CN's, and the plot shows in striking fashion how much closer to the ideal of 2 v.u. the bond strengths to the three oxygens are for the 4,4 CN's for M1 and M2 than they are for any of the higher CN's. The bond strengths with standard deviations for all 14 pyroxenes for CN's of 4 for both M1 and M2 given in Table 3(b) are shown as plots in Fig. 4.

These results are assessed in the next section.

Observations, discussion and conclusions

1. The closeness to the ideal of the olivine results

The results in Table 1 and Fig. 1 show that, for assumed conventional CN's of 4 for Si and 6 for M1 and M2, each of the three oxygen anions in the eight olivines proper receives bond strengths within ~ 0.01 v.u. (i.e. within $\sim \frac{1}{2}\%$) of the ideal of 2 v.u., although in terms of σ the bond strengths to the oxygen anions depart from the ideal of 2 v.u. by a mean of $\sim 11\sigma$ (maximum $\sim 25\sigma$). Thus in answer to the question asked in the Introduction about this application of Pauling's electroneutrality principle, we can say that these olivine structures conform closely but, if the σ values are meaningful, not exactly to the principle applied in this way.

2. The CN's of M1 and M2 in the pyroxene structures and the closeness to the ideal of the pyroxene results

(a) As indicated in an earlier section, from a consideration of valence-bond distributions in their simplest terms in the pyroxenes, one would expect the unorthodox CN's of 4,4 for M1, M2 rather than higher, more orthodox CN's to yield the most satisfactory bond strengths to the oxygens even when the distribution is distance-dependent. The results in Table 3 and Fig. 3 show that this is indeed the case for the eight ordered clinopyroxenes, and they suggest strongly that this would also be the case for the three intermediate pyroxenes and the three orthopyroxenes for which bond strengths were computed for 4, 4 CN's only.

(b) From the results for 4,4 CN's for M1, M2 given in Table 3(b) and Figs. 3 and 4, we can make an observation for the eight ordered clinopyroxenes that is

analogous to that made above for the olivines, namely that each of the three oxygen anions receives bond strengths within ~ 0.05 v.u. (*i.e.* within $\sim 2\frac{1}{2}\%$) of the ideal of 2 v.u.; in terms of σ , the departures from the ideal have a mean value of $\sim 11\sigma$ (surprisingly, the same as for the olivines), with a maximum of $\sim 33\sigma$. We can thus say that for *unorthodox* CN's of 4,4 for M1, M2, these pyroxene structures conform closely (although not as closely as the olivines), but not exactly to the electroneutrality principle applied in this way.

(c) Returning to the matter of possible M1, M2 CN's in the pyroxenes, it would be unwise to take the fact that 4,4 CN's yield better bond strengths than higher CN's, and nearly ideal values, as 'proof' that M1 and M2 are both four-coordinated, that is, bonded only to their nearest two pairs of non-bridging oxygens, but the results suggest that this might conceivably be so.

(d) How likely 4,4 CN's are for the two cation sites in the pyroxenes bears on the closeness to which the electroneutrality principle may be expected to approach the ideal: if the effective CN's of M1, M2 are really the conventional 6,8 or 6,6, then the statement that (non-distance-dependent) bond-strength departures from the ideal can be, in general, as large as $\sim 40\%$, which is Baur's (1970) rule 1, can be said to hold for the pyroxenes because, as Table 3(a) and Fig. 3 show, for 6,8 CN's (which give the least satisfactory results) the departures are, although not 40%, still $\sim 20\%$. If on the other hand it can be established that M1, M2 really are four-coordinated in the pyroxenes so that the bond-strength departures from the ideal are less than $\sim 2\frac{1}{2}\%$, then perhaps it can be shown that the electroneutrality principle holds more closely than Baur's rule 1 would suggest if, for structures generally, other than the most expected cation CN's are considered in deriving bond strengths.

(e) All of the above discussion has been in terms of the possible bonding of M1 and M2 to an integral number of surrounding oxygen anions (4, 6 or 8). It is worth pointing out that the results for the Ca clinopyroxenes both ordered and disordered, for 4,4 CN's given in Table 3 and Fig. 4 could be taken to suggest a small degree of bonding of M2 to its fifth–sixth bridging oxygens: since the four closest oxygens to M2 are one pair each of non-bridging O(1) and O(2) and the next pair are bridging O(3) (Table 3), and since for a CN of 4 the bond strengths to O(3) are < 2 and to O(1) and O(2) are > 2 v.u., if a small amount of the M2 bond strength were contributed to O(3) at the expense of O(1) and O(2), all three oxygens would receive closer to their ideal of 2 v.u. The effect becomes more marked as more tetrahedral Al^{3+} replaces Si^{4+} (in augite and fassaite), that is, there would be a greater degree of bonding between M2 and its fifth–sixth bridging O(3) oxygens as more Al^{3+} replaced Si^{4+} .

(f) The generally accepted picture of the clinopyroxene structures (Zussman, 1968; Clark *et al.*, 1969) is that when M2 is Na or Ca it is eight-coordinated and when it is Li it is six-coordinated. The present bond

strength results (Table 3, Fig. 3) suggest that if there is a difference in the CN of M2 within the different clinopyroxenes, then it occurs not between the Na–Ca members on the one hand and the Li members on the other, but rather between the Li and Na (1+, 3+) on the one hand and the Ca (2+, 2+) on the other because the patterns of bond strengths are of one kind for the Li–Na (1+, 3+) members and of another for the Ca (2+, 2+) members. Despite this fact, however, four-coordinations for M2 (and M1) for all of the Li, Na and Ca members yield the most satisfactory bond strengths to the oxygens.

3. The consistency of certain bond strengths in the olivines and in the pyroxenes

(a) Olivines (Table 1, Fig. 1)

(i) Although the bond strengths to the three oxygens depart from the ideal of 2 v.u. by an overall mean of $\sim 11\sigma$ (point 1 above), there is a marked consistency in the bond strengths to corresponding oxygens within all eight of the true olivine structures: the eight oxygens O(1) and the eight oxygens O(2) both receive with two exceptions, within 2σ of their common mean, 2.009₆ v.u., and the eight oxygens O(3) within 2σ of their mean, 1.990₃ v.u. (where in all cases 1σ is $\leq \sim 0.003$ v.u.). This consistency of the bond strengths shown in Fig. 1(b) may be contrasted with the variation in the cation–anion distances from one olivine to another shown in Fig. 1(a), a matter which is considered below under (c).

(ii) In monticellite (for which the σ 's are not known) O(1) receives 1.973 v.u., much less than any other oxygen in either olivine group; O(2) receives 2.009 v.u., exactly the mean for the eight Mg–Fe O(2) values (and almost exactly for the O(1) values); and O(3) receives, curiously, the same as O(2).

(b) Pyroxenes (Table 3, Figs. 3 and 4)

(i) As with the olivines, the pyroxenes show some marked consistencies in the bond strengths contributed to corresponding oxygens in different structures. Although for M1, M2 coordinations of 4,4, the bond strengths to the three oxygens in the eight ordered clinopyroxenes depart from the ideal by an overall mean of $\sim 11\sigma$ [point 2(b) above], for the six 1+, 3+ (Li, Na) clinopyroxenes, all six oxygens O(1) receive bond strengths within 4σ of their mean, 1.981 v.u.; oxygens O(2) within 2σ of their mean, 2.036 v.u.; and oxygens O(3) within 3σ of their mean of 1.985 v.u. (where 1σ is ~ 0.003 v.u.). This consistency and those noted in (ii) to (v) below are considered later under (c).

(ii) For the two ordered Ca (2+, 2+) clinopyroxenes assuming 4,4 coordinations O(1), O(2) and O(3) receive respective bond strengths that are within 1σ of 2.016, 2.034 and 1.948 v.u. (where 1σ is $\leq \sim 0.005$ v.u.).

(iii) For the Li–Na and the ordered Ca pyroxenes combined, only one of the three oxygens, O(2), has the same bond strength throughout, 2.035 v.u. within 2σ .

(iv) For the three disordered clinopyroxenes, the bond strengths for 4,4 coordination are close to those for the corresponding oxygens in the two ordered Ca pyroxenes to which the three disordered clinopyroxenes are closely related. However, as the proportion of tetrahedral Al increases through omphacite → augite → fassaite, the departures of the bond strengths from those for the corresponding oxygens in ordered diopside progressively increase.

(v) For the three orthopyroxenes, again for 4,4 coordination, related pairs of oxygens [O(1A) and O(1B), *etc.*] within one structure receive the same bond strengths within 2σ ; the bond strengths to corresponding oxygens within the three orthopyroxenes are the same within $\sim 3\sigma$; and the means for related pairs [1.998 v.u. for all oxygens O(1A) and O(1B), *etc.*] fall almost exactly midway between the mean values for all the corresponding single oxygens for the 1+,3+ and the 2+,2+ ordered clinopyroxenes [for O(1), respectively 1.981 and 2.016 v.u. with a mean of 1.998 v.u.].

(vi) Although emphasis has been laid on the results for 4,4 coordinations for M1 and M2 because these lead to the closest to the ideal results, it is important to note that the consistency of the bond strengths to corresponding oxygens in the six 1+,3+ clinopyroxenes as a group and the two ordered 2+,2+ clinopyroxenes as a group holds equally for the higher CN's for M1 and M2 (6 and 6, *etc.*) although the actual bond strengths are not of course as close, in general, to the ideal 2 v.u. as for 4,4 CN's.

(c) General

(i) A natural response to the observation about the consistencies of some of the bond strengths pointed out in (a) and (b) is that these consistencies are only to be expected within a group of closely related structures. It is true that, in an isostructural series like the Mg-Fe olivines, if corresponding cation-anion distances within corresponding polyhedra have the same relative values then the bond strengths evaluated as described here would be the same to corresponding anions throughout the series regardless of the change in size of the chemically variable cations. However, the results suggest that the consistencies of the total bond strengths to certain groups of corresponding oxygens are greater than one might expect from the strikingly different cation-anion distances in most polyhedra. This is illustrated by Table 4(a) where one can see that, for the chemically different olivine pair Mg99(W) and Mg64(W), the anions O(1), O(2), O(3) receive differences in bond strengths from cations Si^{4+} , Mg^{2+} , Mg^{2+} of as much as +0.0023, +0.0018, -0.0034 v.u. respectively whereas their total bond strengths differ by only -0.0013, +0.0008 and +0.0003 v.u. respectively (where 1σ is ~ 0.0005 v.u.). For the (clino) pyroxene pair LiAl and NaFe that differ even more chemically, Table 4(b) shows for CN's of M1, M2 of 4,4 a similar but less convincing effect (perhaps because of the insensitivity of bond strength differences for the low 4,4

CN's). For this same pyroxene pair, Table 4(b) also shows well that, for the higher assumed M1, M2 CN's of 6,8 (for which the bond strengths differences are much more sensitive than for 4,4), the consistency of the total bond strengths is appreciably greater than one might expect considering the differences in comparable strengths to each oxygen from its individual cations; this consistency holds in this case of 6,8 CN's where the total bond strengths are very different from the ideal. Disregarding for the moment the matter of CN in the pyroxenes, one can draw the general conclusion that the consistency of the present results for a number of crystals within one closely related isostructural group, appears to indicate that some characteristic of these structures requires all the comparable anions to receive the same total bond strengths and that the relative cation-anion distances within the different structures of the group are constrained to assure that this is so.

(ii) The final point relates yet again to CN's within the pyroxenes: whereas the closeness of the total bond strengths to the ideal provides a reasonable argument for considering both M1 and M2 to be four coordinated, the *consistency* of the total bond strengths within different ordered clinopyroxenes for M1, M2 CN's of higher than 4,4 appears to suggest that the higher CN's (6,4 or 6,6 or 6,8) are just as likely as 4,4. If M1 and M2 are four-coordinated and bonded to only their closest pairs of non-bridging O(1) and O(2) anions, then one might have expected greater consistency in the total bond strengths for 4,4 CN's than for the higher ones, but such is not the case. Any further interpretation or speculation about these results on my part is to await comparable computations that I plan for related rock-forming silicate structures such as the amphiboles and micas.

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APPENDIX

Comparative expressions for the total bond strengths to the anions for cation valence bonds distributed inversely as the cation-anion distances and as those distances squared*

In the last paragraph of *The general method* in the text of this paper it is pointed out that the question arises whether, in the bond-strength evaluation method described here, the valence bonds from the cations to the anions should be distributed inversely as the cation-anion distances or as those distances squared. In this Appendix are derived comparative expressions for the total bond strengths to the anions under these two conditions in order to explain the relationship between

* I am indebted to E. J. W. Whittaker for derivation of the fundamental equations given here.

two sets of bond strength results that differ only in this way. The derivation is mathematical and involves no physical or bonding considerations.

Using the same nomenclature as in the section of the text entitled *Derivation of the valence-bond distribution relationships*, one can extend symbols $t_k, i z_k$, etc. to

Table 4. *Comparative bond strengths to corresponding oxygens in the olivine pair Mg99(W) and Mg64(W) and in the pyroxene pair LiAl and NaFe*

All cation-anion distances are from the original authors; for the olivines see Fig. 1 and for the pyroxenes Fig. 2. The bond strengths for the olivines are from Table 1 and Fig. 1, and for the pyroxenes from Table 3 and Figs. 3 and 4. Numbers in parentheses are the standard deviations σ in the last place(s).

(a) Olivines

(i) Cation-anion distances d_{ij} and bond strengths $i z_j$ contributed by individual cations

Specimen	Mg99(W)		Mg64(W)		$i z_j(\text{Mg99}) - i z_j(\text{Mg64}) = \Delta i z_j$ (v.u.)
	Distance d_{ij} (Å)	Bond strength $i z_j$ (v.u.)	Distance d_{ij} (Å)	Bond strength $i z_j$ (v.u.)	
Si ⁴⁺ -O(1) (× 1)	1.6131 (10)	1.0137	1.6177 (10)	1.0114	+0.0023
-O(2) (× 1)	1.6545 (9)	0.9884	1.6549 (7)	0.9886	-0.0002
-O(3) (× 2)	1.6370 (7)	0.9989	1.6361 (5)	1.0000	-0.0011
Mean	1.6354 (8)	1.0000	1.6362 (6)	1.0000	—
M1 ²⁺ -O(1) (× 2)	2.0851 (6)	0.3348	2.0992 (5)	0.3363	-0.0015
-O(2) (× 2)	2.0681 (6)	0.3376	2.0891 (5)	0.3380	-0.0004
-O(3) (× 2)	2.1313 (6)	0.3276	2.1678 (5)	0.3257	+0.0019
Mean	2.0948 (6)	0.3333	2.1187 (5)	0.3333	—
M2 ²⁺ -O(1) (× 1)	2.1788 (10)	0.3256	2.1889 (8)	0.3263	-0.0007
-O(2) (× 1)	2.0487 (10)	0.3463	2.0731 (7)	0.3445	+0.0018
-O(3) (× 2)	2.2114 (8)	0.3208	2.2459 (6)	0.3180	+0.0028
-O(3') (× 2)	2.0666 (7)	0.3433	2.0601 (5)	0.3467	-0.0034
Mean	2.1306 (7)	0.3333	2.1456 (6)	0.3333	—

(ii) Total bond strengths t_k to the oxygen anions (v.u.)

Specimen	Mg99(W)	Mg64(W)	$t_k(\text{Mg99}) - t_k(\text{Mg64}) = \Delta t_k$ (v.u.)
O(1)	2.0090 (6)	2.0103 (4)	-0.0013
O(2)	2.0098 (6)	2.0090 (4)	+0.0008
O(3)	1.9906 (6)	1.9903 (4)	+0.0003

(b) Pyroxenes for CN's of M1, M2 of 4, 4 and 6, 8

(i) Cation-anion distances d_{ij} and bond strengths $i z_j$ contributed by individual cations

Specimen	LiAl			NaFe			$i z_j(\text{LiAl}) - i z_j(\text{NaFe}) = \Delta i z_j$ in v.u. for CN's of	
	Distance d_{ij} (Å)	Bond strengths $i z_j$ in v.u. for CN's of		Distance d_{ij} (Å)	Bond strengths $i z_j$ in v.u. for CN's of			
		M1=4, M2=4	M1=6, M2=8		M1=4, M2=4	M1=6, M2=8	M1=4, M2=4	M1=6, M2=8
Si ⁴⁺ -O(1) (× 1)	1.638 (2)	0.988	0.988	1.629 (2)	0.999	0.999	-0.011	-0.011
-O(2) (× 1)	1.586 (2)	1.020	1.020	1.598 (2)	1.018	1.018	+0.002	+0.002
-O(3) (× 1)	1.622 (2)	0.997	0.997	1.637 (2)	0.994	0.994	+0.003	+0.003
-O(3') (× 1)	1.626 (2)	0.995	0.995	1.646 (2)	0.989	0.989	+0.006	+0.006
Mean of 4	1.618	1.000	1.000	1.628	1.000	1.000	—	—
M1 ³⁺ -O(1) (× 2)	1.997 (2)	—	0.480	2.109 (2)	—	0.479	—	-0.001
-O(1') (× 2)	1.943 (2)	0.725	0.493	2.029 (2)	0.732	0.498	-0.007	-0.005
-O(2) (× 2)	1.818 (2)	0.775	0.527	1.936 (2)	0.768	0.522	+0.007	+0.005
Mean of 4	1.880	0.750	—	1.982	0.750	—	—	—
Mean of 6	1.919	—	0.500	2.025	—	0.500	—	—
M2 ²⁺ -O(1) (× 2)	2.105 (6)	0.260	0.142	2.398 (3)	0.251	0.131	+0.009	+0.011
-O(2) (× 2)	2.278 (2)	0.240	0.131	2.415 (2)	0.249	0.130	-0.009	+0.001
-O(3) (× 2)	2.251 (6)	—	0.133	2.430 (3)	—	0.129	—	+0.004
-O(3') (× 2)	3.144 (5)	—	0.095	2.831 (3)	—	0.111	—	-0.016
Mean of 4	2.191	0.250	—	2.406	0.250	—	—	—
Mean of 8	2.444	—	0.125	2.518	0.125	—	—	—

(ii) Total bond strengths t_k to the oxygen anions (v.u.)

Specimen	LiAl		NaFe		$t_k(\text{LiAl}) - t_k(\text{NaFe}) = \Delta t_k$ in v.u. for CN's of	
	M1=4, M2=4	M1=6, M2=8	M1=4, M2=4	M1=6, M2=8	M1=4, M2=4	M1=6, M2=8
O(1)	1.973 (2)	2.102	1.982 (2)	2.107	-0.009	-0.005
O(2)	2.035 (2)	1.678	2.035 (2)	1.670	+0.000	+0.008
O(3)	1.992 (2)	2.220	1.983 (2)	2.222	+0.009	-0.002

symbols ${}^0t_k, {}^0z_k$, etc. to represent the condition when the valence bonds within each cation-anion polyhedron are distributed equally, and in general to symbols ${}^vt_k, {}^vz_k$, etc., when the bonds are distributed inversely as the v th power of the distances. Then

$${}^vt_k = \sum_{i=1}^q {}^vz_k = \sum_{i=1}^q d_{ik}^v \sum_{j=1}^{n_i} 1/d_{ij}^v \quad (\text{A1})$$

whence

$${}^vt_k \approx \sum_{i=1}^q \frac{z_i}{d_{ik}^v \cdot n_i / \bar{d}_i^v} \quad (\text{A2})$$

provided the departures of d_{ij}/\bar{d}_i from unity are all $\ll 1$. Now if

$$d_{ik} = 1 + \varepsilon_{ik} \quad (\text{A3})$$

then

$$\frac{d_{ik}^v}{\bar{d}_i^v} \approx 1 + v\varepsilon_{ik}. \quad (\text{A4})$$

Hence for small ε_{ik}

$${}^1t_k \approx {}^0t_k - \sum_{i=1}^q \frac{z_i \varepsilon_{ik}}{n_i} \quad (\text{A5})$$

and

$${}^2t_k \approx {}^0t_k - 2 \sum_{i=1}^q \frac{z_i \varepsilon_{ik}}{n_i}. \quad (\text{A6})$$

The most valuable conclusion to be drawn from expressions (A5) and (A6) is the one that becomes clear if we compare the two: if the valence bonds are distributed inversely as the cation-anion distances squared (expression A6), the departure of the total bond strength to each anion from what it would be were the bonds within each cation-anion polyhedron distributed equally, is simply twice the corresponding departure relative to a distribution inversely as the distances only (expression A5). This simple relationship was confirmed by a number of actual calculations.

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