

Empirical Bond-Strength–Bond-Length Curves for Oxides

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Bond-strength–bond-length relationships for bonds between oxygen and H^+ , Li^+ , Be^{2+} , B^{3+} , Na^+ , Mg^{2+} , Al^{3+} , Si^{4+} , P^{5+} , S^{6+} , K^+ , Ca^{2+} , Sc^{3+} , Ti^{4+} , V^{5+} , Cr^{6+} , Mn^{2+} , Fe^{3+} , Fe^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Ga^{3+} , Ge^{4+} and As^{5+} have been derived by requiring that the sums of the bond strengths around the cations be equal to their valence in 417 crystals whose structures have been accurately determined. The relationship is of the form $s = (R/R_0)^{-N}$ where s = bond strength, R = bond length and R_0 and N are fitted constants. It is further shown that all ions with an isoelectronic core can be fitted by a single pair of parameters, R_0 and N , that are independent of the ionic character of the bond and the coordination number of the cation. The resulting bond strengths have the property that they are directly related to the covalent character of the bond and that their sum around each atom is, on average, within about 5% of its valence. The bond-strength–bond-length curves are particularly useful in accounting for bonding in cases where the coordination is very distorted (*e.g.* Na^+ , Cu^{2+} and V^{5+}). They can also be used to predict the positions of hydrogen atoms, to analyze for different oxidation states and site occupancies, to calculate ionic radii and to provide an indication of the correctness of crystal structure determinations.

Introduction

The concept of mean bond strength (\bar{s}) was defined by Pauling (1929) as the valence (z) of a cation divided by its coordination (ν). He enunciated the electrostatic valence principle by which the sums ($p = \sum \bar{s}$) of mean bond strengths around the cations and anions are approximately equal to their valence. This principle has been tested frequently by mineralogists, particularly in silicate structures, and is in general only approximately valid with the sum of the bond strengths around the anions deviating by as much as 40% from the valence (Baur, 1970).

In the original formulation of the principle, the variation of bond strength with bond length was determined by the factor $1/\nu$. It is possible, however, to relate bond strength (s) to bond length (R) using analytical expressions (R – s curves). Byström & Wilhelmi (1951) used Pauling's (1947) logarithmic relationship for covalent bonds in the form:

$$R - R_1 = -2k \log n \quad (1)$$

between bond length, R , and bond number n ,[†] to evaluate bond strengths in $(NH_4)_2Cr_2O_7$ and V_2O_5 (R_1 = length of a single bond and k is an arbitrary constant). Evans (1960) revised the value of R_1 for V^{5+} to analyze valence sums in 10 vanadates containing V^{4+} and V^{5+} . The agreement of calculated and observed valences was for the most part excellent although the bond-strength sum, p_V , around vanadium in V_2O_5 was 5.47 and thus deviated considerably from the ideal value of 5.0.

Zachariasen (1954, 1963) and Zachariasen & Plettinger (1959) used the distances in a number of borates and uranates to prepare empirical tables of H^+ –O, B^{3+} –O, and U^{6+} –O ionic bond strengths *vs.* bond lengths and these resulted in bond-strength sums which did not differ by more than 0.1 valence unit (v.u.) from the ideal values. Clark, Appleman & Papike (1969) used an equation of the form $R = a + bs + cs^2$ where R = bond distance, s = bond strength, and a , b , c are variable parameters for each ion pair to evaluate the strengths of the bonds Na^+ –O, Mg^{2+} –O, Ca^{2+} –O, Al^{3+} –O, Fe^{3+} –O and Si^{4+} –O in pyroxenes. Perloff (1970) assumed a linear relationship between bond length and bond strength for Mo^{6+} –O distances in $Na_3(CrMoO_6O_{24}H_6) \cdot 8H_2O$.

Donnay (1969) and Donnay & Allman (1970) have devised a scheme for constructing R – s curves using an equation of the form

$$s = s_0 \left(\frac{\bar{R}}{R} \right)^N \quad (2)$$

where s = strength* of a bond of length R ; s_0 = ideal strength of the bond of length \bar{R} , the mean value of bond length in an individual polyhedron, and N = a constant which is different for each cation–anion pair and in some cases for different cation sites. This expression is used for values of $R < \bar{R}$. When $R > \bar{R}$ they assume a linear relation between s and R ,

$$s = s_0 \frac{R_{\max} - R}{R_{\max} - \bar{R}} \quad (3)$$

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† Bond number is defined as the number of shared electron pairs per bond.

* Although Donnay & Allman (1970) chose to use the term bond valence, we prefer to continue Pauling's original terminology. We have also changed the symbols in equation (2) to be consistent with those of Zachariasen (1931).

Values of R_{\max} were determined for most metal-(O, OH) bonds in the periodic table by extrapolating an empirical $R-s$ curve derived from the ionic radii of Shannon & Prewitt (1969) to $s=0$. They achieve excellent agreement between the valence and the sums of the bond strengths but they are forced to construct unique curves for each structure to be analyzed and in certain cases for even the same cation in different sites, e. g. Ca(1) and Ca(2) in pumpellyite (Allmann & Donnay, 1971).

Baur (1970) uses the deviations from Pauling's electrostatic valence principle to predict which bonds will be longer or shorter than the average in a particular crystal. He relates the bond length (R_{ij}) to the sum (p_j) of the mean bond strengths around the anion (j) using a linear expression of the form

$$R_{ij} = a_i + b_i p_j.$$

He has determined the values of the empirical constants a_i and b_i for fifteen M_i -O atom pairs using the bond lengths observed in some 130 structures but he requires different parameters for the same cation in a different coordination. His approach works well provided the range of R_{ij} values is not large, but for very distorted environments such as are sometimes found around V^{5+} , his method does not work satisfactorily (Gopal, 1972).

We have derived a set of empirical bond-strength-bond-length* curves based on the equation

$$s = s_0 \left(\frac{R}{R_0} \right)^{-N} \quad (4)$$

by fitting the constants, s_0 , R_0 and N , so that the sums of the bond strengths around the cations are set as nearly as possible equal to the valence in a large variety of oxide structures.

While the equation we use [equation (4)] is the same as that [equation (2)] used by Donnay & Allman (1970), our approach differs from theirs in a number of significant ways. First, we use equation (4) over the whole range of bond strengths, thereby avoiding the assignment of R_{\max} (the maximum bonding distance) and the coordination number which they need in order to calculate \bar{R} . Secondly we use the same curve for all bonds between two atomic species wherever they occur. Thirdly, we obtain the values of s_0 , R_0 and N in a different manner, using the information available in a large number of crystal structures rather than tailoring the values to the specific structures under consideration.

* The concept of bond strength as defined by Pauling (1929) is one derived from an ionic model of chemical bonding. In this paper we show that the concept can be used just as well in situations where the bonding is primarily covalent (see below). The fact that the theory works in a given situation cannot be taken as evidence that the bonding is ionic even though for convenience we have continued to use terms such as 'cation' and 'anion'. The term 'electrostatic bond strength' is used in this paper in a formal sense only and it does not imply an ionic model.

Procedure

The bond strength (s) can be calculated from the bond length (R) using the computer program *BOST* which contains a variety of functions of the form $s=f(R)$, [e.g. $s=A((R-B)/c)^{-N}$ or $s=10(A-R)/R_0+c$]. We have chosen to use the following expression

$$s = s_0 \left(\frac{R}{R_0} \right)^{-N} \quad (5)$$

because it gives a good fit and has the advantage of simplicity. The parameter s_0 (the bond strength associated with a bond of length R_0) is assigned arbitrarily by the user and R_0 and N are constants found by least-square fitting as described below.

An initial set of parameters is chosen and used to calculate the bond strength s_{ij} for the bond between atom i and atom j using the observed bond length R_{ij} . The sum (p_i) of these bond strengths around the atom i is given by

$$p_i = \sum_j s_{ij} \quad (6)$$

and in the ideal case this should be equal to the valence z_i of atom i .

The initial set of parameters are then refined by least squares to minimize the function

$$Q = \sum_{i=1}^m w_i (z_i - p_i)^2 \quad (7)$$

where m is the number of atoms of type i used in the calculation and w_i is a weight set equal to $1/\sigma^2(p_i)$, $\sigma(p_i)$ being the standard error in p_i as calculated from $\sigma(R_{ij})$, the standard error in the experimental bond length. Refinement works best if the correlation between the parameters R_0 and N is kept small. This can be done by choosing s_0 so that $R_{ij}/R_0 \sim 1$; R_0 then represents a typical bond length and s_0 the corresponding typical bond strength.

The program calculates a number of measures of the agreement between the valence and the bond strength. In addition to the difference, $(z_i - p_i)$, it calculates the relative difference $(z_i - p_i)/z_i$ and the difference normalized to the standard error $(z_i - p_i)/\sigma(p_i)$, the latter being the quantity which enters into the calculation of Q . The overall agreement for the m atoms around which sums have been made is conveniently measured by the r.m.s. relative deviation $D_i = [(\sum (z_i - p_i)^2 / z_i^2) / m]^{1/2}$.

Three different procedures were followed in determining the parameters R_0 and N . For cations which exist with several different coordination numbers bond-strength sums around all cations for which reasonably accurate bond lengths were available were calculated. The parameters were then refined by fitting the bond strength sums to the valence of the cation. In cases where the cation normally has only one coordination number this procedure is unsatisfactory since almost any value of N will give an equally good fit. In these cases it was necessary to give much greater weight to

structures with atypical coordination numbers. For example the slopes of the $R-s$ curves for $\text{Si}^{4+}\text{-O}$ and $\text{Mg}^{2+}\text{-O}$ were constrained to pass as close as possible to the stishovite and SiP_2O_7 points and to the MgAl_2O_4 and MgV_2O_4 points respectively. Furthermore, since no examples of either tetrahedral Ti^{4+}O_4 or octahedral P^{5+}O_6 are known, we were forced to use data from TiCl_4 , TiBr_4 , and PCl_5 . In these cases Pauling radii for Cl^- and Br^- corrected for CN in a manner similar to that for O^{2-} (Shannon & Prewitt, 1969) were subtracted from the average M-X distances. The resulting radii for ${}^{IV}\text{Ti}^{4+}$ and ${}^{VI}\text{P}^{5+}$ were added to the radius for ${}^{II}\text{O}^{2-}$ to obtain approximate ${}^{IV}\text{Ti}^{4+}\text{-O}$ and ${}^{VI}\text{P}^{5+}\text{-O}$ distances. As in the cases of $\text{Si}^{4+}\text{-O}$ and $\text{Mg}^{2+}\text{-O}$, the $R-s$ curves were constrained to pass through the ${}^{IV}\text{Ti}^{4+}\text{-O}$ and ${}^{VI}\text{P}^{5+}\text{-O}$ points.

The curves for H^+ , S^{6+} and Cr^{6+} were refined in a different way which makes use of the fact that although these atoms normally occur only with one coordination number the bond lengths can vary considerably. In this case the bond-strength sums around the oxygen atoms as well as around the cations were used. This unfortunately restricted the number of structures that could be used to those for which the bond strengths from the oxygen atoms to other cations in the structure could be calculated but on the other hand it gives a much stronger leverage on the value of N . The structures used in the refinements are listed in the Appendix.

Although the interatomic distances published in recent crystal-structure determinations are frequently quoted with standard errors of 0.005 Å or less, it is well known that they are subject to systematic errors larger than this. Principal among these is the error arising from thermal motion which is well understood but difficult to apply because of the need to know how the atomic motions are correlated with each other. In cases of molecular fragments which can be treated as rigid (*e.g.* SO_4^{2-}) it is possible and customary to make these corrections, but for more weakly bonded groups the correction becomes very uncertain. We have therefore only used distances uncorrected for thermal motion, conscious of the fact that these distances are systematically too low (~ 0.01 to 0.02 Å) and will have a true standard error much larger than the values quoted. A more critical evaluation of the effects of thermal motion on the bond distances would, no doubt, improve the agreement between the bond-strength sums and the valence, but such an evaluation is not possible at present.

The $R-s$ curves are particularly useful in accounting for the variation of bond lengths with cation coordination number, a large effect that has long been recognized (Goldschmidt, Barth, Lunde & Zachariasen, 1926; Pauling, 1927; Zachariasen, 1931). Recently, however, the average distances have been found to depend in some measure on the anion coordination number (Jeffreys & Slaughter, 1963; Slaughter, 1966; Shannon & Prewitt, 1969; Brown & Gibbs, 1969) and the nature of the cations surrounding the oxygen ions (Noll, 1963;

Lazarev, 1964; Pant & Cruickshank, 1967; Brown & Gibbs, 1970; Shannon, 1971).

Because this latter dependence is generally not yet well defined, this effect has been ignored. The former dependence can be included by making an *a priori* correction for the anion coordination number using the variation of oxygen radius observed by Shannon & Prewitt (1969). Thus all distances can be 'corrected' to those for two coordinate oxygen by subtraction of the following amounts: 0.01 Å (3 coordination), 0.03 Å (4 coordination) and 0.05 Å (6 coordination), *etc.* For comparison the bond strength parameters have been refined using both the 'corrected' and the 'uncorrected' bond distances.

Kálmán (1971) has shown that the average tetrahedral M-O distances (\bar{R}) for atoms in groups IV to VII of the periodic table can be expressed in terms of the valence (equivalent to bond strength) by the simple relation

$$\bar{R} = 0.0113 n^2 + R' \quad (8)$$

where $n = 8 - z$ and R' is constant for a given row of the periodic table. This suggests that a similar relation might also hold for the standard distances, R_0 . Rather than use equation (8), we have found that we get a good fit with the function

$$s_0 = \left(\frac{R_0}{R_1} \right)^{-N_1} \quad (9)$$

where R_1 and N_1 are constants for a given row. In most cases the value of N_1 obtained does not differ by more than 1 from the individual N 's of the atoms in the row. This allows a single pair of parameters to be used for all the elements in the same row that have isoelectronic ionic cores. Thus one curve of the form

$$s_0 = \left(\frac{R}{R_1} \right)^{-N_1} \quad (10)$$

can be used to calculate bond strengths around Li^+ , Be^{2+} , and B^{3+} and another to calculate bond strengths around Na^+ , Mg^{2+} , Al^{3+} , Si^{4+} , P^{5+} , and S^{6+} *etc.* The fact that such a fit can be made implies that the length of the M-O bond of unit strength (R_1) is the same (or nearly the same) for all ions with the same electron core. To the extent to which this is true one can calculate bond strengths for bonds not included in the table (*e.g.* C-O, N-O, Cl-O; see, for example, Table 15).

Results

Tables 1, 2 and 3 list respectively the refined parameters obtained (1) from 'uncorrected' distances for each individual M-O pair (2) from 'uncorrected' distances for ions having isoelectronic cores and (3) from distances corrected for oxygen coordination for each individual M-O pair. Fig. 1 shows typical $R-s$ curves for Si^{4+} , Ge^{4+} and Ti^{4+} . The points indicate the values of R that were used in the refinement and are, for convenience, plotted along their respective curve. Fig. 2

shows the curves derived from the universal $R-s$ parameters and gives a good indication of the way in which bond strengths fall off with increasing distance.

Table 1. *Individual bond-strength-bond-length parameters for M-O bonds in the expression*
 $s = s_0(R/R_0)^{-N}$

Cation	s_0 (v.u.)	R_0 (Å)	N
H ⁺	0.5	1.184	2.2
Li ⁺	0.25	1.954	3.9
Be ²⁺	0.5	1.639	4.3
B ³⁺	1.0	1.375	3.9
Na ⁺	0.166	2.449	5.6
Mg ²⁺	0.333	2.098	5.0
Al ³⁺	0.5	1.909	5.0
Si ⁴⁺	1.0	1.625	4.5
P ⁵⁺	1.25	1.534	3.2
S ⁶⁺	1.5	1.466	4.0
K ⁺	0.125	2.833	5.0*
Ca ²⁺	0.25	2.468	6.0
Sc ³⁺	0.5	2.121	6.0
Ti ⁴⁺	0.666	1.952	4.0
V ⁵⁺	1.25	1.714	5.1
Cr ⁶⁺	1.5	1.648	4.9†
Mn ²⁺	0.333	2.186	5.5
Fe ³⁺	0.5	2.012	5.3
Fe ²⁺	0.333	2.155	5.5
Co ²⁺	0.333	2.118	5.0
Cu ²⁺	0.333	2.084	5.3
Zn ²⁺	0.5	1.947	5.0
Ga ³⁺	0.75	1.837	4.8
Ge ⁴⁺	1.0	1.750	5.4
As ⁵⁺	1.25	1.681	4.1

* Refines to $N=4.3$ but $N=5.0$ gives as good agreement.

† Refines to $N=6.1$ but $N=4.9$ gives better overall agreement.

Table 2. *Universal bond-strength-bond-length parameters for M-O bonds in the expression*
 $s = (R/R_1)^{-N_1}$

Cations	Number of electrons in cation core	R_1 (Å)	N_1
H ⁺	0	0.86	2.17
Li ⁺ Be ²⁺ B ³⁺	2	1.378	4.065
Na ⁺ Mg ²⁺ Al ³⁺ Si ⁴⁺ P ⁵⁺ S ⁶⁺	10	1.622	4.290
K ⁺ Ca ²⁺ Sc ³⁺ Ti ⁴⁺ V ⁵⁺ Cr ⁶⁺	18	1.799	4.483
Mn ²⁺ Fe ³⁺	23	1.760	5.117
Zn ²⁺ Ga ³⁺ Ge ⁴⁺ As ⁵⁺	28	1.746	6.050

The agreement between the valence and the bond-strength sums is quite sensitive to the value of N (± 0.2) for small ions whose coordination numbers are well defined *e.g.* Be²⁺, B³⁺, Si⁴⁺, Zn²⁺, Ga³⁺ and Ge⁴⁺. In other cases N may be varied within a range of ± 2 without making an appreciable difference to the agreement.* On the other hand the values of R_0 are usually quite well determined, variations of 0.003 Å producing a noticeable change in the observed agreement.

* In certain cases when the refined value of N appears to be unreasonably large or small we have chosen a value different from that obtained by the refinement procedure outlined above. In all these cases, which are explicitly noted in Tables 1 and 3, the agreement is equally good with both values.

Table 3. *Bond-strength-bond-length parameters for M-O bonds (corrected for oxygen coordination) used in the expression* $s = s_0(R/R_0)^{-N}$

Cation	s_0 (v.u.)	R_0 (Å)	N
Li ⁺	0.25	1.925	3.4
Be ²⁺	0.5	1.611	3.8
B ³⁺	1.0	1.343	3.7
Na ⁺	0.166	2.421	5.7
Mg ²⁺	0.333	2.076	5.2
Al ³⁺	0.5	1.888	4.6
Si ⁴⁺	1.0	1.605	4.0
P ⁵⁺	1.25	1.525	3.2
K ⁺	0.125	2.823	6.0*
Ca ²⁺	0.25	2.437	5.5
Sc ³⁺	0.5	2.090	6.0
Ti ⁴⁺	0.666	1.947	4.6
V ⁵⁺	1.25	1.700	4.8
Mn ²⁺	0.333	2.165	5.1
Fe ³⁺	0.5	1.981	5.2
Fe ²⁺	0.333	2.128	4.9
Co ²⁺	0.333	2.087	5.0
Cu ²⁺	0.333	2.068	5.4
Zn ²⁺	0.5	1.946	5.7
Ga ³⁺	0.75	1.822	5.2
Ge ⁴⁺	1.0	1.735	5.3
As ⁵⁺	1.25	1.671	4.9

* Refines to $N=4.7$ but $N=6.0$ gives as good agreement.

The relative merits of the universal and individual curves and the individual curves corrected for oxygen coordination can be judged from the agreement indices (r.m.s. relative deviation) summarized in Table 4. Comparison of the individual *vs.* the universal curves shows better agreement for the individual curves in 15 instances, and worse agreement in only 5 cases.† The mean r.m.s. deviation of 4.0% for the individual curves can be compared with 5.4% for the universal curves. Comparison of individual 'corrected' and 'uncorrected' curves shows better agreement for the 'uncorrected' distances in 10 cases and worse agreement in another 12 cases; the mean r.m.s. deviations being 4.6 and 4.4% respectively. Since calculations involving uncorrected distances are simpler and since the individual curves give a better fit than the universal ones, the 'uncorrected' individual curves with parameters listed in Table 1 are to be preferred for most applications.

Discussion

1. *Electrostatic-valence principle*

We have tried to find a functional relationship which uniquely relates bond strength to bond length, regardless of structure type, with the constraint that the sum of the bond strengths equals the valence as proposed

† The individual curves can always be made to give at least as good a fit as the universal ones since the individual parameters can always be chosen to be the same as the universal parameters. However, the method of fitting the parameters is not one that necessarily minimizes the r.m.s. relative deviation. One would expect the individual parameters to show systematic trends across the periodic table and the universal curves provide a reasonably successful attempt to describe these.

by Pauling (1929). This attempt to evaluate the electrostatic-valence principle follows the general lines adopted by most previous workers but differs from them in that our data, evaluated by least-squares techniques, are more extensive. We have analyzed environments of 884 cations in 417 different structures and have derived $R-s$ curves for M-O bonds for the majority of atoms in the first half of the periodic table in a simple two-parameter form. Table 4 shows that the mean r.m.s. deviation of the valence from the calculated bond-strength sums around cations for individual curves is 4.3%; the agreement is worse for the ions Li^+ , Na^+ , K^+ , Ca^{2+} , Sc^{3+} , and Mn^{2+} . Fig. 3, in which bond-strength sums around most of the cations evaluated in this study are plotted *vs.* their average bond length, shows that although the mean deviation is about 5%, individual variations of 10–15% are still observed.

A detailed examination of the results for V^{5+} shows that while our model accounts for most of the gross features of the structures significant deviations still remain. Table 5 lists the bond sums around the vanadium atoms used in our calculations. For comparison the sums are given using both the individually fitted curve and the curve for 'cations' with the eighteen-electron core. Although the average deviation from 5.00 is only 4.2%, it is apparent that there are individual deviations of 10–20% in some structures. Some of these deviations can be attributed to uncertainties in our knowledge of

the bond lengths (indicated by the errors given for the bond-strength sums) but some have to be attributed to real effects which we cannot as yet explain. That these effects are real is attested, for example, by the bond-

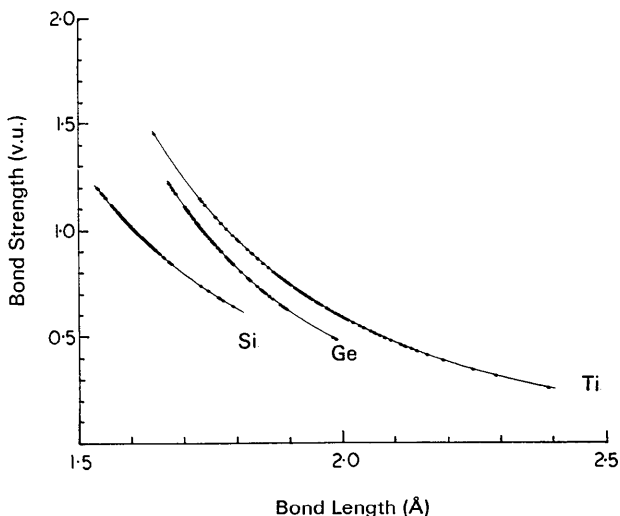


Fig. 1. Individual M-O bond-length-bond-strength curves for M=Si, Ge and Ti. The circles indicate the values of the individual bond lengths used in the calculations. They do not represent the quality of fit between experiment and theory.

Table 4. Statistics concerning the derivation of bond-strength-bond-length parameters

- Method 1. Least squares fit R_0 and N using cation sums only.
 2. N chosen to give good fit for atypical coordination numbers. R_0 refined by least squares.
 3. Least-squares fit of R_0 and N using cation and anion sums.

Cation	Number of structures used	Number of bond strength sums used	Method	R.m.s. relative deviation (%)		
				Individual uncorrected (Table 1)	Universal (Table 2)	Individual corrected (Table 3)
H^+	9 (3)*	38 (24)*	3	4.6	—	—
Li^+	22	29	1	6.4	10.5	5.3
Be^{2+}	11	13	1	3.4	4.0	3.7
B^{3+}	24	44	1	2.6	2.9	4.0
Na^+	31	48	1	7.6	7.5	6.4
Mg^{2+}	27	39	2	5.2	4.9	5.1
Al^{3+}	25	39	1	4.4	4.8	4.0
Si^{4+}	38	50	2	3.1	3.2	2.2
P^{5+}	29	45	2	2.1	3.4	2.7
S^{6+}	33 (3)*	41 (21)*	3	2.4	2.5	—
K^+	29	34	1	8.5	10.9	9.0
Ca^{2+}	30	40	1	6.3	8.4	6.6
Sc^{3+}	8	11	2	7.2	6.1	4.8
Ti^{4+}	21	41	2	3.3	5.1	4.7
V^{5+}	31	46	1	4.2	4.1	3.9
Cr^{6+}	10 (5)*	22 (50)*	3	3.5	3.5	—
Mn^{2+}	20	33	2	6.9	6.5	6.6
Fe^{3+}	36	50	1	2.7	2.9	3.2
Fe^{2+}	15	19	1	5.4	—	4.8
Co^{2+}	18	29	2	6.6	—	3.7
Cu^{2+}	25	40	1	5.8	—	6.5
Zn^{2+}	29	48	1	4.8	4.9	3.9
Ga^{3+}	10	14	1	3.2	6.6	2.8
Ge^{4+}	17	28	1	3.7	5.4	4.4
As^{5+}	24	34	1	3.1	5.4	3.4

* Figures in parentheses indicate the number used in the refinement [marked with * in the Appendix]. The other figures indicate the number of X-O structures and bonds used in calculating the indices quoted in the last 3 columns.

strength sums consistently found in a number of pyroxene structures where $p_{O(2)}$ is typically 1.75 and $p_{O(3)}$ lies between 2.15 and 2.30. Martin & Donnay (1972) attribute the low value of $p_{O(2)}$ to the presence of OH^- ions. However, in the colourless pyroxenes LiVO_3 and NaVO_3 , small amounts of hydroxyl ion would be accompanied by reduction of V^{5+} to V^{4+} which would probably result in darkly coloured compounds. It is likely that the second-nearest neighbours are responsible for some of these deviations but a detailed analysis of their role must await further study.

2. Bond-strength–bond-length curves and implications for chemical bonding

Bond-strength sums calculated using the 10 parameters of the five universal bond-strength curves give al-

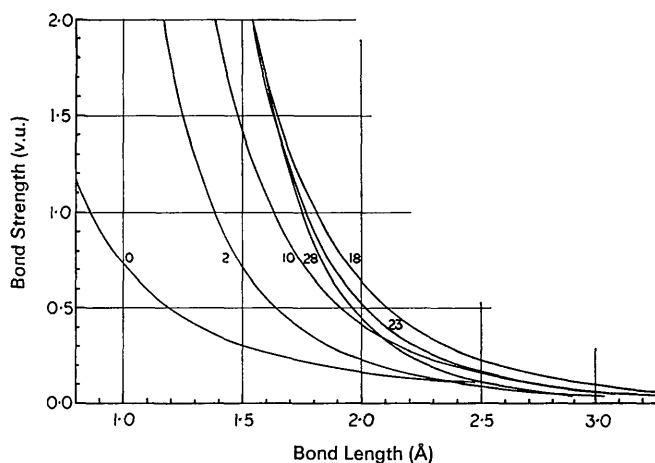


Fig. 2. Universal M–O bond-length–bond-strength curves for isoelectronic series. The numbers associated with each curve indicate the number of electrons on the 'cation' (core electrons).

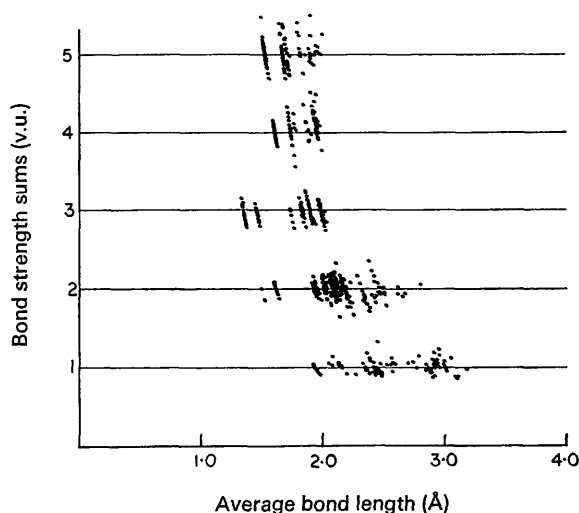


Fig. 3. Experimental bond-length sums vs. average M–O bond length for most of the atoms used in this study.

Table 5. Bond strength sums around V^{5+}

ν = number of bonds used in calculations given in subsequent columns.

\bar{R} = average bond length (Å) around V^{5+} .

P_1 = bond strength sums calculated with individual $R-s$ curve.

$$P_1 = \sum_i 1.25(R_i/1.714)^{-5.1} \text{ v.u.} \quad (\text{Table 1})$$

P_2 = bond-strength sums calculated with universal $R-s$ curve.

$$P_2 = \sum_i (R_i/1.799)^{-4.483} \text{ v.u.} \quad (\text{Table 2})$$

For references see the Appendix.

Figures in parentheses are standard deviations in the last figures quoted.

ν	\bar{R}	P_1	P_2	Crystal
4	1.715	5.04 (7)	5.01 (6)	$\text{Zn}_2\text{V}_2\text{O}_7$
4	1.706	5.12 (6)	5.08 (5)	YVO_4
4	1.721	4.90 (4)	4.89 (3)	NdVO_4
4	1.729	4.84 (4)	4.83 (3)	$\text{Mg}_3\text{V}_2\text{O}_8$
4	1.722	4.91 (19)	4.90 (16)	$\text{Co}_3\text{V}_2\text{O}_8$
4	1.740	4.68 (18)	4.69 (16)	$\text{Ni}_3\text{V}_2\text{O}_8$
4	1.719	4.98 (7)	4.96 (6)	$\text{Zn}_3\text{V}_2\text{O}_8$
4	1.718	4.98 (16)	4.95 (14)	$\text{Cd}_2\text{V}_2\text{O}_7$
4	1.720	5.02 (5)	4.99 (5)	FeVO ₄
4	1.727	4.89 (5)	4.87 (4)	
4	1.720	4.98 (5)	4.96 (4)	Li ₃ VO ₄
4	1.717	4.96 (1)	4.94 (1)	
4	1.727	4.99 (2)	4.95 (2)	LiVO ₃
4	1.730	4.92 (7)	4.89 (6)	Co ₂ V ₂ O ₇
4	1.731	4.84 (7)	4.83 (6)	
4	1.707	5.11 (4)	5.07 (3)	Ca ₂ VO ₄ Cl
4	1.691	5.36 (6)	5.28 (5)	Na ₃ VO ₄ ·12H ₂ O
4	1.702	5.20 (8)	5.14 (7)	Ca ₃ V ₂ O ₈
4	1.694	5.31 (10)	5.24 (9)	
4	1.691	5.36 (9)	5.29 (8)	NH ₄ VO ₃
4	1.725	4.99 (23)	4.95 (20)	
4	1.731	4.89 (7)	4.87 (6)	KVO ₃
5	1.819	5.09 (7)	5.15 (6)	CaV ₂ O ₆
5	1.848	4.84 (22)	4.92 (19)	CaV ₂ O ₆ ·2H ₂ O
5	1.808	5.44 (24)	5.45 (21)	
5	1.952	5.12 (2)	5.12 (1)	Mg ₂ V ₂ O ₇
5	1.883	4.81 (1)	4.89 (1)	
5	1.830	4.99 (15)	5.06 (13)	KVO ₃ ·H ₂ O
6	2.009	5.29 (11)	5.36 (9)	CsV ₃ O ₈
6	1.906	5.03 (2)	5.21 (1)	Ca ₃ V ₁₀ O ₂₈ ·17H ₂ O
6	1.924	5.08 (3)	5.22 (3)	
6	1.911	4.99 (2)	5.17 (2)	
6	1.910	5.05 (2)	5.22 (2)	
6	1.917	4.96 (5)	5.13 (4)	
6	1.913	5.04 (5)	5.20 (5)	
6	1.931	4.94 (6)	5.10 (5)	
6	1.914	4.85 (4)	5.05 (4)	
6	1.932	4.94 (5)	5.10 (4)	
6	1.947	5.25 (5)	5.35 (4)	
6	1.989	5.09 (7)	5.20 (6)	VPO ₅
6	1.917	5.27 (36)	5.38 (31)	V ₂ O ₅
6	1.908	5.64 (46)	5.67 (38)	VO(OCH ₃) ₃
6	1.920	4.88 (12)	5.07 (10)	
6	1.965	5.06 (3)	5.19 (3)	CsV ₃ O ₈
6	1.969	5.13 (1)	5.25 (1)	CoV ₂ O ₆
6	1.944	4.96 (13)	5.12 (12)	MgV ₂ O ₆
				CdV ₂ O ₆

most as good a fit to the valence (5.4% deviation as against 4.0%) as those calculated with the 54 parameters of the 27 individual curves. The universal curves thus lead to a considerable simplification in the concept of bond strength for isoelectronic series of ions. It is perhaps surprising that a single set of parameters can describe bonds ranging from almost completely ionic to largely covalent, particularly as the bond-strength model of chemical bonding has always been regarded

as an ionic model. However, a prior knowledge of the covalent character of a bond is not needed in order to derive or apply the theory. On the other hand, there is a close correlation between the covalence of a bond as calculated (Pauling, 1940, p. 72) from the electronegativity difference between the terminal atoms and the mean bond strength between these atoms. Fig. 4 shows the logarithm of the covalence plotted against the logarithm of the mean cation-oxygen bond strength for 'cations' with 18, 36 and 54 electrons. The relationship between the covalence (f'_c) and the bond strength (s) for M-O bonds can be described by the empirical equation

$$f'_c = as^M \quad (11)$$

where $a = 0.49$ v.u. and $M = 1.57$. Similar curves can be drawn for other isoelectronic series (Fig. 5) with the values of a and M given in Table 6. It follows from equation (10) that the covalence is related also to bond length by

$$f'_c = a \left(\frac{R}{R_1} \right)^{-MN_1} \quad (12)$$

with the values of a and MN_1 given in Table 6. The constancy of the values of MN_1 for the 'ions' with 2, 10 and 18 electrons is rather striking but may be fortuitous.

Table 6. Parameters relating covalence to bond strength and bond length in the equations
 $f'_c = as^M = a(R/R_1)^{-MN_1}$

Number of electrons in core	a (v.u.)	M	MN_1
0	0.67	1.8-2.0*	4*
2	0.60	1.73	7.04
10	0.54	1.64	7.04
18	0.49	1.57	7.04
28	0.60	1.50	9.08
36	0.49	1.57	
46	0.67	1.43	
54	0.49	1.57	

* Estimated from the trends in the value of M in subsequent series.

The relationships between the covalence and the bond strengths of M-O pairs have been calculated on the basis of mean values but it would not be unreasonable to suppose that these relationships could be used to calculate the covalence of an individual bond on the basis of its known bond strength. This would be in accord with the notion that the covalent character of a bond depends amongst other things on the oxidation state and coordination number of its terminal atoms. If these relationships can be applied to individual bonds they would allow a quantitative prediction of the difference in character between the very short and the very long V-O bonds found in V_2O_5 . The short bond ($R = 1.586 \text{ \AA}$) has a bond strength of 1.86 v.u. and a covalence of 1.30 v.u. giving 30% ionic character; on the

other hand the long bond ($R = 2.787 \text{ \AA}$) has a bond strength of 0.103 v.u. and a covalence of 0.013 v.u. giving 87% ionic character.

Hydrogen provides another interesting example of the relationship between bond strength and covalence. Typically it forms two or more bonds between oxygen atoms in crystals. One of these is usually strong ($s \sim 0.85$), the others are weak ($s \lesssim 0.15$). The assignment of the electronegativity of hydrogen is based on a consideration of the strong hydrogen bond and leads to a covalent character of 67% for a single O-H bond. In crystals this covalence is shared very unequally between the two or more bonds. Using a value of 1.8 to 2* for the exponent M in equation (11) the strong bond is calculated to have about 58% and the weak bond 10% covalent character, according well with the view that the weak O-H bond is primarily electrostatic. Both in

* See Table 6. The conclusions drawn here are not very sensitive to the exact value of M chosen.

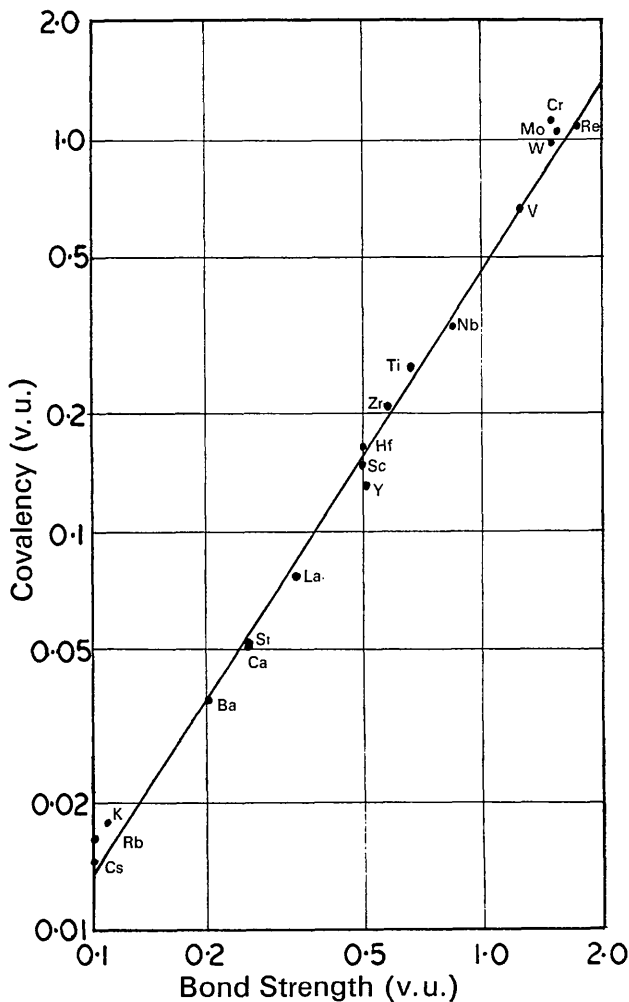


Fig. 4. M-O covalence vs. bond strength for 'cations' with 18, 36 and 54 electrons. The scales are logarithmic.

strength and character the weak O-H bond is similar to a typical Na-O bond, an observation that agrees well with the alkali metal-like behaviour of NH_4^+ .*

The fact that the relations between bond lengths, bond strengths and covalence are the same for all iso-electronic ions suggests a simple model of chemical bonding in which the electrons are divided into core electrons and valence electrons. The latter are all associated with bonds, one electron pair per unit bond strength, and are responsible for the attractive force in the bond. The core electrons give rise to the Born repulsion between atoms. Equilibrium is achieved locally when these two opposing forces are equal, the stronger the bonding force, the closer the distance of approach.

The properties of the core are described by the fitted parameters given in Table 2 and illustrated in Fig. 2. R_1 describes the sum of the radii of the cation and oxygen cores for a unit bond strength and N describes

* Khan & Baur (1972) have recently reviewed the similarities and differences between NH_4^+ and alkali metals.

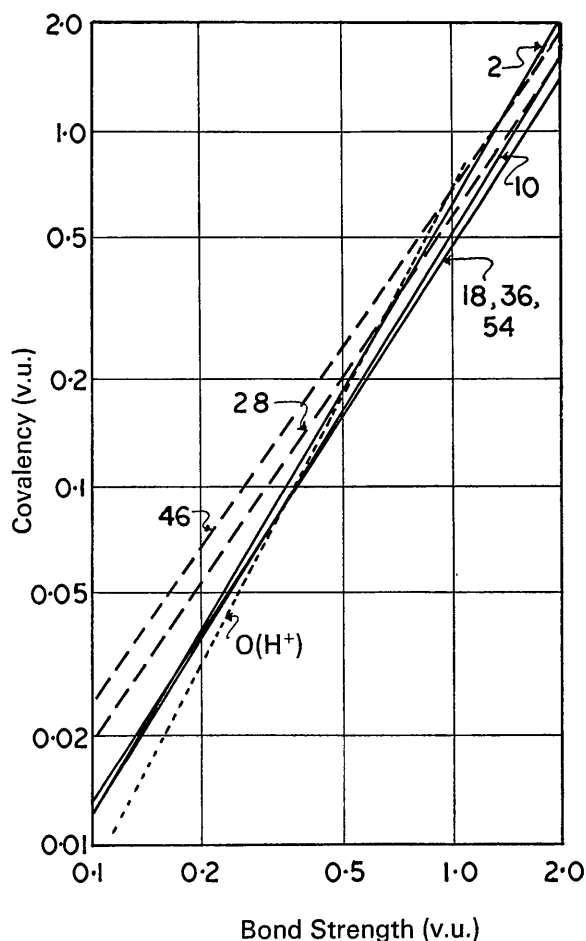


Fig. 5. M-O covalence vs. bond-strength curves for the various iso-electronic series. The numbers associated with each curve indicate the number of electrons in the 'cation' (core electrons). The scales are logarithmic.

the 'hardness' of the core, larger values representing harder cores. Both the properties of the core and the properties of the bond depend only on the numbers of electrons in each, and since these are known from classical valence theory, the prediction of bond lengths becomes remarkably simple.

This model is somewhat different from the ionic picture usually associated with a bond-strength formalism. In the ionic picture no distinction is made between core and valence electrons but the atoms are treated as negatively or positively charged spheres. In our approach all atoms are treated as positively charged spheres (nucleus plus core electrons *e.g.* Li^+ , S^{6+} and O^{2+} rather than O^{2-}) held together by the negative valence electrons. In order to apply the theory it is not necessary to know whether the electrons are placed in the bond symmetrically (covalent bond) or asymmetrically (ionic bond), but the correlation between the covalence and the bond strength suggest that the position of the electrons with respect to the oxygen atom varies in a uniform way with bond strength, residing completely on the oxygen atom at zero strength (ionic limit) and moving towards the centre of the bond for bond strengths of about two (covalent limit).

Our model differs from the Valence Shell Electron Pair Repulsion (VSEPR) theory of Gillespie & Nyholm (1957) in that we assume that the non-bonding electron pair belongs not to the valence shell but to a spherically symmetrical core. However, the VSEPR theory is most useful in discussing angles subtended by the ligands at the cation while our theory is more useful in discussing distances.

3. Distorted coordination polyhedra

The stereochemistry of many elements can be discussed quite effectively using a charged-hard-sphere model in which the properties of an atom are described solely by its ionic charge (valence) and its radius. Such atoms tend to have rather symmetric coordination with bonds of equal length. The stereochemistry of such ions is not difficult to understand in terms of most theories of chemical bonding. More recently the stereochemistry of atoms which typically have rather distorted environments (*e.g.* Cu^{2+} , Sb^{3+} and O^{2-}) have been discussed in terms of the electron configuration in such theories as the ligand field theory (Orgel, 1960) and the valence-shell electron-pair repulsion theory (Gillespie & Nyholm, 1957). In still further cases (*e.g.* alkali metals and V^{5+}) distorted environments occur for which no really predictive theory has yet been proposed. For atoms in such distorted environments the concept of ionic radius has proved difficult to apply and, because of the uncertainty in assigning a coordination number, it has also been difficult to use theories based on mean bond strength.

The use of $R-s$ curves resolves this problem by avoiding the concept of coordination number altogether. In cases where the coordination is regular, the bond strength for each bond can be calculated by divid-

ing the valency by the coordination number (Pauling, 1929; Baur, 1970), and arguments based on average bond length or bond strength lead to the same conclusions. But the method of calculating individual bond strengths can be applied just as easily in cases where the coordination is very irregular. Two examples are given in Tables 7 and 8 and are illustrated in Fig. 6 where the average bond length and the bond-strength sums are plotted as successively longer bonds are added to the coordination spheres around Na^+ and V^{5+} . In the bond-strength-sum graph, regular coordination appears as a straight line and irregular coordination as a curved line, but both level off at values of $\sum s = z$. The inclusion of very long bonds makes little difference to the bond-strength sums but alters the average bond length dramatically indicating that for these ions the concept of average bond length must be used with great caution.

In practice there will always be an arbitrary cut-off in the number of bonds for which strengths are calculated and this makes a small difference to the sums. At 3.0 Å the bond strength for a Na-O bond is 0.05 v.u. and inclusion of bonds in the range 3.0 to 4.0 Å corresponds to change in the value of R_0 of about 0.01

Table 7. Bond lengths in selected sodium compounds

For reference see the Appendix

Ligand number	$\text{Na}_4\text{P}_2\text{O}_7$	$\text{NaAl}(\text{SO}_4)_2$	$\text{Na}_2\text{GeO}_3 \cdot 6\text{H}_2\text{O}$	NaIO_4
1	2.271	2.453	2.36	2.55
2	2.314	2.453	2.37	2.55
3	2.326	2.453	2.43	2.55
4	2.441	2.453	2.45	2.55
5	2.890	2.453	2.46	2.61
6	3.156	2.453	2.52	2.61
7	3.294		3.68	2.61
8			3.85	2.61

Table 8. Bond lengths in selected vanadates

For reference see the Appendix

Ligand number	Li_3VO_4	KVO_3	V_2O_5	$\text{Ca}_3\text{V}_{10}\text{O}_{28} \cdot 17(\text{H}_2\text{O})$
1	1.714	1.652	1.586	1.681
2	1.717	1.661	1.782	1.681
3	1.717	1.806	1.878	1.903
4	1.720	1.806	1.878	1.903
5			2.023	2.135
6			2.787	2.135

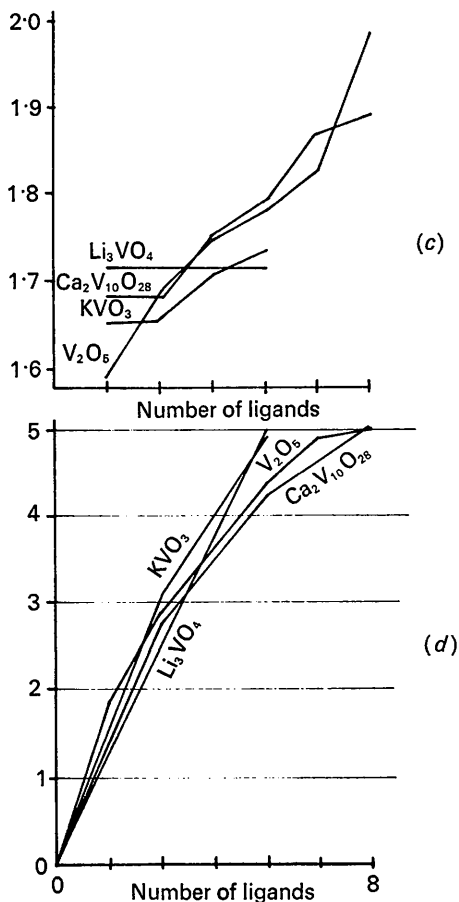
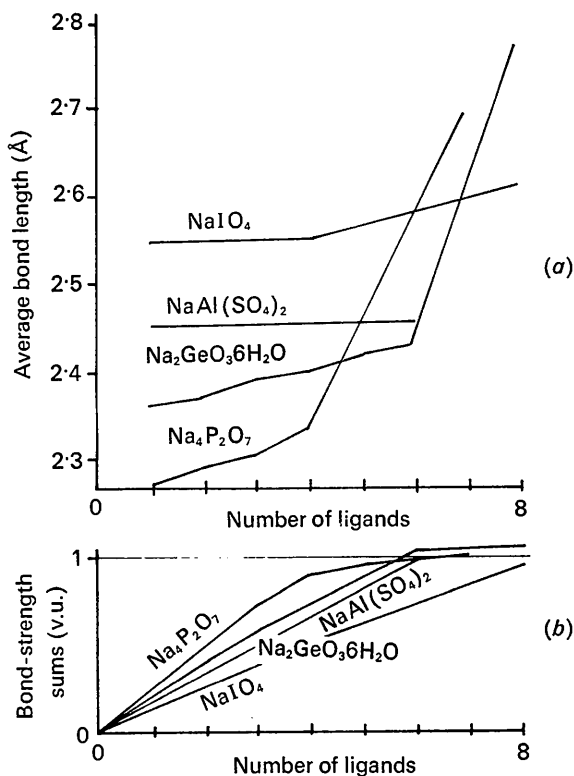


Fig. 6. (a) Average Na-O bond length as successively longer bonds are included. (b) Bond-strength sums around Na as successively longer bonds are included. (c) Average V-O bond length as successively longer bonds are included. (d) Bond-strength sums around V as successively longer bonds are included.

Å. The parameters given in Table 1 were calculated using a cut-off at around 3 Å, the point at which Na-cation distances begin to appear in the coordination sphere. This cut-off point also gives the best agreement with the universal curves.

Baur (1970) is able to predict the variation of the bond lengths in distorted coordination by recognizing that where the sum of Pauling's average bond strengths around the oxygen atom is greater than the valence, the structure will compensate by weakening (lengthening) the bond to it. He obtains linear regressions between the amount of the lengthening and the excess bond strength. Although his method gives a direct prediction of the variation of individual bond lengths from the mean, it requires a knowledge of the coordination numbers in the structure and a separate curve for a given cation for each coordination number. His linear regressions are equivalent to linear $R-s$ curves and for the examples he discusses this approximation is reasonable since the average bond length is constant from one site to another. On the other hand for strongly distorted coordination such as is found in octahedral V^{5+} and Cu^{2+} the average bond lengths show a significant variation. From the non-linear shape of our $R-s$ curve we expect that such highly distorted coordination would lead to a larger average bond length. The correlation between the average bond length (\bar{R}) and the degree of distortion ($\Delta = \text{mean-square relative deviation from the average}$) is shown in Fig. 7 for V^{5+} . Similar data for Cu^{2+} , Mg^{2+} and Li^+ are given by Shannon & Calvo (1973*a, b*). Linear regressions of average bond length on distortion yield the parameters given in Table 9 for V^{5+} , Cu^{2+} , Mg^{2+} , Li^+ , Zn^{2+} and Co^{2+} . For ions showing large distortion the correlation is remarkably high. For only slightly distorted octahedra other effects, such as anion coordination, become more important and this is illustrated by the better fit that is obtained in these cases when the average bond length is replaced by the effective ionic radius which takes anion coordination into account (Shannon & Prewitt, 1969).

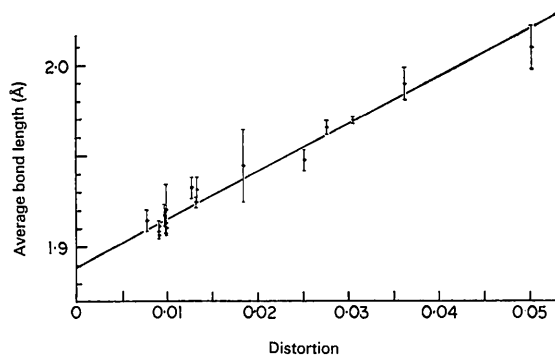


Fig. 7. Average V-O bond length as a function of distortion (mean-square relative deviation of bond length from the average) in VO_6 octahedra.

Table 9. Variation of mean M-O distance and effective ionic radius in octahedral environments as a function of distortion

The first equation given is that fitted to the observed values of \bar{R} and Δ , the second (in parentheses) is that predicted from the $R-s$ curves using equation (13).

The effective ionic radii (\bar{r}) are calculated by subtracting the oxygen radius corrected for anion coordination from the mean bond length (Shannon & Prewitt, 1969).

$$\Delta = \frac{1}{6} \sum_{i=1}^6 [(R_i - \bar{R})/\bar{R}]^2 \text{ where } \bar{R} = \text{average bond length in } \text{Å}.$$

Atom	max Δ	Equation	Correlation coefficient	Goodness of fit
V^{5+}	0.0576	$\bar{R} = 1.887 + 2.62\Delta$ ($\bar{R} = 1.855 + 5.8\Delta$)	0.98	0.008
Cu^{2+}	0.0316	$\bar{R} = 2.095 + 3.60\Delta$ ($\bar{R} = 2.084 + 6.6\Delta$)	0.89	0.016
Mg^{2+}	0.0156	$\bar{R} = 2.094 + 8.31\Delta$ ($\bar{R} = 2.098 + 6.3\Delta$)	0.72	0.021
Li^+	0.0148	$\bar{r} = 0.728 + 8.86\Delta$ $\bar{R} = 2.159 + 8.42\Delta$ ($\bar{R} = 2.167 + 5.3\Delta$)	0.77 0.31	0.018 0.030
Zn^{2+}	0.0071	$\bar{r} = 0.784 + 9.02\Delta$ $\bar{R} = 2.099 + 7.7\Delta$ ($\bar{R} = 2.111 + 6.3\Delta$)	0.79 0.64	0.035 0.021
Co^{2+}	0.0046	$\bar{r} = 0.736 + 8.20\Delta$ $\bar{R} = 2.106 + 7.38\Delta$ ($\bar{R} = 2.118 + 6.4\Delta$) $\bar{r} = 0.734 + 11.7\Delta$	0.74 0.42 0.70	0.016 0.019 0.016

The high correlation between the average bond length and the distortion indicates that the V-O bond-strength-bond-length curve, for example, could be fitted with a quadratic equation. Such an equation can be obtained by expanding equation (5) by the binomial theorem to second order and this in turn leads to the linear relationship between average bond length and distortion:

$$\bar{R} = R_r + \frac{R_r(N+1)}{2} \quad (13)$$

where R_r is the expected bond length for regular coordination. Table 9 list in parentheses the values for the coefficients of equation (13) predicted from the $R-s$ curves. The agreement with the fitted values is satisfactory where the distortion is small but for Li, Mg and particularly Cu and V it is clear that the higher-order terms in the expansion cannot be neglected. As these depend on the nature of the distortion they will vary from one cation site to another and cannot be calculated for a general case.

4. Comparison with elastic properties

The assumption underlying the use of bond lengths to measure bond strength is that the strength of a bond can be measured by its ability to overcome the short-range repulsive force that exists between any two atoms. The parameter which measures this repulsion in an ionic theory is the Born exponent (n).*

* Although the inverse power law is believed to be inferior to the exponential form (Born & Mayer, 1932; Linnett, 1940; Fumi & Tosi, 1964), Anderson (1970) has concluded that it is satisfactory for analysing the pressure derivatives of the bulk modulus of oxides.

Zachariassen (1931) has shown that in an ionic compound which exists in both the NaCl and the CsCl structure,

$$R = \sqrt[n-1]{\frac{nB}{Az_1z_2e^2}} \quad (14)$$

and

$$\frac{R_{\text{CsCl}}}{R_{\text{NaCl}}} = \sqrt[n-1]{\frac{nB_{\text{CsCl}}}{nB_{\text{NaCl}}} \cdot \frac{A_{\text{NaCl}}}{A_{\text{CsCl}}}} \quad (15)$$

where B = Born repulsion coefficient and A = Madelung constant. Zachariassen assumed B to be proportional to the coordination number of the cation and A not to vary greatly from one structure to another. The latter assumption would appear to be fairly drastic but Templeton (1953) has shown that in a variety of structures the reduced Madelung constant ($\bar{\alpha}$ = average atomic Madelung constant) can be expressed as a function of average coordination number ($\bar{\nu}$) in the form:

$$\bar{\alpha} = 1.89 - \frac{1}{\bar{\nu}} \quad .$$

If $\bar{\nu}$ varies from 4 to 6, this results in only a 6% variation in $\bar{\alpha}$. Using equation (15) Zachariassen was able to rationalize the change in interatomic distance with coordination number for a large variety of ions. Because Pauling's (1929) definition of bond strength merely involves z and ν , it is apparent from equation (14) that

$$s = \frac{z}{\nu} = \frac{K}{R^{n-1}} \quad (16)$$

The Born exponent can also be found from compressibility measurements. Anderson (1970) and Anderson & Anderson (1970) have evaluated n using the pressure derivative of the bulk modulus and their values (calculated using the power-law repulsion term) are compared in Table 10 with the values calculated from the R - s curves. With the exceptions of BeO, CaO, SiO₂ and TiO₂ there is satisfactory agreement. Anderson & Anderson have found the elastic behaviour of

SiO₂ and TiO₂ anomalous and attribute the effect to bond bending and directional forces. The values of n determined from the elastic constant for BeO and for CaO (Son & Bartels, 1972) differ by a factor of two from the values we have obtained. Fisher (1973) has suggested that the origin of this discrepancy may be in the derivation of n from the pressure derivative of the bulk moduli. Using the relationships derived by Anderson & Liebermann (1970), Fisher obtains values of n for single-crystal MgO and CaO from the elastic modulus, C_{44} , and the bulk modulus, K . These values agree well with the values of n determined from crystallographic data in Table 10. It would be interesting to see if the discrepancy between the two values of n for BeO could be removed in a similar manner. In the light of the rather drastic assumptions implicit in equation (16), the agreement between the Born exponent determined from the elasticities and that determined from the crystal structures is encouraging.

Uses of bond-strength-bond-length curves

Previous workers have used bond-strength-bond-length curves for a number of practical purposes related to the evaluation of crystal-structure determinations (see Donnay, 1972). Our curves can achieve the same results with considerably more generality and flexibility as is illustrated in the examples given below.

1. Testing for the correctness of a structure

Bond-strength curves provide a convenient method of testing the plausibility of a proposed crystal structure, since the bond-strength sums around any atom should normally lie within 5% of the valence. Larger discrepancies in well refined structures might indicate an incorrect structure. The effect is well illustrated by the structure of Zn₃(BO₃)₂ which was originally refined by Garcia-Blanco & Fayos (1968) in the space group Ic . Baur & Tillmans (1970) subsequently refined it in the space group $I2/c$ and although they obtained the same

Table 10. The Born exponent n evaluated from elastic constants and from bond-strength parameters

Compound	Born exponent			
	From elastic constants	From individual bond-strength curves§	From universal bond-strength curves§	
BeO	9.5*	5.3	5.0	
MgO	6.5,* 4.7†	6.0	5.3	
Al ₂ O ₃	5.0*	6.0		
α -SiO ₂	12.2*	5.5		
SiO ₂ (stishovite)	14.0*			
MgAl ₂ O ₄	5.6*	6.0		
Mg ₂ SiO ₄	6.5*	5.7		
CaO	8.7,* 11.0,† 6.1‡	7.0		
TiO ₂ (rutile)	13.3*	5.0		
Fe ₂ O ₃	6.6*	6.3		6.1
ZnO	7.4*	6.0		7.0

* Anderson (1970) and Anderson & Anderson (1970)

† Son & Bartels (1972)

‡ Fisher (1973)

§ $n = N + 1$

agreement index ($R=0.12$) as Garcia-Blanco & Fayos they preferred their structure on chemical as well as crystallographic grounds (Baur, 1970). The bond-strength calculations confirm Baur & Tillmans's preference, giving a mean deviation of the bond-strength sums from the valence of 13% for the refinement in Ic and only 3.4% for that in $I2/c$ (see Table 11).

Table 11. *Bond-strength sums in two structures proposed for $Zn_3(BO_3)_2$*

Space group	z	Ic		$I2/c$
		Garcia-Blanco & Fayos (1968)	Baur & Tillmans (1970)	
Zn(1)	2	1.99	2.07	1.95
Zn(2)	2	2.24	1.69	1.96
Zn(3)	2	2.08	1.80	1.99
B(1)	3	3.23	3.44	3.12
B(2)	3	2.76	3.67	3.01
O(1)	2	2.39	2.11	2.05
O(2)	2	2.08	1.66	1.95
O(3)	2	1.97	2.55	2.12
O(4)	2	2.31	1.96	2.08
O(5)	2	1.82	1.95	1.91
O(6)	2	1.77	2.39	1.92
Mean deviation from z		13%		3.4%

2. Determining site occupancy in solid solutions

When two atoms of different valence but belonging to the same or neighbouring elements (e.g. Al^{3+} and Si^{4+} ; Fe^{2+} and Fe^{3+}) are present in a crystal, it is usually not possible to determine directly from X-ray diffraction studies the ratio of each on any particular site. The occupancy can be inferred from a study of the bond lengths between the site and its first neighbours since the lower valence ion gives rise to longer bonds

(see for example Evans, 1960; Smith & Bailey, 1963; Ribbe & Gibbs, 1969). Such methods depend on the construction of bond-length-site-occupancy curves for each pair of ions. The use of bond strength provides a more general way of assigning site occupancy since such disordered atoms will normally have the same or very similar $R-s$ curves, and the calculated bond-strength sums will be equal to the average valence of the site. Two examples are given. In Table 12 the distribution of Al^{3+} and Si^{4+} in sanidine, $(Na,K)AlSi_3O_8$, is predicted using the universal bond-strength curve, the bond-strength curve corrected for oxygen coordination, and ionic radii (Shannon & Prewitt, 1969). These are compared with the site occupancy determined from neutron diffraction and the agreement is quite satisfactory. The method can be used with less precision to calculate the ratio of K to Na on the alkali metal site.

Table 13 compares the bond strengths in three ferrospinel. The bond-strength sums at each site have been calculated with the $R-s$ curves appropriate to each species present and the weighted average bond strengths are shown for three cases—(a) normal spinel, (b) inverse spinel and (c) random spinel. In each case these are compared with the expected average valence. Table 13 clearly indicates that Fe_2TiO_4 is an inverse spinel and Fe_2ZnO_4 is normal in agreement with assignments given by other workers. The result for Fe_3O_4 is not quite as unambiguous but suggests that the Fe^{2+} ions are disordered over all sites, a result at variance with accepted view that Fe_3O_4 is an inverse spinel.

3. Prediction of positions of hydrogen atoms

The $R-s$ curve for hydrogen has been calculated using hydrogen positions determined by neutron dif-

Table 12. *Cation distribution in sanidine*

Site	Bond strength sums (universal curves)	Structural information from Prewitt (1973) Estimated errors given in parentheses.			
		Universal bond-strength sums	Bond strength corrected for O coordination	Ionic radii (Shannon & Prewitt, 1969)	Neutron diffraction (Prewitt, 1973)
T1	3.72	72 (10)% Si	73% Si	71% Si	68% Si
T2	3.87	87 (10)% Si	82% Si	92% Si	82% Si
K, Na	1.13 (as K) 0.79 (as Na)	62 (30)% K 38 (30)% Na			88% K 12% Na

Table 13. *Bond strengths in Fe_2XO_4 spinels*

X	Site	$R(\text{\AA})$	$P(Fe^{3+})$	$P(Fe^{2+})$	$P(X)$	$P(\text{normal})$		$P(\text{inverse})$		$P(\text{random})$	
			Table 4-2	Table 4-1	Table 4-2	Theor.	Obs.	Theor.	Obs.	Theor.	Obs.
Ti	A	2.00		2.01	2.49	4.00	2.49	2.00	2.01	2.67	2.17
	B	2.03		2.78	3.49	2.00	2.78	3.00	3.16	2.67	3.02
Zn	A	1.97	2.25		1.93	2.00	1.93	3.00	2.25	2.67	2.14
	B	2.02	2.96		2.48	3.00	2.96	2.50	2.72	2.67	2.80
Fe	A	1.887	2.80	2.59		2.00	2.59	3.00	2.80	2.67	2.73
	B	2.056	2.69	2.76		3.00	2.69	2.50	2.72	2.67	2.71

References

- Fe_2TiO_4 Ishikawa, Sato & Syono (1971).
 Fe_2ZnO_4 Chalyi & Rozhenko (1956); Bałanda, Szyłła, Dimitrijević & Todovović (1969).
 Fe_3O_4 Hamilton (1958)

fraction. In many cases it is not possible to detect hydrogen atoms using X-ray diffraction and where it is possible their positions are not only less accurately known but differ systematically from the positions found by neutron diffraction. Consequently the bond strength curves for H-O bonds quoted in Table 1 are only appropriate for bonds determined by neutron diffraction.

Often it is of interest to know where the hydrogen atoms are to be found in the crystal in those cases where their presence is not detectable by X-ray diffraction. Frequently the presence of short O-O distances is indicative of a hydrogen bond and the hydrogen atoms can be assigned qualitatively without much ambiguity. Donnay & Allman (1970) have shown that the calculation of bond-strength sums provides additional information about the location of hydrogen atoms. Our bond strengths can be used in a similar way but have the additional advantage of ease in calculation. Table 14 shows the calculations of bond strengths for $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ both with and without the inclusion of the hydrogen atoms. Table 15 shows similar calculations for $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ where the hydrogen positions are not known. Estimates of O-H distances based on predicted bond strengths give values for the O-H...O distances that are in striking agreement with those observed. A somewhat different prediction for the positions of the hydrogen atoms based on different considerations has recently been made by Baur (1972).

4. Calculation of effective ionic radii

The $R-s$ functions given in Table 3 allow one to obtain more statistically valid effective ionic radii than were previously possible and in addition allow extrapolation to obtain radii for which no examples have yet been found. Some examples of previously undetermined radii and of radii differing significantly from values in Shannon & Prewitt (1969) are listed in Table 16.

Table 15. Prediction of hydrogen atom positions in $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ using universal bond-strength curves

Structural information from Dickens, Mauer & Brown (1970).

	Bond strength sums without H	Estimated bond strengths for hydrogen		Estimated bond strength sums with H
		H(1)	H(2)	
Na(1)	1.02			1.02
Na(2)	1.11			1.11
C	3.98			3.98
O(1)	1.88	0.16		2.04
O(2)	1.98			1.98
O(3)	1.80		0.24	2.04
O(4)	0.45	0.84	0.76	2.05
		1.00	1.00	
Hydrogen bond				
	Bond strength	Bond length (Å)	Predicted O-H...O	Observed O-H...O
O(4)-H(1)	0.84	0.93	3.0	2.907 (2)
H(1)-O(1)	0.16	2.1		
O(4)-H(2)	0.76	0.96		
H(2)-O(3)	0.24	1.7	2.7	2.684 (2)

Table 16. Effective ionic radii of ions in unusual coordinations

Ion	CN	Radius
Li ⁺	V	0.69
B ³⁺	VI	0.27
P ⁵⁺	VI	0.38
S ⁶⁺	VI	0.29
V ⁵⁺	V	0.43
V ⁵⁺	VI	0.50
Mn ²⁺	IV	0.65
Mn ²⁺	V	0.74
Fe ²⁺	V	0.70
Fe ²⁺	VIII	0.91
Fe ³⁺	V	0.56
Ge ⁴⁺	V	0.46
As ⁵⁺	V	0.40
As ⁵⁺	VI	0.46

Table 14. Bond strengths in $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ calculated using universal curves

	Bond strength sums without H	Structural information from Baur (1964)								Bond strength sums with H
		H(1A)	H(1B)	Bond strengths for hydrogen atoms				H(4A)	H(4B)	
Mg	2.14									2.14
S	6.08									6.08
O(1)	1.84						0.16			2.00
O(2)	1.89				0.07					2.05
					0.09					
O(3)	1.50	0.15	0.17						0.19	2.00
O(4)	1.55			0.14			0.12		0.15	1.97
O(W1)	0.37	0.82	0.86							2.05
O(W2)	0.35			0.82	0.90					2.07
O(W3)	0.36					0.86	0.78			1.99
O(W4)	0.36							0.84	0.79	1.99
Bond strength sums for H		0.97	1.03	0.96	1.06	0.98	0.94	0.99	0.98	
O-H...O distance (Å)		2.884	2.754	2.835	3.282	2.860	2.833	2.831	2.734	
					3.042					

5. Testing for positional disorder or anomalous thermal motion

As mentioned above, thermal motion tends to decrease the apparent bond length as determined by diffraction methods. In the present discussion no allowance has been made for this effect on the assumption that the extent of the shortening will be approximately the same for all bonds. If, however, the thermal motion is anomalously large (or small) the apparent bond lengths will be shortened (or lengthened) from the values used in this study, giving rise to anomalously high (or low) bond strengths. The effect is well illustrated by the bond-strength sums calculated around the bridging oxygen atoms in pyrophosphates (Table 17). All the sums are somewhat high but they tend to increase as the P-O-P angle increases reaching values between 2.3 and 2.4 in those structures where the P-O-P angle is constrained by symmetry to be 180°. In these latter cases the thermal parameters of the bridging oxygen atom are large, indicating that the atom is normally disordered away from the centrosymmetric position. The instantaneous P-O-P angle is thus less than 180° and the corresponding P-O distances longer than the values

of 1.56 Å normally found in these crystals. The large calculated bond-strength sums in this case are thus indicative of either a positional disorder or an anomalous thermal effect.

Table 17. Bond-strength sums around the bridging oxygen atoms in pyrophosphate groups

	Bond-strength sum (Table 4-2)	P-O-P (°)	Reference†
Cd ₂ P ₂ O ₇	1.99 (5)	132	69 CJCHA 47 3409
Na ₄ P ₂ O ₇	2.10 (1)	128	72 CJCHA 50 2519
α-Zn ₂ P ₂ O ₇	2.10 (2)	139	70 JSSCB 1 120
α-Sr ₂ P ₂ O ₇	2.12 (5)	131	68 ACSAA 22 1419
β-Ca ₂ P ₂ O ₇	2.12 (4)	131	66 ACCRA 21 942
α-Ca ₂ P ₂ O ₇	2.14 (3)	130	68 INOCA 7 1345
α-Mg ₂ P ₂ O ₇	2.18 (4)	144	67 ACCRA 23 289
β-Ca ₂ P ₂ O ₇	2.22 (4)	138	66 ACCRA 21 942
α-Zn ₂ P ₂ O ₇	2.23 (3)	148	70 JSSCB 1 120
α-Cu ₂ P ₂ O ₇	2.26 (3)	157	67 ACCRA 22 665
SiP ₂ O ₇ -III	2.27 (4)	139	70 ACBCA 26 233
β-Zn ₂ P ₂ O ₇	2.31 (2)	180	65 CJCHA 43 1147
β-Mg ₂ P ₂ O ₇	2.38 (2)	180	65 CJCHA 43 1139

† The references are given in the same form as in the Appendix.

Table 18. Structures used in the evaluation of bond-strength-bond-lengths parameters

H(1+)	69 ACBCA	25	31J	BE (H2,0) 4 S,04	67 ACCRA	22	37	NA2 SI 03		
	66 ACBCA	20	214	B (0,0) 3	68 ACBCA	24	13	ALPHA-NA2 SI2 05		
	69 ACBCA	20	1804	GD (N,3) 2 (02,0) 4	69 ACBCA	24	1077	BETA-NA2 SI2 05		
	66 ACBCA	20	842	TH (N,3) 4 (H2,0) 5	71 ACBCA	27	2	NA3 P 3L (H2,0) 12		
	67 ACCRA	22	182	NA AL (S,0) 2 (H2,0) 12			REF2	NA4 P2 07		
	66 ACBCA	21	303	CA AL (S,0) 2 (H2,0) 12	67 ACCRA	22	43	NA3 P3 09 (H2,0) 10		
	66 ACBCA	21	303	CA AL (S,0) 2 (H2,0) 12	65 ACCRA	18	43	NA4 P2 07		
	69 ACBCA	23	621	SM (BR,0) 3 (H2,0) 9	69 ACBCA	25	1077	NA5 P3 08 (H2,0) 14		
	66 ACBCA	20	765	H1 I,05	70 ACBCA	26	1584	NA2 H P 04 (H2,0) 7		
					67 ZEKGA	155	238	H2 P2 06 (H2,0) 6		
LI(1+)	66 JCP5A	4	3348	GAMMA-LI B 02	65 ZEKGA	122	175	CA2 NA H S13 09		
	71 ACBCA	27	904	LI3 B,33	67 ACCRA	22	43	CA NA2 (S,0) 2		
	67 ACCRA	22	906	LI C N,3 07	70 ACBCA	24	3657	NA3 P 3L (H2,0) 12		
	65 ACCRA	19	398	GAMMA-LI AL 02	70 INOCA	9	2228	NA2 CR3 08 0,H		
	68 ZEKGA	126	46	LI AL 314 010	61 MOCRA	102	397	NA2 GE 03		
	67 ACCRA	22	399	LI AL 314 010	70 ACBCA	24	1287	NA4 SN2 GE4 012 (0,H) 4		
	67 ACCRA	22	119	LOW-LI3 P,04	67 ACSAA	21	1281	NA8 SN4 GE10 036 (0,H) 4		
	70 ACSAA	24	2803	LI H P2 0,03 09 H2,0	71 ACBCA	27	2124	NA3 AS,04 (H2,0) 12		
	62 ACCRA	15	1491	LI H P2 0,03 09 H2,0			UNPU1	NA4 AS2 07		
	68 CIMYA	18	290	LI FE 0,04	70 ACBCA	26	1574	NA2 H AS,04 (H2,0) 7		
	60 ACCRA	13	325	LI MN 0,02	70 ACBCA	26	1584	NA2 H AS,04 (H2,0) 7		
	60 ACCRA	13	325	LI S,04 H,0	70 ACBCA	26	1792	NA I,04		
	64 ACCRA	17	694	LI N2,15 S,04						
	UNPU1			REF1 LI3 V,04	MG(2+)	57 AMHIA	1966	32	MG 0	
				LI FE 512 06		66 NEMA	142	39	MG 0 4,37 (0,H) 6 (H2,0) 2	
	69 MSAS1	2	31	LI2 CU 02		71 AMHIA	56	1553	MG B6 17	
	71 ZAACA	379	157	LI2 CU 02		65 MIASA	1965	196	MG AL 3,04	
	69 ACBCA	25	147	LI G 12		69 AMHIA	44	196	CA MG 3,04 2	
	65 ACSAA	22	3711	LI MO,02 45,04		69 SPHCA	13	599	MG AL 2 04	
	66 JPP5A	22	997	LI NB,03		65 AMHIA	50	2023	MG3 AL2 SI3 012	
	67 JPP5A	22	997	LI NB,03		68 ACBCA	21	1518	MG AL 2 SI 3 09	
	67 JPP5A	22	1693	LI NB,03		65 ZEKGA	159	55	MG AL 2 04	
	71 ACSAA	25	3337	LI NB3 08		65 TMPHA	10	81	CA MG 3,1,04	
	67 JPP5A	22	1693	LI TA 33		69 AMHIA	53	807	MG1,8 FE0,6 ST,04	
	67 JPP5A	22	1693	LI TA 33		69 ACBCA	26	1429	MG AL 4,04 (2,0) 7	
	70 ZAACA	374	206	LI EU3 04		68 ACSAA	22	1466	MG3 P2 08	
						67 ACCRA	23	418	MG H P,04 (H2,0) 5	
BE(2+)	64 JESAO	111	73	BE 0		70 ACBCA	26	1429	MG N,H4 P,04 (H2,0) 6	
	63 ACCRA	16	1144	BE2 B,33 0,H		70 BSCFA	12	4243	MG S,04 H2,0	
	63 AMHIA	48	804	BE AL2 04		64 ACCRA	17	863	MG S,04 (H2,0) 4	
	65 ZEKGA	117	18	K BE 31,04 0,H		64 ACCRA	17	235	MG S,04 (H2,0) 6	
	69 ACBCA	125	791	Y2 ST 3E2 07 0,H		64 ACCRA	17	1361	MG S,04 (H2,0) 7	
	71 SPHCA	15	999	FE3 BE SI3 09 (0,H,F) 2		62 ZEKGA	117	344	MG (N,4) 2 (S,04) 2 (H2,0) 6	
	65 ZEKGA	117	16	(H,N,FE) BE P,04 0,H		69 ZACA	369	506	MG6 MH 08	
	69 ACBCA	25	310	BE S,04 (H2,0) 4				UNPU1	MG V2 04	
	69 ACBCA	25	1647	S1 BE3 04		71 CJCHA	49	1629	MG3 V2 08	
	67 ACBCA	24	672	LA2 BE2 05		70 JSSCB	12	912	MG28 FE,10 048	
	67 ACBCA	22	354	Y2 BE,34		70 CJCHA	48	893	MG2 AS2 07	
						71 ACBCA	27	845	MG3 TE 06	
B(3+)	70 ACBCA	26	905	B2 03 I II		69 SPHCA	13	933	MG H,04	
	64 ACBCA	24	863	BET 03						
	63 ACCRA	16	389	BET 03 H,02		AL(3+)	62 ZEKGA	117	235	AL2 03
	63 ACCRA	16	389	GAMMA-I B,02			69 ACBCA	24	46	GAMMA I AL 02
	65 ACBCA	19	3349	H2 B,03			69 ZEKGA	126	46	LI AL 512 06
	64 JCP5A	4	3348	GAMMA-LI B,02			63 AMHIA	48	804	BE AL 2 04
	71 ACBCA	27	904	LI3 B,33			65 MIASA	196	196	MG H 3,04
	63 ACBCA	16	594	NA B,03			68 NJHMA	1968	80	CA AL 3,04
	63 ACBCA	16	594	NA B,03			68 ACBCA	24	1518	MG AL 3 SI B 09
	65 AMHIA	50	1827	NA B SI3 08			69 AMHIA	44	196	MG AL 3,04 2
	70 ACBCA	26	1189	K B 05			68 ACBCA	24	1518	MG AL 3 SI B 09
	63 ACCRA	16	376	K2 B4 37 (H2,0) 4			69 AMHIA	44	196	MG AL 3,04 2
	63 ACCRA	16	975	MG AL 3 SI B 09			70 ZEKGA	133	314	NA CA AL SI2 07
	65 MIASA	196	196	MG AL 3 SI B 09			65 AMHIA	150	2023	MG AL 3 SI 012
	63 ACCRA	16	390	CA B2 34 (I)			63 ZEKGA	118	337	*KYANITE* AL 2 SI 05
	69 ACBCA	25	955	CA B2 34 (II)			62 ZEKGA	118	127	*SILIMANITE* AL 2 SI 05
	69 NJHMA	1969	142	CA3 B2 36			63 ACBCA	113	81	CA3 AL SI3 012
	70 ZEKGA	132	241	CA B3 05 (0,H)			66 ZEKGA	123	161	AL P,04
	69 NJHMA	1968	286	CA AL B,04			68 AMHIA	53	1096	AL 2 AL 3 012 (0,H) 3
	69 ACBCA	25	286	B ST 04 0,H			69 ACBCA	19	971	GO3 AL 3 012
	69 ACBCA	25	1811	BA (B (0,H) 4) 2 H2,0			69 ACBCA	19	971	YB3 AL 3 012
	71 ACBCA	29	677	CU B2 34			70 ACBCA	19	971	LU3 AL 3 012
NA(1+)	67 ACCRA	22	906	NA LI S,04			71 AMHIA	56	791	*JLHMAN* LINE GARNET*
	63 ACCRA	16	594	NA B,03			71 AMHIA	56	791	*MN-GRUSSULAR GARNET*
	63 ACCRA	16	594	NA B,03 (H) 4 (H2,0) 2			71 AMHIA	56	791	*SPESSARTINE GARNET*
	65 AMHIA	50	1827	NA B SI3 08						
	62 ACCRA	15	77	NA H C,03						
	69 AMHIA	49	959	NA AL 3,02 06						
	69 ACBCA	25	182	NA AL (S,0) 2 (H2,0) 12						
						SI(4+)	65 ZEKGA	121	369	*CRISTOBALITE* SI 02
							65 ACBCA	19	710	*QUARTZ* SI 02
							67 ACCRA	19	2133	*SILIMANITE* SI 02
							68 ZEKGA	126	46	LI AL 512 06

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Table 18 (cont.)

69	MSAPA	2	31	LI FE Si2 06	
74	SPHCA	1	93	FE3 Si Si3 09 (F, O, H)2	
67	AMHIA	1	1227	NA B Si3 08	
68	ACBCA	1	1512	MC AL3 Si Si B 09	
67	ZEKGA	2	2099	CA B Si3 04 O, H	
67	ACBCA	2	2099	NA2 Si 05	
68	ACBCA	2	2099	ALPHA NA2 Si2 05	
66	AMHIA	1	10	NETA NA2 Si2 05	
66	AMHIA	1	551	CA2 NA H Si3 09	
67	ZEKGA	1	1295	NA FE AL2 Si2 06	
67	ZEKGA	1	1344	NA FE AL2 Si2 06	
76	MSAPA	2	222	NA CR Si3 02	
69	MSAPA	2	14	MG EN Si2 06	
69	ZEKGA	1	179	MG EN Si2 06	
71	AMHIA	1	556	MG7 Si3 012 F O, H	
68	AMHIA	1	119	MG3 AL2 Si3 014	
68	AMHIA	1	2076	MG FE Si3 04 (THREE STRUCTURES)	
65	TMPHA	1	10	CA HG Si3 04	
69	MSAPA	1	23	CA HG Si3 06	
63	ZEKGA	11	228	*ANDALUSITE* AL2 Si 05	
63	ZEKGA	11	337	*KYANITE* AL2 Si 05	
63	ZEKGA	11	127	*SILIMANITE* AL2 Si 05	
66	ZEKGA	1	1348	CA3 AL2 Si3 012	
70	ACBCA	2	233	SI P2 J7 III	
70	PEPTA	2	161	BETA CA2 Si 04	
73	ACBCA	2	553	GAMMA CA2 Si 04	
68	AMHIA	1	807	F12 Si 04	
68	CIMY	1	67	*SUSTONITE* CA MN Si2 06	
67	AMHIA	1	709	*JOHANNSENITE* CA MN Si2 06	
71	ZSICA	1	272	YB2 Si2 07	
71	ALUCA	1	404	E2 Si2 07	
	P (5+)				
55	ACSAA	29	1557	H3 P 04	
65	ZAACA	29	776	(H3 P, O)2 H2 O	
63	ACBCA	368	231	(H3 P, O)2 H2 O	
69	ACBCA	1	325	L13 HN P 04	
67	INOCA	6	119	L13 P 04	
	CJCHA			NA4 P2 07	
65	ACBCA	18	26	NA3 P3 09	
69	ACBCA	13	263	NA5 Si O10	
71	ACBCA	27	2124	NA3 P 04 (H2, O)12	
67	ACBCA	22	43	NA4 P2 07 (H2, O)10	
70	ACBCA	22	1584	NA H P 04 (H2, O)7	
67	ACBCA	26	1429	H C N, H4 P, O4 (H2, O)6	
68	ACBCA	23	289	ALPHA H2 P2 07	
68	ACBCA	21	1466	MG H P 04 (H2, O)3	
67	ACBCA	2	922	ALPHA-CA2 P2 07	
65	ACBCA	2	982	BETA-CA2 P2 07	
69	INOCA	1	239	BE2 P 04 CL 07	
66	ZEKGA	1	161	AL P 04 (O, H)3	
65	AMHIA	1	109	AL P 04 (O, H)3	
69	AMHIA	2	233	SI P2 07	
69	AMHIA	1	132	MN FE2 (P, O)2 (O, H)2 (H2, O)8	
71	ACSAA	2	597	K H S (P, O)2	
69	ZEKGA	1	512	K ZR2 (P, O)2	
69	ZEKGA	1	148	(NH4)3 P, O4 (H2, O)3	
70	ACBCA	26	2826	V P 04	
67	ACBCA	22	665	ALPHA-CU2 P2 07	
70	ZSICB	1	120	ALPHA-ZN2 P2 07	
71	ZAACA	380	51	P CL5	
	S (6+)				
68	ACBCA	24	299	H2 Si 04 H2 O	
65	ACBCA	18	717	LI S 04 H2 O	
	UNPUI			LI S 04 H2 O	
67	ACBCA	22	2985	LI N2 H5 S 04	
74	ACBCA	22	298	N H4 LI S 04	
69	ACBCA	22	298	BE (H2, O)4 S 04	
69	ACBCA	26	310	BE (H2, O)4 S 04	
66	ACBCA	26	335	ZN (C (N, H2)3)2 (S, O)2	
65	ACCSA	19	1612	(N2, H5)2 S 04	
65	ACBCA	22	182	N2 H6 S 04	
65	ZEKGA	1	175	CA NA2 (S, O)2	
70	BSCFA	1	4244	MG S 04 H2 O	
64	ACBCA	17	863	MG S 04 (H2, O)4	
64	ACBCA	17	235	MG S 04 (H2, O)6	
64	ACBCA	17	1361	MG S 04 (H2, O)7	
63	ZEKGA	12	161	MG K2 (S, O)2 (H2, O)6	
	* * *				
62	ZEKGA	117	346	MG (N, H)2 (S, O)2 (H2, O)6	
77	ACBCA	151	151	*COUITE* (AL, FE)2 (S, O)3 (H2, O)9	
66	ACBCA	16	383	CS CA (S, O)2 (H2, O)2	
70	ACBCA	225	1696	K2 CA (S, O)2 H2 O	
67	ACBCA	428	1939	K F F (S, O)2 H2 O	
67	AMHIA	350	1929	K F F (S, O)2 H2 O	
65	AMHIA	350	1929	K F F (S, O)2 H2 O	
68	ZEKGA	129	361	K F F (S, O)2 H2 O	
70	AMHIA	350	1929	*10MERITE* FE3 (S, O)4 (H2, O)14	
68	ACBCA	327	705	NI S 04 (S, O)6	
69	ACBCA	327	705	CU S 04 (S, O)6	
69	ACBCA	325	19	CU (N, H)34 S 04 H2 O	
69	ACBCA	325	676	CU (N, H)2 (S, O)2 (H2, O)6	
71	PHOTA	150	443	PA	
	K (1+)				
70	ACBCA	26	1189	K B O2	
63	ACBCA	16	975	K2 B4 J7 (H2, O)4	
63	ACBCA	16	376	K B O2 O4 (H2, O)4	
7	ACBCA	2	397	K H O2 O4	
53	PRLLA	220	397	K H2 P 04	
74	ACCSA	155	511	K ZR2 (P, O)2	
62	ZEKGA	155	148	K ZR2 (P, O)2	
62	ACBCA	15	1280	LI K2 P3 O9 H2 O	
69	JACSA	162	925	BETA-K2 S 04	
71	AMHIA	556	1917	K F F (S, O)2 H2 O	
65	AMHIA	550	1929	K F F (S, O)2 H2 O	
7	ACBCA	1	133	K F F (S, O)2 (H2, O)4	
60	ZEKGA	114	257	K V O3	
60	ZEKGA	114	257	K V O3 H2 O	
70	ACCSA	24	3627	K2 O3 Fe O28 (H2, O)16	
69	JCSIA	1969	1043	K2 O3 O8 O4 (N, O)2b	
71	ACBCA	26	1451	K2 O3 O8 O4	
69	JCSIA	1969	849	K2 O3 O8 O4	
68	JCSIA	1968	1398	K2 O3 O8 O4	
66	ACCSA	20	2195	K2 O3 O8 O4	
64	INOCA	3	634	K T E O (O, H)5 H2 O	
66	ACCSA	20	2138	K4 FE2 O6 (O, H)4 (H2, O)8	
65	INOCA	3	514	K2 B4 O (N, O)2b	
69	ACBCA	25	1704	K2 W 04	
	CA (2+)				
64	ACBCA	17	685	CA O (H)2	
57	JCP SA	26	563	CA O (H)2	
66	ACBCA	20	295	CA12 BE17 O29	
63	ACBCA	16	399	CA B2 O4 III	
69	ACBCA	25	955	CA B2 O4 III	
69	NJMMA	1969	142	CA3 B2 O6 (O, H)	
73	ACBCA	43	325	CA AL3 O4 (O, H)	
68	NJMMA	1968	86	CA AL3 O4 (O, H)	
67	ZEKGA	125	286	*CALSiO4* (O, H)	
67	ACBCA	125	286	*CALSiO4* (O, H)	
71	JNBAA	75	27	*ARAGONITE* CA C O3	
71	AMHIA	44	679	CA2 H (C, O)3	
67	ZEKGA	29	9	CA2 H (C, O)3	
65	ZEKGA	122	175	CA NA2 (S, O)2	
65	THPHA	3	20	CA Si 04	
66	ACBCA	2	23	CA2 P 05	
66	ZEKGA	123	81	CA3 AL2 Si3 012	
71	ACBCA	27	848	GAMMA CA2 Si 04	
67	ZEKGA	117	331	CA MN Si3 06	
67	AMHIA	52	707	CA MN Si2 06	
71	AMHIA	56	79	CA3 FE2 Si3 012	
66	ACBCA	12	325	INOCA	
66	ACBCA	21	942	BETA-CA P2 07	
70	ACBCA	25	643	CA2 MN (P, O)2 H2 O)2	
70	CHCA	27	0	CA2 MN (P, O)2 H2 O)2	
66	ACBCA	21	397	CA3 V1 O28 (H2, O)17	
70	ACBCA	26	1469	CA2 FE 08	
71	HRUJA	7	725	CA FE 08	
65	ACBCA	18	88	CA W 04	
	SC (3+)				
67	ZEKGA	124	136	SC C2 O3	
67	ARKEA	29	343	SC C2 O3	
65	ZAACA	339	130	LI SC O2	
69	ACBCA	19	493	SC C Si2 O7	
69	ACBCA	19	493	SC C Si2 O7	
65	ZAACA	336	295	CA SC2 O4	
62	JPCHA	56	276	SC V 04	
66	JCP SA	46	276	SC2 W3 O12	

Table 18 (cont.)

CU (2+)		AS (5+)							
70	ACBCA	26	8	CU 0	66	ACCRA	21	808	(AS2 05)3 (H2,0)5
70	ZKGA	379	157	LTP CU 02	70	ACSAA	24	3711	L1 MO,02 AS,04
70	ACBCA	11	169	CU8 HG8 (C,03)4 (0,H)24 (H2,0)8	61	AMHIA	46	1077	CA2 B AS,04 (0,H)4
51	ACBCA	27	677	CU B2 J4	70	ACBCA	26	1574	NA2 H AS,04 (H2,0)7
70	ACBCA	26	1203	CU8 (N,03)212 (H2,0)5	71	ACBCA	27	2124	NA3 AS,04 (H2,0)12
61	ACCRA	14	73	NA8 (C,0)2 (H2,0)2	70	CJCHA	48	891	REF3 NA4 AS2 07
61	AMHIA	14	193	CU2 CA2 S33 010 (H2,0)2	70	CJCHA	48	890	HG2 AS2 07
67	ACCRA	22	665	ALPHA CU2 P2 07	UNPUI	REF9	HG17	AS6 032	
68	CJCHA	14	99	BETA CU2 P2 07	70	ACBCA	26	1889	(N,H4)2 H AS,04
63	ACCRA	16	1009	CU2 O S,04	70	ACBCA	26	403	CA H AS,04
63	NATUA	197	70	CU3 S,04 (0,H)4	69	ACBCA	25	1544	CA H AS,04 (H2,0)2
68	ACBCA	14	909	CU S,04 (H2,0)2	70	INOCA	9	2259	CA2 AS,04 CL
68	PELBA	26	2619	CU S,04 (H2,0)2	70	CJCHA	48	891	CO3 AS2 08
69	ACBCA	25	676	CU (N,H4)2 (S,04)2 (H2,0)6	70	CJCHA	48	3124	CO8 AS3 016
UNPUI	REF9	CU V 03	CU3 V2 08	68	AMHIA	53	733	MN7 (0,H)8 (AS,04)2	
UNPUI	REF1	CU S V2 010	CU3 V2 010	70	AMHIA	55	2023	MN9 (0,H)9 (H2,0)2 AS,03 (AS,04)2	
65	ACCRA	18	477	CU2 AS,04 (0,H)3	65	ACCRA	18	777	MN7 SE AS 012
68	CJCHA	46	917	CU3 AS2 08	65	ACCRA	18	777	CU3 AS,04 (0,H)3
68	ZKGA	130	231	CU ZN2 AS2 08	66	ACCRA	21	437	CU2 AS,04 0,H (H2,0)3
68	JPCSA	48	2619	CU MO 04	68	CJCHA	46	917	CU3 AS2 08
70	ACBCA	27	2066	CU3 MO2 09	69	ZKGA	130	231	CU ZN2 AS2 08
71	ACBCA	26	1020	CU3 W 04	70	ZKGA	132	332	CU3 AS2 08
69	ACSAA	23	15	CU3 W 06	69	ACBCA	25	2658	ZR (H AS,04)2 H2,0
69	ACBCA	25	1233	ZN 0 I	REF1	R.D. SHANNON	UNPUBLISHED		
62	SCIEA	137	993	ZN 0 I	REF2	K. CALVO AND C. CALVO	TO BE PUBLISHED		
70	ZKGA	131	313	ZN3 B2 06	REF3	C. CALVO	PRIVATE COMMUNICATION		
71	ACBCA	27	672	ZN B4 07	REF4	R. GOPAL AND C. CALVO	TO BE PUBLISHED		
70	ACBCA	26	335	ZN (C (N, H2) 3)2 (S,04)2	REF5	I.O. BROWN	UNPUBLISHED		
63	ACBCA	14	73	ZN (C O C H C O C, H3)2 H2,0	REF6	K. CALVO AND C. CALVO	TO BE PUBLISHED		
67	ACBCA	27	1240	ZN (O C C O N, H2)2 (H2,0)2	REF7	BAYSIDE RESEARCH CENTER	GENERAL TELEPHONE AND ELECTRIC LAB. ABSTRACTS		
67	ACBCA	22	240	ZN (O, H2)6 (N,03)2	REF8	R. HAZELL	PRIVATE COMMUNICATION		
70	ACBCA	26	860	ZN5 (0,H)8 (N,03)2 (H2,0)2	REF9	E. KOSTINER	PRIVATE COMMUNICATION		
71	ACBCA	17	1868	ZN S,04	ACACB	ACTA CRYSTALLOGR. SECTION A			
67	ZKGA	124	180	ZN4 S12 07 (0,H)2 H2,0	ACBCA	ACTA CRYSTALLOGR. SECTION B			
67	ZKGA	124	115	PB ZN S1 04	ACSAA	ACTA CHEM. SCAND.			
63	ZKGA	113	321	ZN2 O,H P,04	AMHIA	AMER. MIN. SOC. JAPAN			
69	ZKGA	123	321	ZN2 O,H P,04	JCSJA	BULL. SOC. CHIM. FR.			
70	JSSCB	1	120	ALPHA ZN2 P2 07	JJFCA	BULL. SOC. FR. MINER. CRISTALLOGR.			
65	CJCHA	43	1447	BETA ZN2 P2 07	JMICA	CANAD. MINER. ASSOCIATION			
67	CJCHA	45	2303	CD ZN2 P2 08	JNOCA	C.R. ACAD. SCI. PARIS SECTION C			
68	CJCHA	46	903	CD ZN2 P2 08	JHYA	CARNEGIE INST. WASHINGTON YEARBOOK			
68	ZKGA	126	87	ZN5 (0,H)8 CL2 H2,0	CJCHA	CANAD. J. CHEM.			
68	INOCA	9	97	ZN5 (0,H)8 O 028 (H2,0)16	JNOCA	CANAD. J. CHEM.			
69	ZAACA	369	306	ZN V2 J4	JHYA	CHEM. PHYS. INDUSTRY COMM.			
UNPUI	REF3	ZN2 V2 07		HCACA	HELV. CHIM. ACTA				
71	CJCHA	49	3056	ZN V2 J4	JNOCA	INDUSTR. CHEM.			
69	PHSSA	32	3056	ZN FE2 04 V2 08	JACSA	J. AMER. CHEM. SOC.			
69	ZKGA	130	231	CU ZN2 AS2 08	JPCSA	J. CHEM. PHYS.			
67	AMHIA	56	1147	ZN4 (AS,04)2 (0,H)2 (H2,0)2	JCSIA	J. CHEM. SOC. LOND. SECTION A			
67	JPCSA	48	2052	ALPHA ZN MO 04	JESOA	J. EL. CHEM. SOC.			
66	ACCRA	21	482	ZN2 MO3 08	JINCA	J. INORG. NUCL. CHEM.			
67	JPCSA	46	1862	ALPHA GA2 03	JNBAA	J. RES. NAT. BUREAU STAND. SECTION A			
65	ACCRA	18	676	BETA GA2 03	JPCSA	J. PHYS. CHEM.			
65	ACCRA	18	481	L1 GA 02	JSSCB	J. SOLID STATE CHEM.			
65	JPCSA	42	3957	GA(2-X) FE(X) 03	JURSA	J. SOLID STATE CHEM.			
68	JPCSA	48	1194	EUS FE2 GA3 012	MOCHA	MINER. MAG.			
65	ACCRA	19	971	Y3 GA5 012	YRBUA	MONATSHEFTE CHEM.			
65	ACCRA	18	874	GA NB 04	VSFA	MATERIALS RESEARCH BULLETIN			
68	JENCA	17	1389	YN GA 03	NATUA	MIN. SOC. AMERICA SPEC. PAPERS			
65	ACCRA	19	971	YB3 GA5 012	NJHMA	NATURE LONDON			
65	ACCRA	19	971	LU3 GA5 012	PEP11	NEUES JAHRBUCH MINER. MONATSHEFTE			
64	ACCRA	17	842	GE=02	PHSSA	PHYS. STAT. SOLIDI			
69	MOCHA	100	79	LI NA GE4 09	PRLAA	PROC. ROY. SOC. LONDON SERIES A			
71	MOCHA	102	964	NZ2 GE3 03	SCIEA	SCIENCE			
63	ACSAA	17	617	NA4 GE3 020	SFCOA	SOVIET PHYS. CRYSTALLOGRAPHY (SEE KRISA)			
67	ACCRA	22	507	NA2 GE 03 (H2,0)6	TFSOA	SOLID STATE COMMUNICATIONS			
70	ACSAA	24	1287	NA4 SN2 GE4 012 (0,H)4	TMHMA	TRANS. FARADAY SOC.			
67	ACSAA	21	1281	NA8 SN4 GE10 030 (0,H)4	UNPUI	TSCHERMAKS MINER. PETR. MITT. (UNPUBLISHED REFERENCE)			
70	JSSCB	2	612	HG28 GE10 048	ZAACA	Z. ANORG. ALLGEM. CHEM.			
71	MOCHA	102	1245	K2 GE=09	ZKGA	Z. KRISTALLOGR.			
69	ZKGA	130	139	MN GE=03	ZSTRK	ZH. STRUKT. KHIM.			
69	PEP11	3	181	BETA-MY2 GE=04					
69	ZKGA	129	427	MN3 FE2 GE3 012					
68	ZKGA	126	299	CO GE 03					
70	SEHCA	15	36	FE2 GE2 07					

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