

## Bond-Valence Parameters for Solids

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### Abstract

Bond-valence parameters which relate bond valences and bond lengths have been derived for a large number of bonds. It is shown that there is a strong linear correlation between the parameters for bonds from cations to pairs of anions. This correlation is used to develop an interpolation scheme that allows the estimation of bond-valence parameters for 969 pairs of atoms. A complete listing of these parameters is given.

### Introduction

The concept of *bond valence* has recently found wide applicability in solid-state chemistry. It has developed historically from the concept of *bond number* as applied to metals and intermetallic compounds by Pauling (1947), but was shortly thereafter applied to oxides by Byström & Wilhelmi (1951) and by Zachariassen (1963). The main advantage of the approach is that, to a generally excellent approximation, the bond length is a unique function of bond valence. It therefore provides a powerful method for the prediction and interpretation of bond lengths in crystals (Brown, 1981; O'Keeffe, 1989).

The valence,  $v_{ij}$  of a bond between two atoms  $i$  and  $j$  is defined so that the sum of all the valences from a given atom  $i$  with valence  $V_i$  obeys:

$$\sum_j v_{ij} = V_i. \quad (1)$$

The most commonly adopted empirical expression for the variation of the length  $d_{ij}$  of a bond with valence is

$$v_{ij} = \exp[(R_{ij} - d_{ij})/b]. \quad (2)$$

Here  $b$  is commonly taken to be a 'universal' constant equal to 0.37 Å (Brown & Altermatt, 1985); we use this value of  $b$  throughout.

Equations (1) and (2) serve as a prescription for determining the parameters  $R_{ij}$  for bonds between pairs of atoms in observed crystal (and molecular) structures. We subsequently refer to  $R_{ij}$  as the *bond-valence parameter*. Once obtained, these parameters are useful in a number of ways. The most obvious applications in crystallography are in predicting bond lengths from a given bond valence (Brown,

1977; O'Keeffe, 1990) and the use of bond-valence sums at atoms as a check on the reliability of a determined structure. In this respect the bond-valence method is clearly superior to using sums of radii in most instances. At a lower level, approximate bond-valence parameters are useful in deciding if there is a significant bonding interaction between pairs of atoms, as well as in computer programs as a criterion for determining coordination number (Altermatt & Brown, 1987).

In this paper we are concerned primarily with extending the applicability of the method to a wider range of materials than previously considered. In order to accomplish this we first establish the existence of linear correlations between bond-valence parameters for bonds from cations to different anions.\*

### Determination of bond-valence parameters

Bond-valence parameters have been developed for many chalcides and halides, notably by Brown and his collaborators (Brown, 1981; Brown & Altermatt, 1985). We have supplemented these data by critically examining reported structures in the following journals: *Acta Cryst.* (Vols. C34–C39 and B26–B38), *Z. Kristallogr.* (Vols. 131–175), *Z. Anorg. Allg. Chem.* (Vols. 372–557), and *J. Solid State Chem.* (Vols. 1–73). Data for compounds other than oxides and halides were also obtained from a systematic search of structures in *Pearson's Handbook* (Villars & Calvert, 1985). Bond lengths for some molecular compounds were also taken from the compilations in Wells' (1984) book. We excluded crystal structures with disorder and partial occupancy and those in which we felt that there might be ambiguity about atomic valences (as for some compounds containing transition elements). In cases where there was ambiguity about reported bond lengths these were recalculated from the original crystallographic data. As well over 1000 structures have been considered,

\* We emphasize that the terms *cation* and *anion* are used only for want of better expressions for 'the more electropositive element' and 'the more electronegative element' respectively. We definitely want to apply the method to cases where an ionic model of bonding would be quite inappropriate.

their enumeration and reference are clearly not practical.

For each structure where a central atom was bound only to atoms of the same kind,  $R_{ij}$  was found from equation (2) which may be written

$$R_{ij} = b \ln[V_i / \sum_j \exp(-d_{ij}/b)]. \quad (3)$$

We evaluated this expression for each appropriate atom in each structure using a constant value of  $b = 0.37 \text{ \AA}$ . We then averaged the bond-valence parameters thus determined for each type of bond, rejecting any obvious outliers.

It is our belief that, despite claims to the contrary, bond lengths are rarely determined with an accuracy better than  $0.01 \text{ \AA}$ . For many bonds,  $R_{ij}$  determined from different structures varied by several times this amount so that in general we only consider bond-valence parameters significant to an accuracy of about  $\pm 0.02 \text{ \AA}$ , although data for many oxides and fluorides justify higher precision.

Initially we distinguished atoms by oxidation state. Previous work had shown that for many bonds to oxygen the bond-valence parameter did not depend strongly on oxidation state in many instances\* and our own experience showed that this was a satisfactory approximation for bonds from atoms such as S to more electronegative elements. However for some atoms such as Cu, Ag and Au the bond-valence parameters do depend significantly on oxidation state.

The data considered here refer to bonds from cations to as many as 12 anions (H, F, Cl, Br, I, O, S, Se, Te, N, P, As). Some elements (*e.g.* As) are considered as both cations and anions.

### Linear relationships between bond-valence parameters

The hypothesis that bond lengths can be expressed as a sum of radii (which may be specific to a given coordination number) implies that the difference between bond lengths from a given atom with a given coordination number to *e.g.* O and F will be a constant. In the language of the bond-valence method a 'given coordination number' translates to 'given bond valence'. As  $d_{ij} = R_{ij} - b \ln(v_{ij})$ , it is clear that the hypothesis also implies that (referring to the same example)  $R_{iO} - R_{iF}$  is a constant.

Fig. 1 shows a plot of  $R_{ij}$  ( $j = F, N, S$ ) against  $R_{iO}$ . The line drawn through the points is that which minimizes the sum of the absolute deviations of the points from the line (see *Appendix*). Clearly a linear trend is well developed. For  $j = F$ , the average absolute deviation is  $0.011 \text{ \AA}$ . Interestingly, however,

\* For example Brown & Altermatt (1985) give the following bond-valence parameters for bonds to oxygen from metal atoms in different oxidation states: Fe<sup>II</sup> 1.73, Fe<sup>III</sup> 1.76; Mn<sup>II</sup> 1.79, Mn<sup>III</sup> 1.76, Mn<sup>IV</sup> 1.75; As<sup>III</sup> 1.79, As<sup>V</sup> 1.77.

the equation of the line is:

$$R_{iF} = 0.021 + 0.940R_{iO} \text{ \AA}. \quad (4)$$

Thus the intercept is (in this instance) very close to zero and the bond-valence parameters are very nearly in constant ratio. The corresponding fit for oxides and nitrides (average absolute deviation =  $0.017 \text{ \AA}$ ) is:

$$R_{iN} = -0.027 + 1.090R_{iO} \text{ \AA}. \quad (5)$$

Equations (4) and (5) are derived from raw data only. The fact that bond lengths in oxides, fluorides and nitrides could not be described using additive radii has been noted before (O'Keeffe, 1979).

The strong linear correlation of bond-valence parameters for bonds to different anions suggests that bond-valence parameters that are not readily available could be obtained by linear interpolation. Accordingly we have developed a scheme for doing this which utilizes all the input data and which is described fully in the *Appendix*. The essence of the scheme is that we assume a linear relationship between the  $R_{ij}$  and the  $R_{jk}$  and find the linear relationships that minimize the sum of the weighted absolute deviations from the line.

As a result of the analysis we obtain a set of 66 'best' equations relating bond-valence parameters for bonds from cations to pairs of the 12 anions. The parameters of the equations  $R_{ij} = a_{jk} + b_{jk}R_{ik}$  are presented in Table 1. In cases such as for bonds to O and F where there was a large set of original input data, these equations do not differ significantly from those derived from the original data for O and F only. However the parameters presented are those derived using the full set of data as described in the *Appendix*.

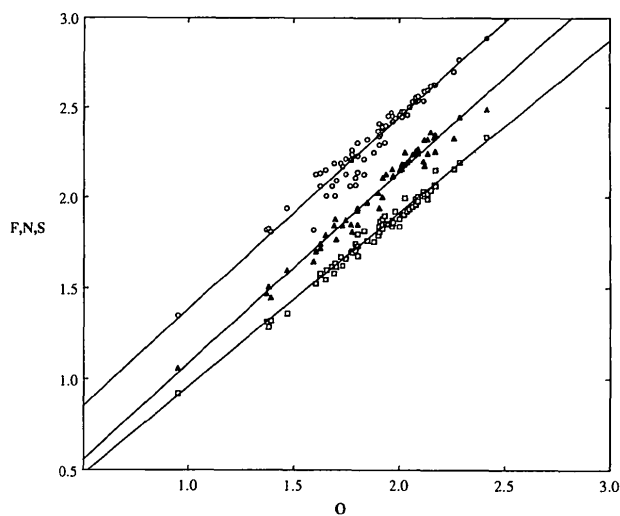


Fig. 1. Bond-valence parameters for bonds to F (squares), N (triangles) and S (circles) as a function of the bond-valence parameter for the same cation to oxygen using raw data only.

Table 1. *Parameters a (upper) and b (lower)*

To be used to obtain bond-valence parameters for bonds to anions at the top of the table from bond-valence parameters for bonds to anions in the left-hand column.

	O	S	Se	Te	F	Cl	Br	I	N	P	As	H
O	0.0	0.361	0.560	0.910	0.016	0.341	0.464	0.652	-0.006	0.524	0.543	-0.629
	1.0	1.049	1.014	0.936	0.942	1.020	1.034	1.048	1.077	1.010	1.041	1.243
S	-0.344	0.0	0.171	0.560	-0.321	-0.057	0.058	0.240	-0.410	0.176	0.185	-1.061
	0.953	1.0	0.982	0.903	0.903	0.991	1.006	1.020	1.037	0.962	0.992	1.185
Se	-0.552	-0.174	0.0	0.416	-0.500	-0.226	-0.100	0.071	-0.606	-0.020	0.020	-1.230
	0.986	1.018	1.0	0.914	0.928	1.008	1.018	1.035	1.065	0.990	1.006	1.192
Te	-0.972	-0.620	-0.455	0.0	-0.900	-0.660	-0.568	-0.411	-1.054	-0.459	-0.430	-1.803
	1.068	1.107	1.094	1.0	1.007	1.093	1.116	1.136	1.151	1.080	1.099	1.317
F	-0.017	0.355	0.539	0.894	0.0	0.330	0.449	0.628	0.007	0.503	0.523	-0.647
	1.061	1.107	1.078	0.993	1.0	1.079	1.098	1.117	1.124	1.073	1.104	1.316
Cl	-0.334	0.056	0.224	0.604	-0.306	0.0	0.113	0.294	-0.339	0.222	0.238	-0.994
	0.980	1.009	0.992	0.915	0.927	1.0	1.017	1.031	1.044	0.976	1.003	1.197
Br	-0.449	-0.058	0.099	0.509	-0.103	-0.111	0.0	0.158	-0.505	0.099	0.133	-1.116
	0.967	0.994	0.994	0.896	0.911	0.983	1.0	1.023	1.048	0.965	0.982	1.173
I	-0.622	-0.235	-0.068	-0.553	-0.562	-0.153	-0.154	0.0	-0.686	-0.030	-0.021	-1.313
	0.952	0.980	0.966	0.880	0.895	0.970	0.973	1.0	1.032	0.936	0.962	1.153
N	0.056	0.395	0.569	0.916	-0.006	0.325	0.482	0.665	0.0	0.495	0.538	-0.595
	0.923	0.964	0.939	0.869	0.890	0.958	0.954	0.969	1.0	0.955	0.974	1.142
P	-0.519	-0.183	0.020	0.425	-0.469	-0.227	-0.130	0.032	-0.518	0.0	0.071	-1.214
	0.990	1.040	1.010	0.926	0.932	1.025	1.036	1.068	1.047	1.0	1.003	1.207
As	-0.522	-0.186	-0.020	0.391	-0.473	-0.237	-0.135	0.022	-0.552	-0.071	0.0	-1.282
	0.961	1.008	0.994	0.910	0.906	0.997	1.108	1.040	1.026	0.997	1.0	1.197
H	0.506	0.506	1.032	1.369	0.492	0.830	0.951	1.139	0.521	1.062	1.071	0.0
	0.805	0.805	0.839	0.759	0.760	0.835	0.853	0.867	0.876	0.829	0.835	1.0

We also obtain bond-valence parameters predicted on the basis of the assumed linear relationships. In general where there were original input data the predicted and observed values are in very good agreement (some exceptions are noted below). For presentation the data have been split into two groups. For bonds to F, O and Cl, high-oxidation states are common and cations are distinguished by oxidation state. For bonds to the rest of the atoms, the data refer to the lowest common oxidation state.

#### Data for oxides, fluorides and chlorides

Our recommended values of bond-valence parameters for oxides, fluorides and chlorides are presented in Table 2. These are derived directly from structural data except as noted. The missing values were obtained using the appropriate interpolation parameters from Table 1. Data for bonds from the actinide elements to oxygen were obtained from the lattice parameters of the oxides which interpolate between those for the lanthanide oxides. We have followed Brown & Altermatt (1985) in not distinguishing different electronic configurations of  $3d^n$  cations as this information is generally not available, although bond lengths to high-spin and low-spin states may differ by as much as 0.05 Å (Shannon, 1976). The presence of a third decimal place is intended to signify more-accurate parameters.

Almost one third of the 330 entries in Table 2 have also been reported by Brown & Altermatt (1985). Our independent determinations are in generally excellent agreement with theirs and we have been content to retain many of their values; others are changed by less than 0.02 Å (except for  $\text{Ag}^{\text{I}}-\text{O}$  and

$\text{H}-\text{O}$ ). Accordingly our table should be considered as supplementing, rather than replacing, their compilation.

#### Data for anions other than O, F, Cl

In general with less electronegative anions, high-oxidation states of cations are not achieved, so data for the lowest common oxidation state ( $\text{Cu}^{\text{I}}$ ,  $\text{Pd}^{\text{II}}$  etc.) were only used for transition elements in the final analysis. Little is lost in this process as  $R$  is not very different for different oxidation states in general (e.g. for the important case of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  in sulfides). The input data were not very different from the final predicted data in most instances (average absolute difference  $< 0.03$  Å). The main discrepancies were for hydrides; for bonds to alkali-metal hydrides, the predicted values were smaller than observed, and for hydrides of electronegative elements the predicted values were larger than observed. After some soul searching we decided to average predicted and observed values in all instances and this average is reported in the table.

We did not use data for bonds from 'cations' such as P to equally or less electronegative 'anions' such as P and As. Nevertheless, the value of  $R$  found for such bonds is close to the single-bond distance. The only exception was for the  $\text{H}-\text{H}$  bond for which the predicted distance is 0.55 Å instead of the 0.74 Å observed. The latter value is used in the table and is the only value changed in hindsight.

Brown & Altermatt (1985) report values corresponding to only 19 (mainly sulfides) of the 639 entries of Table 3. Most are in very good agreement and only two differ by more than 0.05 Å (for  $\text{Tl}-\text{I}$  and  $\text{Tl}-\text{S}$ ).

Table 2. Recommended bond-valence parameters for oxides, fluorides and chlorides

Directly determined except for those values in italics (see text).

Cation	O			F			Cl		
	O	F	Cl	O	F	Cl	O	F	Cl
Ac <sup>III</sup>	2.24	<i>2.13</i>	<i>2.63</i>	Mn <sup>IV</sup>	1.753	1.71	<i>2.13</i>		
Ag <sup>I</sup>	1.805	1.80	2.09	Mn <sup>VII</sup>	1.79	1.72	<i>2.17</i>		
Al <sup>III</sup>	1.651	1.545	2.03	Mo <sup>VI</sup>	1.907	<i>1.81</i>	2.28		
Am <sup>III</sup>	2.11	<i>2.00</i>	<i>2.48</i>	N <sup>III</sup>	1.361	1.37	1.75		
As <sup>III</sup>	1.789	1.70	2.16	N <sup>V</sup>	1.432	<i>1.36</i>	<i>1.80</i>		
As <sup>V</sup>	1.767	1.62	<i>2.14</i>	Na <sup>I</sup>	1.80	1.677	2.15		
Au <sup>III</sup>	1.833	1.81	2.17	Nb <sup>V</sup>	1.911	1.87	2.27		
B <sup>III</sup>	1.371	1.31	1.74	Nd <sup>III</sup>	2.117	2.008	<i>2.492</i>		
Ba <sup>II</sup>	2.29	2.19	2.69	Ni <sup>II</sup>	1.654	1.599	2.02		
Be <sup>II</sup>	1.381	1.28	<i>1.76</i>	Os <sup>IV</sup>	1.811	<i>1.72</i>	<i>2.19</i>		
Bi <sup>III</sup>	2.09	1.99	2.48	P <sup>V</sup>	1.604	1.521	1.99		
Bi <sup>V</sup>	2.06	1.97	<i>2.44</i>	Pb <sup>II</sup>	2.112	2.03	2.53		
Bk <sup>III</sup>	2.08	<i>1.96</i>	<i>2.46</i>	Pb <sup>IV</sup>	2.042	<i>1.94</i>	2.43		
Br <sup>VII</sup>	1.81	<i>1.72</i>	<i>2.19</i>	Pd <sup>II</sup>	1.792	1.74	2.05		
C <sup>IV</sup>	1.39	1.32	1.76	Pr <sup>II</sup>	2.135	2.022	2.50		
Ca <sup>II</sup>	1.967	1.842	2.37	Pr <sup>III</sup>	1.768	1.68	2.05		
Cd <sup>II</sup>	1.904	1.811	2.23	Pt <sup>II</sup>	1.879	1.759	2.17		
Ce <sup>III</sup>	2.151	2.036	2.52	Pu <sup>III</sup>	2.11	2.00	2.48		
Ce <sup>IV</sup>	2.028	1.995	<i>2.41</i>	Rb <sup>I</sup>	2.26	2.16	2.65		
Cf <sup>III</sup>	2.07	1.95	2.45	Re <sup>VII</sup>	1.97	1.86	2.23		
Cf <sup>VII</sup>	1.632	<i>1.55</i>	<i>2.00</i>	Rh <sup>III</sup>	1.791	1.71	<i>2.17</i>		
Cm <sup>III</sup>	2.23	2.12	2.62	Ru <sup>IV</sup>	1.834	1.74	2.21		
Co <sup>II</sup>	1.692	1.64	2.01	S <sup>IV</sup>	1.644	1.60	2.02		
Co <sup>III</sup>	1.70	1.62	2.05	S <sup>VI</sup>	1.624	1.56	2.03		
Cr <sup>II</sup>	<i>1.73</i>	1.67	2.09	Sb <sup>III</sup>	1.973	1.90	2.35		
Cr <sup>III</sup>	1.724	1.64	2.08	Sb <sup>V</sup>	1.942	1.80	2.30		
Cr <sup>VI</sup>	1.794	1.74	2.12	Sc <sup>III</sup>	1.849	1.76	<i>2.23</i>		
Cs <sup>I</sup>	2.42	2.33	2.79	Se <sup>IV</sup>	1.811	1.73	2.22		
Cu <sup>I</sup>	1.593	<i>1.6</i>	1.85	Se <sup>VI</sup>	1.788	1.69	<i>2.16</i>		
Cu <sup>II</sup>	1.679	1.60	2.00	Si <sup>IV</sup>	1.624	1.58	2.03		
Dy <sup>III</sup>	2.036	1.922	2.41	Sm <sup>III</sup>	2.088	1.977	<i>2.466</i>		
Er <sup>III</sup>	2.010	1.906	2.39	Sn <sup>II</sup>	1.984	1.925	<i>2.36</i>		
Eu <sup>II</sup>	2.147	2.04	2.53	Sn <sup>IV</sup>	1.905	1.84	2.28		
Eu <sup>III</sup>	2.076	1.961	2.455	Sr <sup>II</sup>	2.118	2.019	2.51		
Fe <sup>II</sup>	1.734	1.65	2.06	Ta <sup>V</sup>	1.920	1.88	2.30		
Fe <sup>III</sup>	1.759	1.67	2.09	Tb <sup>III</sup>	2.049	1.936	<i>2.427</i>		
Ga <sup>III</sup>	1.730	1.62	2.07	Te <sup>IV</sup>	1.977	1.87	2.37		
Gd <sup>III</sup>	2.065	1.95	2.445	Te <sup>VI</sup>	1.917	1.82	<i>2.30</i>		
Ge <sup>IV</sup>	1.748	1.66	2.14	Th <sup>IV</sup>	2.167	2.07	<i>2.55</i>		
H <sup>I</sup>	0.95	0.92	1.28	Ti <sup>III</sup>	1.791	1.723	<i>2.17</i>		
Hf <sup>IV</sup>	1.923	1.85	2.30	Ti <sup>IV</sup>	1.815	1.76	<i>2.19</i>		
Hg <sup>I</sup>	1.90	<i>1.81</i>	<i>2.28</i>	Tl <sup>I</sup>	2.172	2.15	<i>2.56</i>		
Hg <sup>II</sup>	1.93	1.90	2.25	Tl <sup>III</sup>	2.003	1.88	2.32		
Ho <sup>III</sup>	2.023	1.908	2.401	Tm <sup>III</sup>	2.000	1.842	2.38		
I <sup>V</sup>	2.00	<i>1.90</i>	<i>2.38</i>	U <sup>VI</sup>	2.112	2.034	2.48		
I <sup>VII</sup>	1.93	1.83	<i>2.31</i>	U <sup>VI</sup>	2.075	1.966	2.46		
In <sup>III</sup>	1.902	1.79	2.28	V <sup>III</sup>	1.743	1.702	<i>2.19</i>		
Ir <sup>V</sup>	1.916	1.82	2.30	V <sup>IV</sup>	1.784	1.70	<i>2.16</i>		
K <sup>I</sup>	2.13	1.99	2.52	V <sup>V</sup>	1.803	1.71	2.16		
La <sup>III</sup>	2.172	2.057	2.545	W <sup>VI</sup>	1.921	1.83	2.27		
Li <sup>I</sup>	1.466	1.360	1.91	Y <sup>III</sup>	2.014	1.904	2.40		
Lu <sup>III</sup>	1.971	1.876	2.361	Yb <sup>III</sup>	1.985	1.875	<i>2.371</i>		
Mg <sup>II</sup>	1.693	1.581	2.08	Zn <sup>II</sup>	1.704	1.62	2.01		
Mn <sup>II</sup>	1.790	1.698	2.13	Zr <sup>IV</sup>	1.937	1.854	2.33		
Mn <sup>III</sup>	1.760	1.66	<i>2.14</i>						

### Bonds to metals in high oxidation states

Application of the bond-valence method to oxides of Cu in high oxidation states is currently of great interest (O'Keeffe & Hansen, 1988; Brown, 1989). For Cu<sup>III</sup>—O bonds a value of  $R = 1.724 \text{ \AA}$  has been recommended (Brese, O'Keeffe, Von Dreele & Young, 1989), but see the next paragraph. For Ag<sup>III</sup>—O a value of  $R = 1.91 \text{ \AA}$  is calculated from the structure of Ag<sub>2</sub>O<sub>3</sub> (Standke & Jansen, 1986).

The strong variation of  $R$  with oxidation state for the coinage metals is to be noted, as is the fact that in general  $R$  for bonds to oxygen and fluorine from these elements were notable outliers in the linear correlations. For this reason we are reluctant to recommend a value of  $R$  for Cu<sup>I</sup>—F bonds. We note

Table 3. Bond-valence parameters for anions other than O, F, Cl

	Br	I	S	Se	Te	N	P	As	H
Ag	2.22	2.38	2.15	2.26	2.51	1.85	2.22	2.30	1.50
Al	2.20	2.41	2.13	2.27	2.48	1.79	2.24	2.32	1.45
As	2.32	2.54	2.26	2.39	2.61	1.93	2.34	2.41	1.56
Au	2.12	2.34	2.03	2.18	2.41	1.72	2.14	2.22	1.37
B	1.88	2.10	1.82	1.95	2.20	1.47	1.88	1.97	1.14
Ba	2.88	3.13	2.77	2.88	3.08	2.47	2.88	2.96	2.22
Be	1.90	2.10	1.83	1.97	2.21	1.50	1.95	2.00	1.11
Bi	2.62	2.84	2.55	2.72	2.87	2.24	2.63	2.72	1.97
C	1.90	2.12	1.82	1.97	2.21	1.47	1.89	1.99	1.10
Ca	2.49	2.72	2.45	2.56	2.76	2.14	2.55	2.62	1.83
Cd	2.35	2.57	2.29	2.40	2.59	1.96	2.34	2.43	1.66
Ce	2.69	2.92	2.62	2.74	2.92	2.34	2.70	2.78	2.04
Co	2.18	2.37	2.06	2.24	2.46	1.84	2.21	2.28	1.44
Cr	2.26	2.45	2.18	2.29	2.52	1.85	2.27	2.34	1.52
Cs	2.95	3.18	2.89	2.98	3.16	2.53	2.93	3.04	2.44
Cu	1.99	2.16	1.86	2.02	2.27	1.61	1.97	2.08	1.21
Dy	2.56	2.77	2.47	2.61	2.80	2.18	2.57	2.64	1.89
Er	2.54	2.75	2.46	2.59	2.78	2.16	2.55	2.63	1.86
Eu	2.61	2.83	2.53	2.66	2.85	2.24	2.62	2.70	1.95
Fe	2.26	2.47	2.16	2.28	2.53	1.86	2.27	2.35	1.53
Ga	2.24	2.45	2.17	2.30	2.54	1.84	2.26	2.34	1.51
Gd	2.60	2.82	2.53	2.65	2.84	2.22	2.61	2.68	1.93
Ge	2.30	2.50	2.22	2.35	2.56	1.88	2.32	2.43	1.55
H	1.42	1.61	1.35	1.48	1.78	1.03	1.48	1.52	0.74
Hf	2.47	2.68	2.39	2.52	2.72	2.09	2.48	2.56	1.78
Hg	2.40	2.59	2.32	2.47	2.61	2.02	2.42	2.50	1.71
Ho	2.55	2.77	2.48	2.61	2.80	2.18	2.56	2.64	1.88
In	2.41	2.63	2.36	2.47	2.69	2.03	2.43	2.51	1.72
Ir	2.45	2.66	2.38	2.51	2.71	2.06	2.46	2.54	1.76
K	2.66	2.88	2.59	2.72	2.93	2.26	2.64	2.83	2.10
La	2.72	2.93	2.64	2.74	2.94	2.34	2.73	2.80	2.06
Li	2.02	2.22	1.94	2.09	2.30	1.61	2.04	2.11	1.31
Lu	2.50	2.72	2.43	2.56	2.75	2.11	2.51	2.59	1.82
Mg	2.28	2.46	2.18	2.32	2.53	1.85	2.29	2.38	1.53
Mn	2.26	2.49	2.20	2.32	2.55	1.87	2.24	2.36	1.55
Mo	2.43	2.64	2.35	2.49	2.69	2.04	2.44	2.52	1.73
Na	2.33	2.56	2.28	2.41	2.64	1.93	2.36	2.53	1.68
Nb	2.45	2.68	2.37	2.51	2.70	2.06	2.46	2.54	1.75
Nd	2.66	2.87	2.59	2.71	2.89	2.30	2.66	2.74	2.00
Ni	2.16	2.34	2.04	2.14	2.43	1.75	2.17	2.24	1.40
P	2.15	2.40	2.11	2.26	2.44	1.73	2.19	2.25	1.41
Pb	2.64	2.78	2.55	2.67	2.84	2.22	2.64	2.72	1.97
Pd	2.19	2.38	2.10	2.22	2.48	1.81	2.22	2.30	1.47
Pr	2.67	2.89	2.60	2.72	2.90	2.30	2.68	2.75	2.02
Pt	2.18	2.37	2.08	2.19	2.45	1.77	2.19	2.26	1.40
Rb	2.78	3.01	2.70	2.81	3.00	2.37	2.76	2.87	2.26
Re	2.45	2.61	2.37	2.50	2.70	2.06	2.46	2.54	1.75
Rh	2.25	2.48	2.15	2.33	2.55	1.88	2.29	2.37	1.55
Ru	2.26	2.48	2.16	2.33	2.54	1.88	2.29	2.36	1.61
S	2.17	2.36	2.07	2.21	2.45	1.74	2.15	2.25	1.38
Sb	2.50	2.72	2.45	2.57	2.78	2.12	2.52	2.60	1.77
Sc	2.38	2.59	2.32	2.44	2.64	1.98	2.40	2.48	1.68
Se	2.33	2.54	2.25	2.36	2.55	1.93	2.34	2.42	1.54
Si	2.20	2.41	2.13	2.26	2.49	1.77	2.23	2.31	1.47
Sm	2.62	2.84	2.55	2.67	2.86	2.24	2.63	2.70	1.96
Sn	2.55	2.76	2.45	2.59	2.76	2.14	2.45	2.62	1.85
Sr	2.68	2.88	2.59	2.72	2.87	2.23	2.67	2.76	2.01
Ta	2.45	2.66	2.39	2.51	2.70	2.01	2.47	2.55	1.76
Tb	2.58	2.80	2.51	2.63	2.82	2.20	2.59	2.66	1.91
Te	2.53	2.76	2.45	2.53	2.76	2.12	2.52	2.60	1.83
Th	2.71	2.93	2.64	2.76	2.94	2.34	2.73	2.80	2.07
Ti	2.32	2.54	2.24	2.38	2.60	1.93	2.36	2.42	1.61
Tl	2.70	2.91	2.63	2.70	2.93	2.29	2.71	2.79	2.05
Tm	2.53	2.74	2.45	2.58	2.77	2.14	2.53	2.62	1.85
U	2.63	2.84	2.56	2.70	2.86	2.24	2.64	2.72	1.97
V	2.30	2.51	2.23	2.33	2.57	1.86	2.31	2.39	1.58
W	2.45	2.66	2.39	2.51	2.71	2.06	2.46	2.54	1.76
Y	2.55	2.77	2.48	2.61	2.80	2.17	2.57	2.64	1.86
Yb	2.51	2.72	2.43	2.56	2.76	2.12	2.53	2.59	1.82
Zn	2.15	2.36	2.09	2.22	2.45	1.77	2.15	2.24	1.42
Zr	2.48	2.69	2.41	2.53	2.67	2.11	2.52	2.57	1.79

also that for Cu<sup>III</sup>—F the value of  $R$  calculated from the structure of Cs<sub>2</sub>KCuF<sub>6</sub> (Kissel & Hoppe, 1986) is 1.58 Å. Likewise for Cu<sup>IV</sup>—F the value of  $R$  calculated from the structure of Cs<sub>2</sub>CuF<sub>6</sub> (Kissel & Hoppe, 1988) is 1.61 Å. These low values of

$\text{Cu}^{\text{III}}\text{—O}$  bonds and suggest that  $\text{Cu}^{\text{III}}\text{—O}$  bonds might have less than their formal valence.

The oddities seen for highly oxidized coinage metals are not mirrored in the other transition metals in their high oxidation states. Generally,  $R$  parameters are only slightly larger for metals in higher oxidation states.

The  $R$  parameter for low-spin  $\text{Ni}^{\text{III}}\text{—O}$  calculated from  $\text{HoNiO}_3$  (Demazeau, Marbeuf, Pouchard & Hagenmuller, 1971), low-spin  $\text{AgNiO}_2$  (Wichainchai, Dordor, Doumerc, Marquestaut, Pouchard & Hagenmuller, 1988), and  $\text{SrLaNiO}_4$  (Demazeau, Pouchard & Hagenmuller, 1976) is 1.68 Å, while that for  $\text{Ni}^{\text{IV}}\text{—O}$  from  $\text{BaNiO}_3$  (Takeda, Kanamaru, Shimada & Koizumi, 1976) is 1.72 Å (compare  $\text{Ni}^{\text{II}}\text{—O}$  at 1.654 Å). The  $R$  parameter for  $\text{Ni}^{\text{III}}\text{—F}$  is 1.65 Å [from  $\text{BaNiF}_6$  (Müller & Hoppe, 1983)] and is accordingly smaller than for  $\text{Ni}^{\text{III}}\text{—O}$  but larger than for  $\text{Ni}^{\text{II}}\text{—F}$  (1.599 Å).

The  $R$  parameters for  $\text{Fe}^{\text{II}}\text{—O}$  and  $\text{Fe}^{\text{III}}\text{—O}$  are 1.734 and 1.759 Å, respectively. The value for  $\text{Fe}^{\text{IV}}\text{—O}$  is calculated to be 1.78 Å from the cubic perovskite  $\text{SrFeO}_3$  (MacChesney, Sherwood & Potter, 1965). Mössbauer measurements show that at low temperatures  $\text{Fe}^{\text{IV}}$  disproportionates to  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{V}}$  [for example, see Takeda, Naka, Takano, Shinjo, Takada & Shimada (1978)], but we could find no reliable  $\text{Fe}^{\text{V}}\text{—O}$  bond lengths.

The  $R$  parameter for  $\text{Co}^{\text{IV}}\text{—O}$  calculated from  $\text{Li}_8\text{CoO}_6$  (Jansen & Hoppe, 1973),  $\text{Cs}_2\text{CoO}_3$  (Jansen & Hoppe, 1974a),  $\text{K}_6\text{Co}_2\text{O}_7$  (Jansen & Hoppe, 1974b), and  $\text{SrCoO}_3$  (Taguchi, Shimada & Koizumi, 1979) is 1.75 Å. This value seems high, since the  $\text{Co}^{\text{II}}\text{—O}$  and  $\text{Co}^{\text{III}}\text{—O}$  parameters are 1.692 and 1.70 Å, respectively.

### Concluding remarks

The tables in this paper are intended for the uses indicated in the *Introduction*. For detailed interpretation of bond lengths in a particular crystal, one should preferably examine well-determined structures of related materials. Note that a combined error of 0.01 Å in  $R$  and the bond length results in an error of 2.7% in the derived valence; for an error of 0.05 Å the corresponding error in the valence is 14%. Despite this caution we feel that the tables should be generally useful in crystal chemistry. They are available on a Macintosh diskette from the authors as a FORTRAN callable subroutine.

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## APPENDIX

### Interpolation scheme for bond-valence parameters

First we wish to fit the bond-valence parameters  $R_{ij} = x$  and  $R_{jk} = y$  to a line  $y = a + bx$ . Let the points have weights  $w_{xi}$  and  $w_{yi}$ . It is not expected that the deviations will be normally distributed so we adopt the procedure of minimizing the sum of the absolute deviations from the line multiplied by  $w_{xi}w_{yi}$ . The direction of the deviation from the line is chosen so that the ratio of the deviations in  $x$  and  $y$  is  $\delta x_i/\delta y_i = w_{yi}/w_{xi}$ . This procedure is equivalent to minimizing

$$\sum_i \frac{|y_i - a - bx_i|(w_{xi}^2 + w_{yi}^2)^{1/2}}{b/w_{xi} + 1/w_{yi}}$$

Initially lines are fitted in this way using only the input values of  $R_{ij}$  each assigned unit weight. However for the interpolation scheme we need to develop weights for the points.

Let there be  $n$  points fitted out of a possible  $N$  (= number of cations). If the average deviation for a line is  $\langle\delta\rangle_l$  and  $\langle\delta\rangle_i$  is the average deviation of all the lines, then with each line is associated a weight  $W_l = (n/N)(\langle\delta\rangle_l/\langle\delta\rangle_i)$ . The  $x$  and  $y$  are now given new weights obtained by summing  $W_l\langle\delta\rangle_l/(\langle\delta\rangle_l + \delta_l)$  over all the lines  $l$  in which there is an  $x, y$  point (here  $\delta_l$  is the deviation of the point from the individual line).

The next step is to recalculate  $a$  and  $b$  for all lines using the individual weights obtained. From each of these lines we obtain predicted  $x_p$  and  $y_p$  which are points on the line. If there are values of both  $x$  and  $y$  then  $x_p$  and  $y_p$  are obtained by shifting according to  $\delta x_i/\delta y_i = w_{yi}/w_{xi}$  otherwise  $y_p = a + bx$ . The predicted  $R_{ij}$  are now averaged with weights equal to the product of their individual weights and the line weights.

Finally we repeat the procedure of the above two paragraphs to get a second set of predicted  $R_{ij}$  mainly as a check that we have achieved self consistency. These differ from the first set by less than 0.01 Å on average. This second set was used in conjunction with input data where available in derivation of the data reported in Table 3.

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## Aluminate Sodalites: $\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{MoO}_4)_2$ (SAM) at 293, 423, 523, 623 and 723 K and $\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{WO}_4)_2$ (SAW) at 293 K

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### Abstract

The crystal structure of the aluminate sodalite  $\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{MoO}_4)_2$  (SAM) has been determined at 293 K from single-crystal X-ray data. The structure refinement was also performed employing the Rietveld method with neutron powder-diffraction data collected at nominally 293, 423, 523, 623 and 723 K. SAM is tetragonal below, but cubic above, 571 K. Crystal data:  $\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{MoO}_4)_2$ ,  $M_r = 1728.6$ ,  $F(000) = 800$ ; at 293 K,  $I4_1/acd$ ,  $a = 18.8751$  (6),  $c = 18.7839$  (9) Å,  $V = 6692.1$  (7) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 3.43$  Mg m<sup>-3</sup>; at 423 K,  $I4_1/acd$ ,  $a = 18.9056$  (8),  $c = 18.822$  (1) Å,  $V = 6727$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 3.41$  Mg m<sup>-3</sup>; at 523 K,  $I4_1/acd$ ,  $a = 18.9218$  (8),  $c = 18.850$  (1) Å,  $V = 6749$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 3.40$  Mg m<sup>-3</sup>; at 623 K,  $Im\bar{3}m$ ,  $a = 9.4643$  (3) Å,  $V = 847.7$  (1) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 3.39$  Mg m<sup>-3</sup>; at 723 K,  $Im\bar{3}m$ ,  $a = 9.4725$  (3) Å,  $V = 850.0$  (1) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 3.38$  Mg m<sup>-3</sup>. The tetragonal phase is pyroelastic with a spontaneous-strain coefficient of about  $16 \times 10^{-4}$ . Structurally it is characterized by ordered arrangements of the cage anions  $\text{MoO}_4$ , which adopt

the 'tetragonal orientation'. This results in conformational distortion of the sodalite framework and in displacive modulation of the Sr atoms. The cubic phase exhibits reorientational disorder of the  $\text{MoO}_4$  tetrahedra. The temperature dependencies of lattice parameters, spontaneous-strain and atomic displacement parameters have been determined. The mean linear thermal-expansion coefficient is  $12 \times 10^{-6}$  K<sup>-1</sup>. Structural changes, within a given phase, are smaller than the e.s.d.'s of this powder experiment. At 293 K, SAW corresponds almost perfectly to its Mo analogue:  $\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{WO}_4)_2$ ,  $M_r = 1904.4$ ,  $F(000) = 864$ ,  $I4_1/acd$ ,  $a = 18.8771$  (6),  $c = 18.7819$  (9) Å,  $V = 6692.8$  (7) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 3.78$  Mg m<sup>-3</sup>.

### Introduction

SAM and SAW belong to the structural family of aluminate sodalites with general formula  $M_8[\text{Al}_{12}\text{O}_{24}](\text{XO}_4)_2$ ,  $M = \text{Ca}, \text{Sr} \dots$  and  $X = \text{S}, \text{Cr}, \text{Mo}, \text{W} \dots$ . The structure is characterized by corner-