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Alternative presentation of the Brown–Wu bond-valence parameters for some s^2 cation/O^{2-} ion pairs

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Using the least-squares refinement procedure, high-performance Brown–Wu bond-valence parameters, r_0 and n, reported for the Sn^{2+}/O^{2-}, Sb^{3+}/O^{2-}, Te^{4+}/O^{2-} and I^{5+}/O^{2-} ion pairs have been converted into the commonly used bond-valence parameters, r_0 and b. The r_0 and b values obtained can be recommended as a replacement for the conventional bond-valence parameters based on the 'universal constant' b = 0.37 Å.

The modern bond-valence model (BVM) is a powerful and easy-to-use tool for detecting errors in crystal structure determinations and for predicting interatomic distances in the crystal structures of known chemical composition and presupposed topology (Brown, 2002). The bond valence (BV) s is defined as the classical atomic valence shared with each bond. According to the bond-valence sum rule, the oxidation state (atomic valence) V_i can be calculated from the sum of the individual bond valences s_{ij} (where i denotes an atom bonded to j), as given by

$$V_i = \sum_j s_{ij}. \qquad (1)$$

The valence of a bond (measured in valence units, v.u.) is considered to be a unique function of the bond length; the most commonly adopted empirical expressions for the relationship between the bond valences s_{ij} and the bond lengths r_{ij} are the Brown–Altermatt formula (2) and the Brown–Shannon formula (3)

$$s_{ij} = \exp[(r_0 - r_{ij})/b] \qquad (2)$$

and

$$s_{ij} = (r_0/r_{ij})^n, \qquad (3)$$

where r_0, b and n are the empirically determined parameters for a given ion pair, r_0 being the length of the bond of unit valence (Brown & Shannon, 1973; Brown & Altermatt, 1985).

However, the Brown–Altermatt formula (2) is used in almost all recent works describing applications of the BVM. The b parameter in (2) is commonly taken to be the 'universal constant' equal to 0.37 Å, and the r_0 parameters have been determined for a large number (~1000) of ion pairs, assuming b = 0.37 Å (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). Hereafter, the BV parameters determined using the 'universal constant' will be referred to as the conventional BV parameters.

The r_0 and n parameters for use in the Brown–Shannon formula (3) were reported for a much smaller number (< 200) of ion pairs (Brown & Wu, 1976; Brown, 1981; Slupecki & Brown, 1982); systematic determination of these parameters stopped in the 1980s because of the much greater popularity of the Brown–Altermatt formula.

In well determined stable crystal structures, the bond-valence sums (BVSs) calculated for all crystallographically non-equivalent atoms are usually very close to the expected V_i values; therefore, large deviations between the BVS and V_i values can really be a symptom of the errors in the structural model obtained.

It must be noted, however, that the efficiency of the BVM in detecting errors of crystal structures and in predicting bond lengths is

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Table 1
Brese–O'Keeffe conventional BV parameters reported for the ion pairs considered, the Brown–Wu parameters for the same ion pairs, r_0 and b values obtained in this work from the corresponding Brown–Wu parameters, and the ranges of bond lengths r_{ij} used in the calculations.

	Brese & O'Keeffe (1991)		Brown & Wu (1976)		This work		
Ion pair	r_0 (Å)	b (Å)	r_0 (Å)	n	r_0 (Å)	b (Å)	r_{ij} range (Å)
Sn^{2+}/O^{2-}	1.984	0.37	1.860	4.5	1.849 (4)	0.50	1.8–4.1
Sb^{3+}/O^{2-}	1.973	0.37	1.910	4.5	1.924 (4)	0.47	1.7–3.9
Te^{4+}/O^{2-}	1.977	0.37	1.933	4.5	1.955 (4)	0.44	1.6–4.0
I^{5+}/O^{2-}	2.00	0.37	1.967	4.5	1.990 (4)	0.44	1.6–3.9

critically dependent on the *quality* of the BV parameters: high-quality BV parameters are expected to give close approximations of the real (observed) '$s_{ij} - r_{ij}$' curves within the *full* range of observed bond lengths. In most cases, the commonly used *monoparametric* (with b = 0.37 Å) Brown–Altermatt formula (4)

$$s_{ij} = \exp[(r_0 - r_{ij})/0.37] \qquad (4)$$

can give close approximations of the real '$s_{ij} - r_{ij}$' curves; however, for certain ion pairs (especially for those having a wide range of coordination numbers, CNs) close approximations of the real '$s_{ij} - r_{ij}$' correlations are possible only by simultaneous fitting of both r_0 and b.

In preparation of his recently published article (Sidey, 2008), the author of the present work has found that the conventional BV parameters (Brese & O'Keeffe, 1991) reported for some s^2 cation/O^{2-} ion pairs[1] (Tl^{+}/O^{2-}, Sn^{2+}/O^{2-}, Pb^{2+}/O^{2-}, Sb^{3+}/O^{2-}, Te^{4+}/O^{2-} and I^{5+}/O^{2-}) give very poor approximations (especially within the short-bond ranges) of the real '$s_{ij} - r_{ij}$' curves. However, the Brown–Wu parameters, r_0 and n, reported for the same ion pairs (Brown, 1974; Brown & Wu, 1976) have been fitted simultaneously and demonstrate a much higher performance. In other words, the two-parameter function (3) was able to approximate the real '$s_{ij} - r_{ij}$' curves for the above ion pairs reasonably well, whereas the highly popular monoparametric function (4) was unable to give close approximations for these curves.

The unsatisfactory performance of the conventional BV parameters reported for some s^2 cation/O^{2-} ion pairs has stimulated the appearance of new research works dedicated to the improvement of the r_0 and b values. Thus, Krivovichev & Brown (2001) and Locock & Burns (2004) have simultaneously refined the r_0 and b parameters, and have greatly improved approximations of the real '$s_{ij} - r_{ij}$' correlations for the Pb^{2+}/O^{2-} and Tl^{+}/O^{2-} ion pairs.

Unfortunately, determination of the improved values of the r_0 and b parameters (with the free b parameter) is extremely time-consuming, so researchers usually improve the BV parameters only for the ion pairs of personal scientific interest. For this reason, poorly determined conventional BV parameters can be routinely used for a long time, and can lead to serious misinterpretations of the peculiarities of the chemical bonding observed in certain crystal structures [see, for example, two different interpretations made by Krivovichev (1999) and Krivovichev & Brown (2001) for the chemical bonding in the OPb_4 coordination tetrahedra].

In principle, the Brown–Wu parameters r_0 and n can still be successfully used for the BV analysis of the structures containing coordination polyhedra formed by the aforementioned s^2 cation/O^{2-} ion pairs. However, calculations of the BVS values from the Brown–Wu parameters can only be done *manually* because all modern crystallographic programs for performing the BV analysis use only the Brown–Altermatt formula (2) (see, for example, Brown, 1996; Spek, 2008; Wills, 2008). Hence, in order to use the high-quality BV parameters r_0 and n with modern crystallographic software, these parameters should be converted, as accurately as possible, into the r_0 and b parameters of the Brown–Altermatt formula (2).

Since the performances of the Brown–Shannon formula (3) and the 'canonical' (*i.e.* two-parameter) Brown–Altermatt formula (2) in approximating the real '$s_{ij} - r_{ij}$' curves are virtually the same (Brown, 2002), it was assumed that the '$s_{ij} - r_{ij}$' curves defined by (3) with the r_0 and n parameters can be very closely approximated using (2) with the fitted r_0 and b values. The r_0 and b values determined in this way should demonstrate nearly the same performance as that demonstrated by the original Brown–Wu parameters. Thus, the main goal of this work is to present the r_0 and b parameters obtained by the author for some s^2 cation/O^{2-} ion pairs from the corresponding high-quality Brown–Wu parameters r_0 and n (Brown & Wu, 1976), and also to describe a potentially useful procedure for conversion of the r_0 and n parameters into the r_0 and b parameters (or *vice versa*).

In the paper by Brown & Wu (1976), the BV parameters r_0 and n were reported for the following s^2 cation/O^{2-} ion pairs: Tl^{+}/O^{2-}, Sn^{2+}/O^{2-}, Pb^{2+}/O^{2-}, Sb^{3+}/O^{2-}, Bi^{3+}/O^{2-}, S^{4+}/O^{2-}, Se^{4+}/O^{2-}, Te^{4+}/O^{2-} and I^{5+}/O^{2-}.

The BV parameters r_0 and b reported by Krivovichev & Brown (2001) for the Pb^{2+}/O^{2-} ion pair (r_0 = 1.963 Å and b = 0.49 Å) and by Locock & Burns (2004) for the Tl^{+}/O^{2-} ion pair (r_0 = 1.927 Å and b = 0.50 Å) are definitely the best parameters currently available for these ion pairs. Hence, there was no reason to convert the Brown–Wu parameters r_0 and n reported in 1976 for the Pb^{2+}/O^{2-} and Tl^{+}/O^{2-} ion pairs into the r_0 and b parameters; although the Brown–Wu parameters work much better than the conventional parameters reported by Brese & O'Keeffe (1991) for the same ion pairs.

Furthermore, the performances of the conventional and Brown–Wu parameters reported for the ion pairs S^{4+}/O^{2-}, Se^{4+}/O^{2-} and Bi^{3+}/O^{2-} have been found to be similar and reasonably high; so no significant gain was expected from the use of the Brown–Wu parameters rather than the conventional BV parameters.

In order to find the r_0 and b values giving the best possible approximations of the Brown–Wu '$s_{ij} - r_{ij}$' curves for the remaining ion pairs (Sn^{2+}/O^{2-}, Sb^{3+}/O^{2-}, Te^{4+}/O^{2-} and I^{5+}/O^{2-}), the following procedure has been used.

As a first step, the minimum and maximum bond lengths r_{ij} were set for each ion pair under consideration. The minimum bond length for a given ion pair $r_{\min}$ was estimated as $\sim 0.9 \times r'_{\min}$, where $r'_{\min}$ is the typical bond length in the smallest observed CN of a given ion pair. The maximum bond length for a given ion pair $r_{\max}$ was estimated as $\sim 1.1 \times \sum R_{\rm vdW}$, where $\sum R_{\rm vdW}$ is the sum of the van der Waals radii of the elements of the ion pair (van der Waals radii were taken from the Cambridge Structural Database;[2] Allen, 2002).

At the second step, the '$s_{ij} - r_{ij}$' curves defined by (3) with the Brown–Wu r_0 and n parameters were plotted within the limits from $r_{\min}$ to $r_{\max}$.

Finally, the plotted '$s_{ij} - r_{ij}$' curves were closely approximated by (2) using the least-squares refinement of the r_0 and b parameters. In order to avoid the superfluous and unjustified precision for the b

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[1] The term 's^2 cation' is used to denote the cations with one lone electron pair s^2.

[2] The table containing the van der Waals radii is available online at http://www.ccdc.cam.ac.uk/products/csd/radii/table.php4.

Table 2
Typical relations between the BVS values calculated for different CNs of the considered ion pairs from the Brese–O'Keeffe conventional BV parameters and from the BV parameters obtained in this work.

			BVS (v.u.)†	
Compound	Reference	Coordination shell‡	Brese & O'Keeffe (1991)	This work
K_4SnO_3	Röhr (1995)	SnO_3	2.530 (+27%)	2.019 (+1%)
Rb_2SnO_2	Braun & Hoppe (1982)	SnO_3	2.478 (+24%)	1.986 (−1%)
SnO	Pannetier & Denes (1980)	SnO_4	2.091 (+5%)	1.889 (−6%)
$SnWO_4$	Jeitschko & Sleight (1972)	SnO_8	2.070 (+4%)	2.063 (+3%)
Na_3SbO_3	Stöver & Hoppe (1980)	SbO_3	3.724 (+24%)	3.205 (+7%)
K_3SbO_3	Emmerling & Röhr (2001)	SbO_3	3.434 (+14%)	3.006 (+0%)
$CsSbO_2$	Hirschle & Röhr (1998)	SbO_4	3.286 (+10%)	3.066 (+2%)
Sb_2O_3	Svensson (1974)	SbO_5	3.151 (+5%)	3.032 (+1%)
K_2TeO_3	Andersen *et al.* (1989)	TeO_3	4.598 (+15%)	4.087 (+2%)
Cs_2TeO_3	Loopstra & Goubitz (1986)	TeO_3	4.274 (+7%)	3.843 (−4%)
$BaTeO_3$	Folger (1975)	TeO_6	4.204 (+5%)	3.885 (−3%)
TeO_2	Kondratyuk *et al.* (1987)	TeO_8	4.169 (+4%)	4.056 (+1%)
$Ba(IO_3)_2\cdot(H_2O)$	Lutz *et al.* (1985)	IO_5	5.27 (+5%)	4.825 (−4%)
β-$LiIO_3$	Schulz (1973)	IO_5	5.47 (+9%)	4.990 (−0%)
α-$RbIO_3$	Alcock (1972)	IO_6	5.40 (+8%)	5.064 (+1%)
$NaIO_3$	Svensson & Ståhl (1988)	IO_8	5.31 (+6%)	4.925 (−2%)

† The relative BVS errors calculated as $[(\mathrm{BVS}-V_i)/V_i] \times 100\%$ are given in parentheses. ‡ The shortest distance from the central cation to another cation in a given crystal structure was assumed to be the physical limit of the coordination sphere under consideration.

parameters, in the last refinement cycles the fitted values of the b parameters were rounded to and fixed at the nearest two-decimal values.

All calculations of the second and final steps were performed using a common plotting/spreadsheet program.

The r_0 and b parameters obtained for the considered s^2 cation/O^{2-} ion pairs by using the above procedure (along with some additional data) are given in Table 1. Fig. 1 shows typical relations between the '$s_{ij} - r_{ij}$' curves defined by (3) and by optimized (2). Some typical examples of the BVS values calculated for different CNs of the considered ion pairs from the conventional BV parameters (Brese & O'Keeffe, 1991) and from the BV parameters obtained in this work are given in Table 2. All the crystal structures selected for Table 2 are well determined, investigated at the ambient conditions, ordered, stoichiometric and stable; so large differences between the BVS and V_i values are not expected for these structures. It can be seen that the performances of the BV parameters r_0 and b determined in this work for the ion pairs Sn^{2+}/O^{2-}, Sb^{3+}/O^{2-}, Te^{4+}/O^{2-} and I^{5+}/O^{2-} are reasonably high for *all* CNs observed, including the smallest ones in the short-bond ranges; this fact clearly indicates that the r_0 and b values obtained give *better* approximations of the real '$s_{ij} - r_{ij}$' curves than the conventional BV parameters.

Being based on the structural information available in the mid 1970s (Brown & Wu, 1976), the r_0 and b parameters reported in this work cannot be regarded as the best possible parameters. Nevertheless, the r_0 and b values reported here for the ion pairs Sn^{2+}/O^{2-}, Sb^{3+}/O^{2-}, Te^{4+}/O^{2-} and I^{5+}/O^{2-} demonstrate high reliability, and can be recommended for routine BVS calculations as a replacement for the conventional BV parameters (Brese & O'Keeffe, 1991) reported for the same ion pairs. The conversion procedure used in this work to obtain the r_0 and b parameters from the corresponding r_0 and n values should be considered by a researcher if the conventional BV parameters reported for a given ion pair seem to fail and if the Brown–Wu parameters (or other r_0 and n parameters) reported for the same ion pair work significantly better.

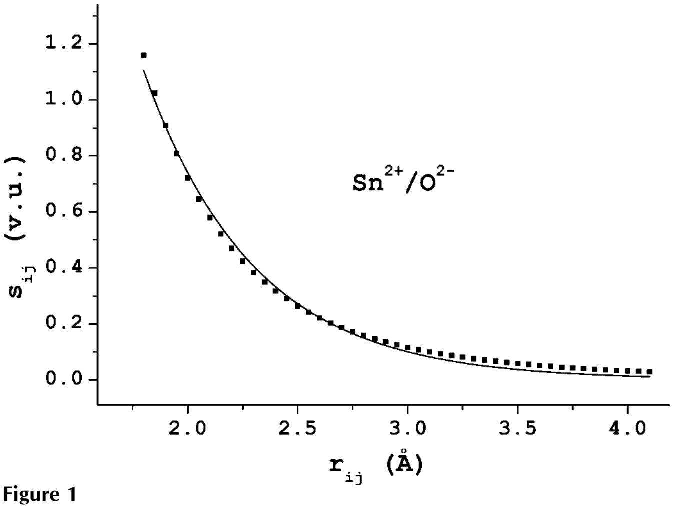

Figure 1
Relations between the '$s_{ij} - r_{ij}$' curves defined for the Sn^{2+}/O^{2-} ion pair as $s_{ij} = (1.860/r_{ij})^{4.5}$ (dotted line; Brown & Wu, 1976) and as $s_{ij} = \exp[(1.849 - r_{ij})/0.50]$ (solid line; this work).

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