

Acta Crystallographica Section B

**Structural
Science**

ISSN 0108-7681

Editor: **Carolyn P. Brock**

On the optimization of bond-valence parameters: artifacts conceal chemical effects

Xiqu Wang and Friedrich Liebau*Acta Cryst.* (2009). **B65**, 96–98

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Reproduction of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see <http://journals.iucr.org/services/authorrights.html>



Acta Crystallographica Section B: Structural Science publishes papers in structural chemistry and solid-state physics in which structure is the primary focus of the work reported. The central themes are the acquisition of structural knowledge from novel experimental observations or from existing data, the correlation of structural knowledge with physico-chemical and other properties, and the application of this knowledge to solve problems in the structural domain. The journal covers metals and alloys, inorganics and minerals, metal-organics and purely organic compounds.

Crystallography Journals **Online** is available from journals.iucr.org

On the optimization of bond-valence parameters:
artifacts conceal chemical effectsXiqu Wang^{a*} and Friedrich
Liebau^b^aDepartment of Chemistry, University of
Houston, Houston, TX 77204, USA, and^bInstitut für Geowissenschaften, AG Kristallographie,
Universität Kiel, Olshausenstrasse 40,
D-24098 Kiel, GermanyCorrespondence e-mail:
xiqu.wang@mail.uh.edu

Received 12 September 2008

Accepted 3 December 2008

We recently proposed that calculated bond-valence sums, BVS, represent a non-integer structural valence, ${}^{\text{struct}}V$, rather than the integer-value stoichiometric valence, ${}^{\text{stoich}}V$. Therefore, the usual attempts to 'optimize' bond-valence parameters r_0 and b by adjusting them to ${}^{\text{stoich}}V$ are based on the false assumption that numerical values of ${}^{\text{struct}}V$ and ${}^{\text{stoich}}V$ are always equal. Bond-valence calculations for several compounds with stereoactive cations Sn^{II} , Sb^{III} and Bi^{III} reveal the balanced distribution of the bonding power ${}^{\text{struct}}V$ between atoms of each structure.

In a recent paper we described the linear correlation

$$(\text{BVS})_i = E|\Phi| + F' \quad (1)$$

between the values of the polyhedron-eccentricity parameter, Φ , and the bond-valence sum, BVS, for cations with one lone electron pair (LEP; Wang & Liebau, 2007). The bond-valence sums are calculated with the well known bond-valence formula

$$(\text{BVS})_i = \sum_j s_{ij} = \sum_j \exp[(r_0 - D_{ij})/b]. \quad (2)$$

Here D_{ij} are the experimental bond lengths, r_0 and b the empirical bond-valence parameter values from Brown & Altermatt (1985) and Brese & O'Keeffe (1991). $(\text{BVS})_i$ is usually assumed to be equal to the classical integer-number stoichiometric valence ${}^{\text{stoich}}V_i$ of the element under consideration. In a communication recently published in this journal, Sidey (2008) concluded that the correlations described by us are probably an artifact of poorly determined bond-valence parameters. He further pointed out that by using the bond-valence parameters of Brown & Wu (1976), a better fit between the calculated BVS values and the values of the stoichiometric valence ${}^{\text{stoich}}V_i$ can be achieved for some of the cations with one LEP. There have been reports in which the bond-valence parameter values were modified in order to eliminate some significant deviations between the calculated BVS and the values of ${}^{\text{stoich}}V_i$ for specific bond types, without thoroughly analyzing structural reasons for the deviations. The improvement in fitting which is claimed is often achieved by increasing the number of variables from one to two (Burns *et al.*, 1997; Krivovichev & Brown, 2001; Locock & Burns, 2004; Palenik *et al.*, 2005; Sidey, 2006; Malcherek & Schlüter, 2007; Sidey *et al.*, 2008). As briefly pointed out (Wang & Liebau, 2005, 2007), such 'optimization' of bond-valence parameters, which is based on a specific type of coordination polyhedra that are separated from whole structures, may simply shift the problem from one type of atom to another in the structures, because the underlying chemical reasons are not addressed.

If the large observed deviations between the values of BVS and the stoichiometric valence of the lone-pair cations are caused by incorrectly calculated bond valences for their bonds, the corresponding deviations should also be seen in the BVS values of the anions bonded to them. Table 1 lists calculated BVS values for eight compounds from Tables 2 and 3 of Sidey (2008). It can be seen that when the Brese & O'Keeffe (1991) parameters are used, the calculated BVS values for the oxygen anions do not show any abnormal

Table 1
BVS values calculated using the Brese & O'Keeffe (1991) and Brown & Wu (1976) bond-valence parameters.

Deviations of BVS from the stoichiometric valence are given in parentheses. Values with less than 10% deviation are marked in bold.

Compound	ICSD code	Atoms	BVS(v.u.)	
			Brese & O'Keeffe	Brown & Wu
Na ₄ SnO ₃	49624	Sn1	2.733 (+37%)	2.077 (+4%)
		Na1	0.532 (-47%)	0.456 (-54%)
		Na2	0.853 (-15%)	0.840 (-16%)
		Na3	0.859 (-14%)	0.848 (-15%)
		Na4	0.849 (-15%)	0.713 (-29%)
		O1	1.978 (-1%)	1.669 (-17%)
		O2	1.858 (-7%)	1.594 (-20%)
		O3	1.990 (-1%)	1.670 (-17%)
Na ₃ SbO ₃	23346	Sb1	3.724 (+24%)	3.123 (+4%)
		Na1	0.883 (-12%)	0.862 (-14%)
		O1	2.124 (+6%)	1.903 (-5%)
K ₃ SbO ₃	279579	Sb1	3.434 (+14%)	2.910 (-3%)
		K1	0.902 (-10%)	0.831 (-17%)
		K2	0.904 (-10%)	0.839 (-16%)
		K3	0.702 (-30%)	0.731 (-27%)
		O1	1.987 (-1%)	1.770 (-12%)
Cs ₃ SbO ₃	279580	Sb1	3.388 (+13%)	2.876 (4%)
		Cs1	0.881 (-12%)	0.867 (-13%)
		Cs2	0.878 (-12%)	0.863 (-14%)
		Cs3	0.845 (-15%)	0.736 (-26%)
		O1	1.997 (0%)	1.781 (-11%)
		O2	0.862 (-14%)	0.852 (-15%)
Na ₃ BiO ₃	23347	Bi1	3.307 (+10%)	2.692 (-10%)
		Na1	0.862 (-14%)	0.852 (-15%)
		O1	1.964 (-2%)	1.749 (-13%)
K ₃ BiO ₃	407293	Bi1	3.227 (+8%)	2.634 (-12%)
		K1	0.929 (-7%)	0.893 (-11%)
		O1	2.004 (0%)	1.771 (-12%)
Rb ₃ BiO ₃	407294	Bi1	3.324 (+11%)	2.705 (-10%)
		Rb1	0.718 (-28%)	0.607 (-39%)
		Rb2	0.906 (-9%)	0.802 (-20%)
		Rb3	0.889 (-11%)	0.789 (-21%)
		O1	1.946 (-3%)	1.634 (-18%)
Cs ₃ BiO ₃	406563	Bi1	3.471 (+16%)	2.813 (-6%)
		Cs1	0.818 (-18%)	0.716 (-28%)
		Cs2	0.843 (-16%)	0.838 (-16%)
		Cs3	0.911 (-9%)	0.888 (-11%)
		O1	2.014 (+1%)	1.752 (-13%)

deviations from the stoichiometric valence values. Instead, the positive deviations of BVS values for the lone-pair cations are largely counterbalanced by negative deviations for the alkali cations in the

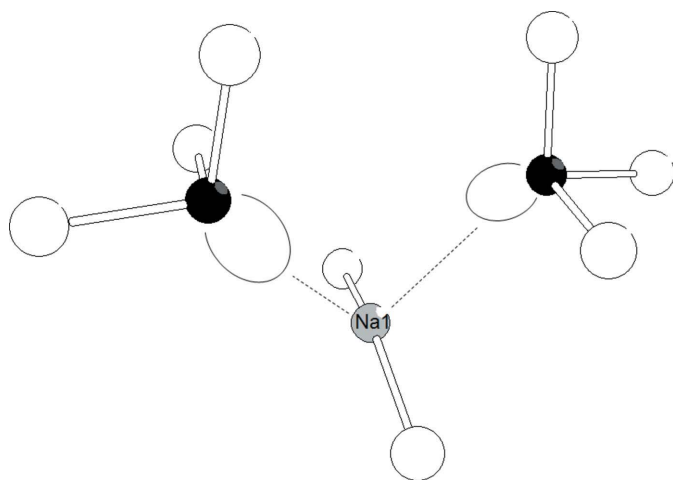


Figure 1
The coordination of the Na1 cations in the structure of Na₄SnO₃ (Nowitzki & Hoppe, 1984). Open and solid circles represent O and Sn atoms, respectively. Two lone electron pairs of Sn atoms, drawn schematically, complement the tetrahedral coordination of Na1.

structures. Similar results are also found for other compounds with lone-pair cations, including those in Tables 2 and 3 of Sidey (2008). The chemical reasons for such cooperative deviations were previously interpreted as being due to the transfer of bonding power from the alkali cations to the lone-pair cations by the lone electron pairs (Wang & Liebau, 2005). The asymmetric distribution of the LEP around the core of the *p*-block cation withdraws negative charge from the core and leaves the more positive charge of the core exposed to the bonding anions. This leads to the enhanced bonding capability of the lone-pair cation. The stereoactive LEP with its negative charge may join the coordination sphere of other cations such as the alkali cations shown in Figs. 1 and 2. In Na₄SnO₃ and Rb₃BiO₃, the positive charge of an alkali cation is partially balanced by the negative charges of two or three LEPs of the *p*-block cations, respectively. Thus, the bonding power of the alkali cations is reduced, because the LEPs transfer bonding power from the alkali cations to the surrounding lone-pair cations. Although usually an LEP cannot be located through X-ray crystal-structure refinement, its effect is reflected in the calculated BVS values of the involved atoms. This is similar to the situation in O—H...X hydrogen bonds if the H atom is not located. Table 1 shows that a replacement of the bond-valence parameters of Brese & O'Keeffe (1991) by those of Brown & Wu (1976) simply shifts the 'overbonding' of the lone-pair cations to 'underbonding' of the oxygen anions, with little change for the alkali cations. Apparently, any 'optimization' of bond-valence parameters, which is based on lone-pair cation-centered polyhedra without taking into consideration the bonding-power change, will lead to results similar to those obtained when the parameters of Brown & Wu (1976) are used. The degree of change of the bonding power of the atoms owing to LEP depends on the specific structures, but does not depend on the stoichiometric valence of the atoms. If in such cases one insists on a fit between calculated BVS and the stoichiometric valence, a cation–anion bond with a bond valence that must be counted negative for the lone-pair cation but positive for the alkali cation may be assumed. Such treatment has been proposed for coordination complexes such as [Cu(NO₂)₆]⁴⁻, where the Cu atom is octahedrally coordinated by six N atoms (Brown, 2002, p. 37).

However, it was recently shown (Liebau & Wang, 2008*a*) that in the isostructural series of garnet-type phases Ln^{III}Te₂^{VI}Li₃O₁₂, where the trailing Roman-number superscripts describe the stoichiometric valence values of the corresponding atoms, the calculated BVS values of the lanthanide atoms do not represent their integer-value stoi-

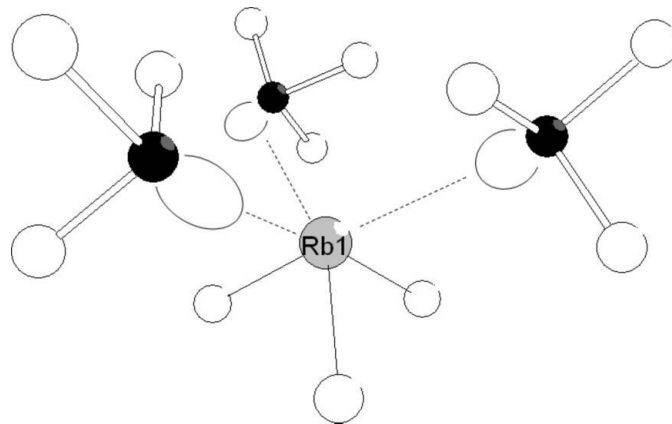


Figure 2
The coordination of the Rb1 cation in the structure of Rb₃BiO₃ (Zoche & Jansen, 1997). Open and solid circles represent O and Bi atoms, respectively. Three lone electron pairs of Bi atoms, drawn schematically, complement the octahedral coordination of Rb1.

chiometric valence +III. Instead, these non-integer BVS values are equivalent to the valence values that were calculated by Strange *et al.* (1999) with quantum-chemical methods for Ln in their sulfides and in their metallic state. Moreover, both calculated $(\text{BVS})_{\text{Ln}}$ values for the garnet-type phases and quantum-chemically calculated Ln valence values show the same irregular variation with atomic number as the third ionization potential of Ln. This proves that the stoichiometric valence, $\text{stoich}V$, and the bond-valence sum, BVS, are two distinct properties useful for describing the bonding power of atoms. In order to avoid confusion, we proposed to use the term 'structural valence' and the symbol $\text{struct}V$ for the bonding power of atoms in a compound which is represented by the structure-based BVS, and the symbol $\text{stoich}V$ for the composition-based stoichiometric valence (Liebau & Wang, 2005).

Since $\text{stoich}V$ and $\text{struct}V$ are two distinct properties and since BVS is related to $\text{struct}V$ and not to $\text{stoich}V$, any attempt to reduce differences between BVS and $\text{stoich}V$ in specific structures by 'improving' r_0 and b by fitting calculated BVS values to the integer-number $\text{stoich}V$, is based on the false assumption that $\text{stoich}V$ and $\text{struct}V$ are equivalent.

The fact that in the majority of structures the bond-valence parameters r_0 and b of Brown & Altermatt (1985) and Brese & O'Keeffe (1991) nevertheless lead to good agreement between BVS and $\text{stoich}V$, although they are derived under the false assumption $\text{BVS} \propto \text{stoich}V$, is due to the following reason. These r_0 and b values are based on a large number of accurately determined structures in which the majority of atoms have bonding-power values close to the mean value of their kind, averaged over all structures. The values of these parameters can in fact be derived by scaling the mean bonding power of the atoms to their stoichiometric valence. For atoms having bonding-power values equal to the mean value of their kind, the numerical values of $\text{struct}V$ and $\text{stoich}V$ are equal, although they have essentially different meanings (Liebau & Wang, 2005, 2008b). In the calculation of bond-valence parameters, two types of structures should be considered:

(i) in structures in which values of $\text{struct}V$ are equal to those of $\text{stoich}V$, BVS values are numerically equal to the values of $\text{stoich}V$ for all the atoms in the structures.

(ii) in structures with at least some atoms for which $\text{struct}V$ deviates considerably from $\text{stoich}V$, due to reasons such as electronic and steric effects, BVS values should reflect the differences between $\text{struct}V$ and $\text{stoich}V$ proportionally.

Apparently, only for type (i) structures can fitting BVS to $\text{stoich}V$ lead to correct bond-valence parameters. The errors in the bond-valence parameters of Brown & Altermatt (1985) and Brese & O'Keeffe (1991) that are caused by type (ii) structures are likely not substantial because of the relatively small percentages of such structures. Therefore, BVS values calculated using these parameters are good estimates for $\text{struct}V$, and can be used for screening structures of type (i) or close to type (i) for further refinement of these parameters.

In conclusion, systematic differences between calculated values of BVS and $\text{stoich}V$, observed for structures such as those containing lone pair cations, are reflections of the differences between the values of $\text{struct}V$ and $\text{stoich}V$ caused by electronic and steric effects. Such differences cannot be explained by inaccuracy of the bond-valence parameters. Refinements of bond-valence parameters should be based on values of $\text{struct}V$ instead of $\text{stoich}V$.

XW thanks Professor A. J. Jacobson for his continuous support.

References

- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
 Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. Oxford University Press.
 Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
 Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.
 Burns, P. C., Ewing, R. C. & Hawthorne, F. C. (1997). *Can. Mineral.* **35**, 1551–1570.
 Krivovichev, S. V. & Brown, I. D. (2001). *Z. Kristallogr.* **216**, 245–247.
 Liebau, F. & Wang, X. (2005). *Z. Kristallogr.* **220**, 589–591.
 Liebau, F. & Wang, X. (2008a). *Acta Cryst.* **B64**, 299–304.
 Liebau, F. & Wang, X. (2008b). *Chem. Eur. J.* In the press.
 Locock, A. J. & Burns, P. C. (2004). *Z. Kristallogr.* **219**, 259–266.
 Malcherek, T. & Schlüter, J. (2007). *Acta Cryst.* **B63**, 157–160.
 Nowitzki, B. & Hoppe, R. (1984). *Z. Anorg. Allg. Chem.* **515**, 114–126.
 Palenik, R. C., Abboud, K. A. & Palenik, G. J. (2005). *Inorg. Chim. Acta*, **358**, 1034–1040.
 Sidey, V. (2006). *Acta Cryst.* **B62**, 949–951.
 Sidey, V. (2008). *Acta Cryst.* **B64**, 515–518.
 Sidey, V. I., Milyan, P. M., Semrad, O. O. & Solomon, A. M. (2008). *J. Alloys Compd.* **457**, 480–484.
 Strange, P., Svane, A., Temmerman, W. M., Szotek, Z. & Winter, H. (1999). *Nature*, **399**, 756–758.
 Wang, X. & Liebau, F. (2005). *Mater. Res. Soc. Symp. Proc.* **848**, 345–350.
 Wang, X. & Liebau, F. (2007). *Acta Cryst.* **B63**, 216–228.
 Zoche, N. & Jansen, M. (1997). *Z. Naturforsch. B*, **52**, 1031–1036.