Bond-Valence Parameters for Anion–Anion Bonds in Solids

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Abstract

Bond-valence parameters relating bond valences and bond lengths are given for bonds between pairs of atoms each of which is one of H, B, C, Si, Ge, N, P, As, Sb, O, S, Se, Te, F, Cl, Br and I. A suggested use of existing tables of bond-valence parameters is outlined.

Bond-valence parameters

Bond-valence parameters R_{ij} relate the length d_{ij} of a bond between atoms i and j to the bond valence v_{ij}. A 'standard' form for this relationship is (Brown & Altermatt, 1985):

$$d_{ij} = R_{ij} - b\ln v_{ij} \qquad (1)$$

with $b = 0.37$ Å.

Recently (Brese & O'Keeffe, 1991) we presented extensive tables for bond-valence parameters to be used in equation (1) for the prediction and interpretation of bond lengths in crystals. These parameters were to be used for bonds between electropositive atoms ('cations') and electronegative atoms ('anions'). We subsequently (O'Keeffe & Brese, 1991) showed that, to a good approximation, bond-valence parameters for heteropolar, homopolar and metallic bonds formed one population and could be obtained from an empirical expression involving two parameters (a 'size' and an 'electronegativity') for each atom.

With the increasing interest in compounds with anion–anion bonding – so-called 'polycompounds' (Hulliger, 1981) – it is useful also to have parameters for these bonds. These are presented here in a paper that should be considered as a supplement to Brese & O'Keeffe (1991). Readers unfamiliar with the bond-valence method will find a fuller account and references to earlier work in that paper and in recent reviews (Brown, 1981; O'Keeffe, 1989). We have considered 17 elements as anions: H, B, C, Si, Ge, N, P, As, Sb, O, S, Se, Te, F, Cl, Br and I. Data for bonds between some of these (*e.g.* Si—O) are in our earlier compilation; in some instances there are minor differences (≤ 0.02 Å) as the parameters in the present compilation are designed for use with bonds with valences close to unity. The bond-valence

parameters were calculated from data obtained as described earlier (Brese & O'Keeffe, 1991) or (for bonds between more electronegative elements) from compilations of bond lengths found in Wells (1984); these data form part of the database used by O'Keeffe & Brese (1991). Missing or uncertain values have been estimated from the empirical expression given by O'Keeffe & Brese (1991) and are italicized in Table 1 which presents the resulting 153 independent values of R_{ij}. These are to be used in equation (1) either to calculate bond valences from known bond lengths or to calculate expected bond lengths from predicted bond valences.

Unfortunately, it is less obvious how to proceed with metal–metal bonding, also a topic of considerable interest. The difficulty arises particularly with the most electropositive metals; for these it is commonly observed that the metal–metal distance in compounds such as oxides (where one presumes that there is no metal–metal bonding) is less than in the element (where now one assumes that the atoms are bonded together). For transition metals, the empirical relationship given by O'Keeffe & Brese (1991) should be of some use. This relationship expresses the bond-valence parameter as a sum of 'single-bond radii' minus a generally small correction term.

Use of tables of bond-valence parameters

It may be helpful for the reader to know how we use the tables of bond-valence parameters at Arizona State University. We use a locally generated suite of four programs for analysis and interpretation of crystal structures. This is known collectively as *EUTAX*. *EUTAX*1 and *EUTAX*2 use bond-valence parameters obtained by calling a subroutine *RZERO*. *EUTAX*1 calculates bond valences and bond-valence sums in a routine manner and *EUTAX*2 is an implementation of an algorithm (O'Keeffe, 1990) for calculating expected bond lengths in crystals. The input to these programs is a typical crystallographic input file (space group, lattice parameters, atomic coordinates) except that every atom is required to have a valence, *V*. 'Cations' have $V > 0$ and 'anions' have $V < 0$.

RZERO returns bond-valence parameters by searching its data in the following sequence.

Table 1. *Bond-valence parameters for anion–anion bonds*

	H	B	C	Si	Ge	N	P	As	Sb	O	S	Se	Te	F	Cl	Br	I
H	0.74	1.19	1.09	1.48	1.53	1.01	1.42	1.52	1.71	0.95	1.35	1.46	*1.72*	0.92	1.28	1.41	1.60
B	1.19	1.55	1.58	*1.91*	*2.00*	1.47	1.86	1.96	*2.19*	1.37	1.82	*1.96*	*2.16*	1.31	1.74	1.89	2.11
C	1.09	1.58	1.54	1.85	1.95	1.44	1.85	1.96	2.20	1.39	1.81	1.98	*2.16*	1.32	1.76	1.92	2.14
Si	1.48	*1.91*	1.85	2.34	2.38	1.75	*2.21*	2.33	*2.53*	1.62	2.14	2.27	2.50	1.58	2.03	2.20	2.42
Ge	1.53	*2.00*	1.95	2.38	2.45	1.88	*2.29*	2.47	2.62	1.75	2.22	2.35	2.56	1.66	2.14	2.31	2.50
N	1.01	1.47	1.44	1.75	1.88	1.49	1.70	*1.93*	2.11	1.36	1.72	*1.90*	2.12	1.37	1.75	*1.85*	2.03
P	1.42	1.86	1.85	*2.21*	*2.29*	1.70	2.21	*2.31*	2.48	1.60	2.13	2.29	2.48	1.55	1.99	2.14	2.44
As	1.52	1.96	1.96	2.33	2.47	*1.93*	*2.31*	2.44	2.61	1.78	2.26	2.40	2.63	1.70	2.16	2.33	2.55
Sb	1.71	*2.19*	2.20	*2.53*	2.62	*2.11*	2.48	2.61	2.82	1.96	2.47	2.58	2.81	1.85	2.35	2.49	2.72
O	0.95	1.37	1.39	1.62	1.75	1.36	1.60	1.78	1.96	1.48	1.62	1.80	1.95	1.45	1.63	1.81	2.00
S	1.35	1.82	1.81	2.14	2.22	1.72	2.13	2.26	2.47	1.62	2.06	2.23	2.46	1.57	2.03	2.19	*2.36*
Se	1.46	*1.96*	1.98	2.27	2.35	*1.90*	2.29	2.40	2.58	1.80	2.23	2.33	2.50	1.73	2.22	*2.31*	2.51
Te	*1.72*	*2.16*	*2.16*	2.50	2.56	2.12	2.48	2.63	2.81	1.95	2.46	2.50	2.83	1.86	2.37	2.55	2.79
F	0.92	1.31	1.32	1.58	1.66	1.37	1.55	1.70	1.85	1.45	1.57	1.73	1.86	1.40	1.63	1.76	1.91
Cl	1.28	1.74	1.76	2.03	2.14	1.75	1.99	2.16	2.35	1.63	2.03	2.22	2.37	1.63	1.99	2.14	2.30
Br	1.41	1.89	1.92	2.20	2.31	*1.85*	2.14	2.33	2.49	1.81	2.19	*2.31*	2.55	1.76	2.14	2.28	2.45
I	1.60	2.11	2.14	2.42	2.50	2.03	2.44	2.55	2.72	2.00	*2.36*	*2.51*	2.79	1.91	2.30	2.45	2.66

Cation–anion bonds

(a) If the anion is O, F or Cl, the cation symbol *and valence* are tested. The bond-valence parameter returned (if one is found) is from Table 1 of Brese & O'Keeffe (1991).

(b) If the anion is H, N, P, As, S, Se, Br or I the cation symbol is tested. The bond-valence parameter returned (if one is found) is from Table 2 of Brese & O'Keeffe (1991).

(c) If the anion is B, C, Si, Ge or Sb, the empirical equation of O'Keeffe & Brese (1991) is used.

Anion–anion bonds

(d) If both anions are one of H, B, C, Si, Ge, N, P, As, Sb, O, S, Se, Te, F, Br, Cl or I, the bond-valence parameter returned is taken from Table 1 of the present paper. To avoid reporting a lot of weak bonds, valences calculated to be less than a cut-off value are subsequently set equal to zero. As an example, O···O distances of 2.5 Å are commonly encountered in oxides and correspond to a calculated valence of 0.03. We currently cut off anion–anion valences at 0.25, so that only strong bonds are reported by EUTAX1.

The present implementation of EUTAX2 considers only cation–anion bonds so that in calculating expected bond lengths using this program for e.g. a peroxide the valence of oxygen is set equal to − 1 rather than − 2. The reason for this is that the O—O bond in peroxides has a formal valence of 1.0, so that the remaining bonds from each the O atoms (with valence 2.0) to the cations have bond valences that ideally sum to 1.0. (The negative charge is assigned solely so that the program recognizes the O atoms as anions.) For an azide the valence of the central nitrogen is set equal to + 5 (and is therefore treated as a cation) and those of the other two are set equal to − 3. This ensures that the bonds from the central N atom each have a valence $v = 2.5$ [and a predicted bond length of 1.15 Å using equation (1) with $R = 1.49$ Å from Table 1]; the bonds from the terminal N atoms to other cations then have a bond-valence sum of 0.5 and the bonds from the two terminal N atoms have a bond-valence sum of 1.0 in accord with the formal valence of 1.0 for the N_3^- anion.

A simple example of application to structures of polycompounds is afforded by $Ta_4P_4S_{29}$ (Evian, Queignec, Brec & Rouxel, 1985) in which sulfur occurs in three oxidation states (− 2, − 1 and 0); although there are 15 crystallographically distinct S atoms in the structure they are of only three topologically distinct types. The first, just labelled S, is bonded to Ta and P; the second (S′) is bonded to Ta (2 ×) and to another S′; the third (S″) is bonded to two other S″ atoms. Table 2 displays the average valences [calculated from equation (1) using the observed bond lengths] of the different types of bond in the structure and the resulting bond-valence sums at the atoms. It can be seen clearly that S′ forms a single bond to another S′ and that S″ forms two single bonds to other S″ atoms. The bond-valence sums are close to those expected for Ta (5), P (5) and S (2). The main source of departure from exact agreement is the higher than expected valence of the Ta—S bonds.

Metal–metal bonds

(e) Bond-valence parameters are calculated from the empirical relation of O'Keeffe & Brese (1991). As mentioned above, the interpretation of apparent valences for metal···metal interactions has to be carried out with caution. Valences are calculated and values greater than 0.25 are reported (by EUTAX1) as a flag to alert the user of possible metal–metal bonding. Normally one would ignore this for electropositive elements, but consider it seriously for close distances between transition elements.

Table 2. *Average bond valences and bond-valence sums for* $Ta_4P_4S_{29}$

The number preceeding the atom symbol is the number of atoms in the formula unit, and the entries in the table are the numbers of bonds per formula unit and their average valence. The last column is the bond-valence sum for the atoms in the left column.

	4Ta	4P	16S	8S'	5S''	Sum
4Ta	–	–	16 × 0.73	16 × 0.63	–	4 × 5.46
4P	–	–	16 × 1.23	–	–	4 × 4.95
16S	16 × 0.73	16 × 1.23	–	–	–	16 × 1.97
8S'	16 × 0.63	–	–	8 × 1.06	–	8 × 2.33
5S''	–	–	–	–	10 × 1.02	5 × 2.04

Table 3. *Average bond valences and bond-valence sums for* $FePS_3$

The entries in the table have the same significance as for Table 2.

	Fe	P	3S	Sum
Fe	–	–	6 × 0.35	2.09
P	–	1.00	3 × 1.24	4.72
3S	6 × 0.35	3 × 1.24	–	3 × 1.98

A simple example of a case where 'cation'–'cation' bonding *is* unambiguous is afforded by the structure of $FePS_3$ (Klingen, Eulenberger & Hahn, 1973). In this structure P_2 groups center octahedra of S atoms and act as 'cations' with each P atom bonded to one P and three S atoms. This interpretation of the structure is supported by the bond valences [again calculated from equation (1) using the

observed bond lengths] reported in Table 3. The P—P bond has a valence of 1.0; the bond-valence sums have the values expected for Fe octahedrally coordinated by S (2) and for P acting as a cation (5) and for S acting as an anion (2).

RZERO is available from the authors as a subroutine written in ANSI standard FORTRAN77.

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Deformation Density in Lithium Triborate, LiB3O5

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Abstract

An accurate set of X-ray data collected at 293 K was used to refine the structure and study the deformation density of the title compound, LiB_3O_5. $M_r = 119.371$, orthorhombic, $Pna2_1$, $a = 8.447$ (1), $b = 7.3789$ (8), $c = 5.1408$ (6) Å, $V = 320.4$ (1) Å^3, $Z = 4$, $D_x = 2.47$ g cm^{-3}, $\mu = 2.5$ cm^{-1}, $\lambda(Mo\ K\alpha) = 0.71076$ Å, $F(000) = 232$, $R = 0.0188$, $wR = 0.0190$ for 1130 reflections ($s > 0.4$ Å^{-1}). According to the deformation electron density distribution, the vacant $2p$ orbital of the triangularly coordinated B(1) atom is mainly populated by electrons belonging to lone pairs of the O(1) and O(2) atoms which are linked by