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Influence of polyhedron distortions on calculated bond-valence sums for cations with one lone electron pair

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Dedicated to the late Linus Pauling who, more than 75 years ago, founded the bond-valence model, and to David Brown who transformed this model into a readily and successfully applicable method in inorganic crystal chemistry.

In the present bond-valence model (BVM), the bond-valence parameters r_0 and b are, in general, supposed to be constant for each **A**–**X** pair and equal to 0.37 Å for all **A**–**X** pairs, respectively. For $[\mathbf{A}_i(\mathbf{X}_j)_n]$ coordination polyhedra that do not deviate strongly from regularity, these suppositions are well fulfilled and calculated values for the bond-valence sums $(\mathrm{BVS})_i$ are nearly equal to the whole-number values of the stoichiometric valence. However, application of the BVM to 2591 $[\mathbf{L}_i(\mathbf{X}_j)_n]$ polyhedra, where **L** are *p*-block cations, *i.e.* cations of the 13th to 17th group of the periodic system of elements, with one lone electron pair and $\mathbf{X} = \mathrm{O}^{-\mathrm{II}}$, $\mathrm{S}^{-\mathrm{II}}$ and $\mathrm{Se}^{-\mathrm{II}}$, shows that r_{0i} values of individual $[\mathbf{LX}_n]$ polyhedra are correlated with the absolute value $|\mathbf{\Phi}_i|$ of an eccentricity parameter, $\mathbf{\Phi}_i$, which is higher for more distorted $[\mathbf{LX}_n]$ polyhedra. As a consequence, calculated $(\mathrm{BVS})_i$ values for these polyhedra are also correlated with $|\mathbf{\Phi}_i|$, rather than being numerically equal to the stoichiometric valence of **L**. This is interpreted as the stereochemical influence of the lone electron pair of **L**. It is shown that the values of the correlation parameters and the R^2 values of the correlation equations depend on the position of the **L** cation in the periodic system of elements, if the correlations are assumed to be linear. This observation suggests that $(\mathrm{BVS})_\mathbf{L}$ describes a chemical quantity that is different from the stoichiometric valence of **L**.

1. Introduction

The bond-valence model (BVM) in its present form is a powerful tool for analysing inorganic crystal structures on the basis of the valence distribution between the atoms. It can be traced back to Pauling's (1929) proposal that the valence of an atom is distributed among the bonds to its neighbours.

In the majority of structures, values of the bond-valence sums (BVS), calculated using the empirical bond-valence/bond-length relations, are within 0.1 v.u. (valence units) of the whole-number values of the classical atomic valence. Various authors have, however, noticed that in some cases agreement between such BVS values and the corresponding atomic valence is poor and that deviations of up to 1 v.u. are sometimes observed. This is true for structures containing small cations located in larger voids of a relatively rigid framework (Brown, 1992), for structures containing complexes in which the central metal atoms have valences $V \leq 0$, such as $\mathrm{NaCo(CO)_4}$ (Naskar *et al.*, 1997), for structures with strong hydrogen bonds, $\mathrm{O{-}H\cdots O}$ (*e.g.* Brown, 1992), and for structures containing cations with lone electron pairs such as $\mathrm{Tl^{I}}$, $\mathrm{Sn^{II}}$, $\mathrm{Pb^{II}}$ and $\mathrm{Sb^{III}}$[1] (Brown, 1992; Wang, 1993; Krivovichev & Brown, 2001).

Such discrepancies, although rather small in number compared with the much larger number of successful analyses, indicate limitations inherent in the present BVM. In this report the present BVM is re-examined in order to find the reasons behind its insufficiencies.

Valence, which in bond-valence theory has so far been ascribed to each atom within a compound, is the classical valence that is derived from the stoichiometry of the compound and is, throughout this paper, called the *stoichiometric valence*,[2] ${}^{\rm stoich}V$. Because of the chemical laws of constant and multiple proportions, the values of ${}^{\rm stoich}V$ are whole numbers, ${}^{\rm stoich}V$ = ..., −2, −1, 0, +1, +2, ... (v.u.).

2. Historical development of the BVM

As a detailed review of the present BVM is available (Brown, 2002), only a brief review with special emphasis on those aspects shall be given that are necessary to recognize possible insufficiencies and to suggest improvements.

Crystal structures of inorganic compounds are usually described as frameworks of cation-centred coordination polyhedra $[\mathbf{AX}_n]$[3] or of anion-centred polyhedra $[\mathbf{XA}_m]$. Although descriptions of a crystal structure on the basis of $[\mathbf{AX}_n]$ and of $[\mathbf{XA}_m]$ coordination polyhedra are equivalent, we shall prefer, in the following discussion, descriptions based on $[\mathbf{AX}_n]$ polyhedra.

According to Pauling's (1929) electrostatic valence principle, the valence V_i of a cation $\mathbf{A}_i$ is distributed among its $\mathbf{A}_i$—$\mathbf{X}_j$ bonds such that

$$V_i = \sum_j^n s_{ij} = ({\rm BVS})_i \ [{\rm v.u.}], \tag{1}$$

where $({\rm BVS})_i$ is the *bond-valence sum*, *i.e.* the sum over all bond valences, s_{ij}, of $\mathbf{A}_i$. For s_{ij} Pauling introduced the term *bond order*, which has been replaced by the term bond valence, which was introduced by Donnay & Allmann (1970).

If all bonds $\mathbf{A}_i$—$\mathbf{X}_j$ of a coordination polyhedron (CP) are equivalent, n is equal to the coordination number $({\rm CN})_i$ of the cation $\mathbf{A}_i$

$$V_i = ({\rm BVS})_i = \sum_{j=1}^{({\rm CN})_i} s_{ij} = ({\rm CN})_i \times s_{ij} \tag{2}$$

and

$$s_{ij} = V_i/({\rm CN})_i. \tag{2a}$$

For example, the mineral zircon $\mathrm{Zr}^{[8cb]}\mathrm{Si}^{[4t]}\mathrm{O}_4^{[3]}$[4] (Kolesov *et al.*, 2001) contains zirconium ions in cubical and silicon in tetrahedral coordination. Applying (2) and (2*a*) and assuming that $V_i = {}^{\rm stoich}V_i$

$$s_{\rm Zr-O} = {}^{\rm stoich}V_{\rm Zr}/({\rm CN})_{\rm Zr} = 4\,{\rm v.u.}/8 = \frac{4}{8}\ {\rm v.u.},$$

$$s_{\rm Si-O} = {}^{\rm stoich}V_{\rm Si}/({\rm CN})_{\rm Si} = 4\,{\rm v.u.}/4 = \frac{4}{4}\ {\rm v.u.}$$

and

$$({\rm BVS})_{\rm O} = \sum_1^3 s_{\rm O-(Zr,\,Si)} = -\left[2 \times \frac{4}{8} + \frac{4}{4}\right] = -2\,{\rm v.u.} = V_{\rm O}$$

is derived, which is equal to the corresponding stoichiometric valence of the oxygen anion.

This result is not trivial, as the application of (2) and (2*a*) to the structure of hedenbergite, $\mathrm{CaFe[Si_2O_6]}$ (Zhang *et al.*, 1997), or, with additional information, $\mathrm{Ca}^{[8cb]}\mathrm{Fe}^{[6o]}\mathrm{Si}_2^{[4t]}\mathrm{O1}_2^{[4]}\mathrm{O2}_2^{[3]}\mathrm{O3}_2^{[4]}$, shows. With cation size increasing from Si to Ca, the corresponding CPs in hedenbergite are increasingly distorted with regard to their cation–oxygen distances. If the bond valences are calculated with (2*a*) and $V_i = {}^{\rm stoich}V_i$, calculated $({\rm BVS})_j$ values of −1.917, −1.583 and −2.500 v.u. of the three crystallographically non-equivalent kinds of O atoms deviate considerably from the stoichiometric valence −2 v.u. of oxygen.

Pauling (1947) realised that, for a given $[\mathbf{AX}_n]$ polyhedron, the bond valences $s_{\mathbf{A-X}}$ are smaller the longer their interatomic distances, $D_{\mathbf{A-X}}$. For bonds between two metal atoms of the same element or between two C atoms of radius R, he derived the equation

$$R(n=1) - R(n) = 0.300 \times \log n,$$

where n is the *bond order*, which does not necessarily have whole-number values. For n = 1, 2, 3, ... (single, double, triple, ... bonds) n is called the *bond number*. Since, for these bonds, the interatomic distance D equals twice the atomic radii R, this equation can be rewritten as

$$D(n=1) - D(n) = k \times \ln n \ \text{with} \ k = 0.26\ \text{Å}. \tag{3}$$

Corresponding equations have been derived for chromates by Byström & Wilhelmi (1951) and for borates by Donnay & Donnay (1973) with k = 0.34 and 0.37 Å, respectively.

The logarithmic function (3) can be transformed into the exponential one

$$n = \exp[(D(n=1) - D(n))/k],$$

which is now usually written as

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[1] Throughout this paper, distinction is made between the classical stoichiometric valence, ${}^{\rm stoich}V$, and the calculated bond-valence sum, BVS, of an atom or ion. Within a given chemical formula, the particular values of these quantities are given as, for example, $\mathrm{Sb^{III}}$ and $\mathrm{O^{-II}}$, and $\mathrm{Sb}^{+3.24}$ and $\mathrm{O}^{-1.89}$, respectively, and are measured in v.u. The two quantities, stoichiometric valence and bond-valence sum, should not be confused with the charge, Q, of an ion, which is usually given as, for example, $\mathrm{Si^{2.33+}}$ and $\mathrm{O^{1.23-}}$, and measured in units of the elementary charge.

[2] Where a term is introduced and defined in the text it is given in italics.

[3] The use of bold-face letters has been suggested for structure-site symbols to distinguish them from the usual element symbols, which are given as normal-face letters (Smith *et al.*, 1998). For example, **A** and **L** represent cations regardless of coordination and with lone electron pairs, respectively, and **X** represents monatomic anions.

[4] Coordination numbers and coordination symbols are given as trailing superscripts to the element symbols (Lima-de-Faria *et al.*, 1990).

$$s_{ij} = \exp[(r_0 - D_{ij})/b], \tag{4}$$

where D_{ij} is the *experimental bond length*.[5] Combining (4) with (1) leads to

$$(\mathrm{BVS})_i = \sum_j s_{ij} = \sum_j \exp[(r_0 - D_{ij})/b] = V_i, \tag{5}$$

which was first used by Brown & Altermatt (1985). Here, r_0 and b are called *bond-valence parameters*. This empirical equation (5) is presently the most widely used. It is the fundamental equation of the present BVM.

Based on a large number M of $[\mathbf{AX}_n]$ polyhedra from structures filed in the Inorganic Crystal Structure Database ICSD, Brown & Altermatt (1985) derived numerical values for the bond-valence parameters r_0 and b by minimizing

$$\sum_M \left\{ {}^{\mathrm{stoich}}V_i - \sum_j s_{ij} \right\}^2 = \sum_M \left\{ {}^{\mathrm{stoich}}V_i - \sum_j \exp[(r_{0i} - D_{ij})/b] \right\}^2. \tag{6}$$

Here, r_{0i} is the individual r_0 value of a particular $[\mathbf{A}_i(\mathbf{X}_j)_n]$ polyhedron. It is calculated *via*

$$r_{0i} = b \times \ln \left[{}^{\mathrm{stoich}}V_i / \sum_j \exp(-D_{ij}/b) \right], \tag{7}$$

which is derived by the transformation of (5).

Although r_{0i} and b are correlated, Brown & Altermatt (1985) observed that for a large number of **A**–**X** pairs the values of b varied between 0.32 and 0.42 Å. They decided to fix the value of b at 0.37 Å (Brown, 2002, p. 227). When they used this value b = 0.37 Å to calculate with (7) individual r_{0i}, they, in addition, observed that, for the large majority of atom pairs **A**–**X**, the calculated r_{0i} values of a particular **A**–**X** bond type vary only within a rather small range. This led them to take the arithmetical mean value of the r_{0i} values of M polyhedra $[\mathbf{A}_i(\mathbf{X}_j)_n]$,

$$r_0(\mathbf{A}{-}\mathbf{X}) = {}^M\langle r_{0i}(\mathbf{A}{-}\mathbf{X})\rangle = \frac{1}{M} \times \sum_1^M [r_{0i}(\mathbf{A}{-}\mathbf{X})], \tag{8}$$

as the value of the bond-valence parameter, r_0, for a particular **A**–**X** type of bond.

Applying this procedure, Brown & Altermatt (1985) derived r_0 values for a large number of **A**—**X** type bonds. The same procedure was also applied by Brese & O'Keeffe (1991) to improve some of Brown & Altermatt's r_0 values and to include r_0 values for other **A**—**X** pairs, in particular for homoatomic bonds **A**—**A** and **X**—**X**. The r_0 values tabulated by Brown & Altermatt (1985) and Brese & O'Keeffe (1991) are now generally applied. Several workers have determined additional or improved r_0 values for specific **A**—**X** bond types. A comprehensive list of r_0 values has been compiled by Brown and is available at http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown.

The procedure applied by Brown & Altermatt and Brese & O'Keeffe implies that for each **A**—**X** atom pair, the right-hand sides of (4) and (5) contain, besides the constants r_0 and b, the experimental bond length D_{ij} as the only variable. Provided that it is justified to set r_0 and b as constant, (4) and (5) should allow one to calculate unequivocally bond valences s_{ij} and BVS from crystal structure data.

Taking into consideration the experimental bond lengths D_{ij} and the values $r_0(\mathbf{A}{-}\mathbf{X})$ tabulated by Brese & O'Keeffe to calculate, using (5), the BVS values of the atoms in hedenbergite, $\mathrm{CaFe[Si_2O_6]}$, led to 2.04, 2.08, 3.92, −2.07, −1.87 and −2.03 v.u. for the symmetrically non-equivalent atoms. The corresponding structural formula of hedenbergite then is $\mathrm{Ca}^{+2.04}\,\mathrm{Fe}^{+2.08}\,[\mathrm{Si}_2^{+3.92}\,\mathrm{O}_2^{-2.07}\,\mathrm{O}_2^{-1.87}\,\mathrm{O}_2^{-2.03}]$. The BVS values obtained for the O atoms are considerably closer to the stoichiometric valence of oxygen value −2 v.u. than the BVS values −1.92, −1.58 and −2.50 v.u. derived with (2).

Instead of using logarithmic or exponential functions to describe the relation between experimental bond length and bond valence, Clark *et al.* (1969) used, to calculate bond valence values, a third degree polynomial given by

$$D_{ij} = a_0 + a_1 s_{ij} + a_2 (s_{ij})^2 + a_3 (s_{ij})^3, \tag{9}$$

while others (*e.g.* Brown & Shannon, 1973) employed the power function

$$s_{ij} = [R_0/D_{ij}]^N \tag{10a}$$

that can be traced back to Donnay & Allmann (1970) and in which R_0 approximates r_0 of (4). A similar empirical function

$$s_{ij} = (s_{ij})_0 (R^0 - \lambda)^3 / (D_{ij} - \lambda)^3 \tag{10b}$$

has been derived by Mohri (2000), where $(s_{ij})_0 = V_i/(\mathrm{CN})_i$ is the bond valence in a regular polyhedron, R^0 is essentially the same as r_0 in (4) and λ is taken as the sum of the cation radii of both **A** and **X**.

Since (4) and (5) are the most widely used functions, the following discussion shall be restricted to them.

3. Accuracies of calculated bond valences and bond-valence sums

3.1. Expected mean errors of calculated bond valences and bond-valence sums

From (4) it follows that the expected mean error of the calculated bond valence is

$$\begin{aligned} |\delta(s_{ij})| &= \{[\delta(r_0)]^2 (\partial s_{ij}/\partial r_0)^2 + [\delta(D_{ij})]^2 (\partial s_{ij}/\partial D_{ij})^2\}^{1/2} \\ &= (s_{ij}/b) \times \{[\delta(r_0)]^2 + [\delta(D_{ij})]^2\}^{1/2}, \end{aligned} \tag{11}$$

and its relative mean error is

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[5] D_{ij} is usually called 'bond length'. It should, however, be pointed out that a bond length, in the original sense of the word, is the distance between two atoms that are linked by a chemical bond. Because of the thermal vibrations of the atoms, the length of a bond varies with time. Therefore, D_{ij} values derived from structure determinations with diffraction methods do not represent bond lengths. They, instead, represent distances between either atomic nuclei (neutron diffraction) or between centres of gravity of the electron clouds (X-ray diffraction), both averaged over time and space. We, therefore, prefer to term D_{ij} the experimental bond length over bond length. Correspondingly, we prefer to term experimental bond angle over bond angle.

Table 1
Values of the expected mean errors of $(\mathrm{BVS})_i$ calculated with (13*a*) for various $[\mathbf{AX}_n]$ polyhedra.

Polyhedra	${}^{\mathrm{stoich}}V_i$ (v.u.)	${}^{\mathrm{expect}}\lvert\delta(V_i)\rvert$ (v.u.)
$[\mathrm{BO}_3]^{3-}$, $[\mathrm{SbO}_3]^{3-}$	3	0.066
$[\mathrm{CO}_3]^{2-}$	4	0.088
$[\mathrm{NO}_3]^{-}$	5	0.110
$[\mathrm{LiO}_4]^{7-}$	1	0.019
$[\mathrm{ZnO}_4]^{6-}$	2	0.038
$[\mathrm{BO}_4]^{5-}$, $[\mathrm{AlO}_4]^{5-}$	3	0.057
$[\mathrm{SiO}_4]^{4-}$, $[\mathrm{SiN}_4]^{8-}$	4	0.076
$[\mathrm{PO}_4]^{3-}$, $[\mathrm{PN}_4]^{7-}$	5	0.095
$[\mathrm{SO}_4]^{2-}$	6	0.114
$[\mathrm{ClO}_4]^{-}$	7	0.133
$[\mathrm{NaO}_6]^{11-}$	1	0.016
$[\mathrm{MgO}_6]^{10-}$	2	0.031
$[\mathrm{AlO}_6]^{9-}$	3	0.047
$[\mathrm{SiO}_6]^{8-}$	4	0.062
$[\mathrm{CaF}_8]^{6-}$	2	0.027
$[\mathrm{ZrO}_8]^{12-}$	4	0.054

$$|\delta(s_{ij})/s_{ij}| = 1/b\{[\delta(r_0)]^2 + [\delta(D_{ij})]^2\}^{1/2}$$

with b = 0.37 Å. If the accuracy of both r_0 and experimental bond-length values, derived from modern structure analyses, is assumed to be 0.01 Å or better, the expected mean error of the bond valence is

$$ {}^{\mathrm{expect}}|\delta(s_{ij})| \leq 0.038 \times s_{ij}, \qquad (12)$$

and the relative error of a bond valence should be less than 4%.

From (5) it follows that the mean error of the calculated BVS is

$$|\delta(\mathrm{BVS})_i| = \left[\sum_{j=1}^{n} \delta(s_{ij})^2\right]^{1/2}. \qquad (13)$$

For $[\mathbf{AX}_n]$ polyhedra in which D_{ij} values vary only slightly, the corresponding bond-valence errors for each bond are expected to be similar so that the expected error is

$$ {}^{\mathrm{expect}}|\delta(V_i)| \leq (\mathrm{CN})_i^{1/2}|\delta(s_{ij})|. \qquad (13a)$$

In Table 1, the expected errors of the cation valences for a number of frequently occurring polyhedra, as calculated with (13*a*), are listed. When a BVS of a cation, which is calculated from crystal structure data using (5) with b = 0.37 Å and the tabulated r_0 values, deviates from its ${}^{\mathrm{stoich}}V_i$ value by more than its ${}^{\mathrm{expect}}|\delta(V_i)|$ value calculated with (13) or (13*a*), the deviation has to be explained.

For $[\mathbf{AX}_n]$ polyhedra in which experimental bond length values D_{ij} vary considerably, corresponding errors have to be calculated with (13).

3.2. Reasons for larger deviations of calculated BVS values from stoichiometric atom valences

If for a coordination polyhedron $[\mathbf{A}_i(\mathbf{X}_j)_n]$

$$\Delta V_i = |{}^{\mathrm{calc}}(\mathrm{BVS})_i - {}^{\mathrm{stoich}}V_i| > {}^{\mathrm{expect}}|\delta(V_i)|, \qquad (14)$$

that is, if the difference between the value of the stoichiometric valence of a cation and its BVS, as calculated with (5), is larger than the value of the expected error, ${}^{\mathrm{expect}}|\delta(V_i)|$, calculated with (13) or (13*a*), one of the following explanations may be correct.

(i) The determined crystal structure is wrong or incomplete. In the latter case, Donnay & Allmann (1970) used such observed deviations to distinguish between $\mathrm{O}^{-\mathrm{II}}$, $\mathrm{OH}^{-\mathrm{I}}$ and $\mathrm{H_2O}$ in structures where the H atoms are difficult to locate experimentally.

(ii) Only atoms of the inner coordination shell were considered in calculating the BVS values. The omission of more distant atoms that form so-called secondary bonds between a central atom and its surrounding ligands leads necessarily to calculated BVS values that are too low. This effect of bond-distance cut-off has recently been discussed for alkali halide and chalcogenide polyhedra (Adams, 2001).

(iii) A crystallographic Wyckoff position is statistically occupied by atoms of different elements or vacancies, or by atoms of the same element having different stoichiometric valences. For example, at temperatures below 120 K magnetite, $\mathrm{Fe_3O_4}$ is essentially an inverse spinel in which, according to its structural formula $(\mathrm{Fe^{III}})^{[4t]}$ $(\mathrm{Fe^{II}Fe^{III}})^{[6o]}$ $\mathrm{O}_4^{-\mathrm{II}}$, the octahedrally coordinated structure site is occupied by stoichiometrically divalent and trivalent iron cations in the ratio 1:1, whereas the tetrahedrally coordinated site is exclusively occupied by trivalent iron (Fleet, 1981). With the atomic coordinates given by Fleet and the bond-valence parameters of Brese & O'Keeffe, $(\mathrm{BVS})_i$ values of 2.82 and 2.59 v.u. are derived using (5) for the Fe cations in the tetrahedrally and octahedrally coordinated positions, respectively. With diffraction methods alone, no distinction can be made between statistical occupation of the octahedral site by cations that are permanently stoichiometrically divalent and trivalent, and a situation where fast electron hopping between $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ ions occurs. Such questions can only be answered by spectroscopic methods, such as Mössbauer spectroscopy.

(iv) Values of bond-valence parameters r_0 and b that have been used to calculate the bond-valence sums are inaccurate.

(v) The structure belongs to one of the groups of compounds mentioned in the second paragraph of §1.

4. The influence of coordination-polyhedron distortions on calculated BVS values for cations with one lone electron pair

4.1. Atoms of *p*-block elements with one lone electron pair

Various authors have observed that cations with large differences between ${}^{\mathrm{stoich}}V_i$ and the values of their BVSs calculated with (5), *i.e.* cations with large values of ΔV_i, have distorted CPs. It is noteworthy that this is particularly true for CPs in structures belonging to the group of compounds mentioned in §1. However, a systematic analysis of the influence of CP distortion on ΔV_i is lacking.

To study such an influence, a class of chemical compounds is needed that covers a large range of CP distortions, and for which these distortions have the same chemical and structural reason. Such a class is formed by inorganic compounds that contain the so-called *p*-block elements of the periodic system of elements (PSE). These elements have a valence-shell electron configuration of $ns^2\, np^m$, where n = 3, 4, 5, 6 is the principle quantum number (period number of the PSE) and m = 1, 2,..., 5 is the number of *p* electrons of the neutral atom. These elements can have, in addition to negative stoichiometric valences $^{\rm stoich}V_i = N - 18$, positive valences $^{\rm stoich}V_i = N - 10 - 2\mu$. Here, N is the group number of the cation and μ is its number of lone electron pairs. These lone electron pairs (LEP) are more or less stereoactive and can distort their CPs considerably.

After Wang & Liebau (1996*a*) had, by accident, discovered that calculated $(\mathrm{BVS})_i$ values for trivalent antimony in $[\mathrm{Sb^{III}S}_n]$ and $[\mathrm{Sb^{III}Se}_n]$ coordination polyhedra depend on the geometry of the CPs, they performed a systematic study of the influence of the distortion of $[\mathbf{L}\mathbf{X}_n^{-\mathrm{II}}]$ polyhedra on $^{\rm calc}(\mathrm{BVS})_i$, where $\mathbf{L}$ are cations of *p*-block elements with one LEP and $\mathbf{X}^{-\mathrm{II}} = \mathrm{O}^{-\mathrm{II}}$, $\mathrm{S}^{-\mathrm{II}}$ and $\mathrm{Se}^{-\mathrm{II}}$. First results of these studies were published as a short letter without details (Wang & Liebau, 1996*b*). These studies have now been confirmed and interpreted.

4.2. Application of the BVM to structures with [LX$_n$] polyhedra

During studies of cetineite-type phases of the general formula $\mathbf{A}[\mathrm{Sb2_6Sb3_6O_{18}}][\mathrm{Sb1}\mathbf{X}_3]_2\,[\mathbf{D}_x\mathbf{Y}_{6-y}]$, with $\mathbf{A}$ = Na$^{\rm I}$, K$^{\rm I}$, Rb$^{\rm I}$, Sr$^{\rm II}$, Ba$^{\rm II}$; $\mathbf{X}$ = S$^{-\rm II}$, Se$^{-\rm II}$; $\mathbf{D}$ = Na$^{\rm I}$, Sb$^{\rm III}$, C$^{\rm IV}$; $\mathbf{Y}$ = H$_2$O, OH$^{-\rm I}$ and O$^{-\rm II}$, Wang (1993, Tables 7, 28*b*–32*b*) observed that $(\mathrm{BVS})_i$ values of the Sb1 atoms, calculated with (4) and bond-valence parameters b = 0.37 Å and r_0 as tabulated by Brese & O'Keeffe, varied between 3.61 and 4.04 v.u. although these atoms are stoichiometrically trivalent. In addition, a positive correlation between the $(\mathrm{BVS})_i$ values and the experimental bond angles $\alpha_i = \angle\ \mathbf{X}{-}\mathrm{Sb1}{-}\mathbf{X}$ of the trigonal $[\mathrm{Sb^{III}}\mathbf{X}_3]$ pyramids was found. In comparison, $(\mathrm{BVS})_i$ values for the Sb2 and Sb3 atoms forming $[\mathrm{Sb^{III}O_3}]$ pyramids were found to scatter much less around $^{\rm stoich}V_{\rm Sb^{III}}$ = 3 v.u. Using a more accurate and larger set of 24 $[\mathrm{Sb^{III}}\mathbf{X}_3^{-\mathrm{II}}]$ polyhedra from eight cetineites, $(\mathrm{BVS})_{\rm Sb^{III}}$ values between 3.00 and 3.99 v.u. were derived (Liebau, 2000). From these $(\mathrm{BVS})_{\rm Sb^{III}}$ values and the $^3\langle\alpha_{\rm Sb^{III}}\rangle$ values given in Wang & Liebau (1999), the correlation

$$(\mathrm{BVS})_{\rm Sb^{III}} = -1.4871\cos{}^3\langle\alpha_{\rm Sb(1,2,3)}\rangle + 3.1612$$

with a correlation coefficient R^2 = 0.63 is obtained. Here, $^3\langle\alpha_i\rangle$ is the average of the three experimental bond angles α_i at the Sb$^{\rm III}$ atoms of each $[\mathrm{Sb^{III}}\mathbf{X}_3]$ pyramid.

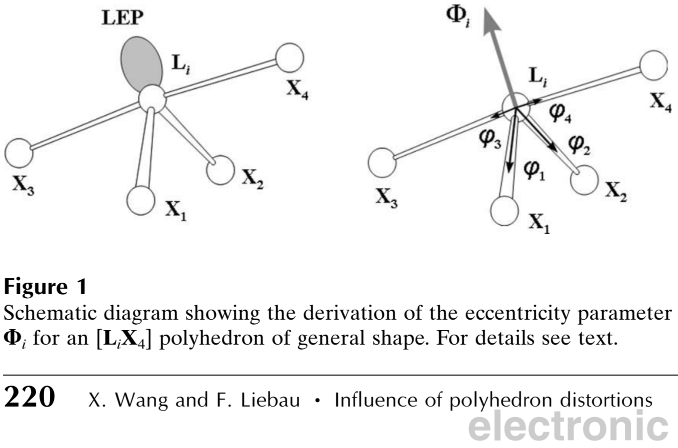

Figure 1
Schematic diagram showing the derivation of the eccentricity parameter $\boldsymbol{\Phi}_i$ for an $[\mathbf{L}_i\mathbf{X}_4]$ polyhedron of general shape. For details see text.

4.2.1. Correlations between r$_{0i}$ and experimental bond angles α_i and polyhedron eccentricity

A statistical analysis based on 76 $[\mathrm{Sb^{III}S}_n]$ and 14 $[\mathrm{Sb^{III}Se}_n]$ polyhedra with $n \geq 3$, as extracted from the literature, was performed by Wang & Liebau (1996*a*). Fig. 1 of that paper gives clear evidence that the r_{0i} values for the Sb$^{\rm III}$—S and Sb$^{\rm III}$—Se bonds, although calculated with (7) and b = 0.37 Å, are strongly correlated with the cosine of the average $^3\langle\alpha_i\rangle$ of the three experimental bond angles $\angle\ \mathbf{X}{-}\mathrm{Sb^{III}}{-}\mathbf{X}$ between the three shortest bonds of a $[\mathrm{Sb^{III}}\mathbf{X}_n]$ polyhedron

$$r_{0i} = P\cos{}^3\langle\alpha_i\rangle + Q. \tag{15}$$

This result contradicts the assumption of Brown & Altermatt (1985) that the r_{0i} values scatter only slightly and statistically around their arithmetic mean value.[6]

Wang & Liebau (1996*a*) concluded that the correlation (15) between r_{0i} and $^3\langle\alpha_i\rangle$ for various cetineites reflects the stereochemical influence of the LEP of the Sb$^{\rm III}$ atoms on the geometry of the $[\mathrm{Sb^{III}}\mathbf{X}_n^{-\mathrm{II}}]$ polyhedra. If this interpretation is correct, it should also apply to $\mathbf{L}$ cations other than Sb$^{\rm III}$, *i.e.* to all *p*-block elements of the PSE, which have one lone electron pair. To check this hypothesis a statistical analysis, analoguous to that used for the $[\mathrm{Sb^{III}}\mathbf{X}_n^{-\mathrm{II}}]$ polyhedra, was performed with all *p*-block cations with a stoichiometric valence of $^{\rm stoich}V = N - 12$. Altogether, 1924 $[\mathbf{L}\mathbf{X}_n^{-\mathrm{II}}]$ polyhedra with $\mathbf{X}^{-\mathrm{II}} = \mathrm{O}^{-\mathrm{II}}$, S$^{-\rm II}$ and Se$^{-\rm II}$ from 1058 crystal structures were extracted from the ICSD, representing 22 different $\mathbf{L}{-}\mathbf{X}$ bond types. Each of these 22 data sets consists of at least ten $[\mathbf{L}\mathbf{X}_n]$ polyhedra.

Linear correlations between individual r_{0i} values and the mean values $^m\langle\alpha_i\rangle$ of the m experimental bond angles $\alpha_i = \angle(\mathbf{X}{-}\mathbf{L}_i{-}\mathbf{X})$ between the strongest bonds in the $[\mathbf{L}\mathbf{X}_n^{-\mathrm{II}}]$ polyhedra are significant only for CPs that do not deviate considerably from m-fold rotation symmetry, so that averaging over the m experimental bond angles α_i is justified. Therefore, for CPs of general shape, cos $^m\langle\alpha_i\rangle$ was replaced by the absolute value of an *eccentricity parameter*,[7] $\boldsymbol{\Phi}_i$, which is a vector defined as

$$\boldsymbol{\Phi}_i = -\sum_j \boldsymbol{\varphi}_{ij}. \tag{16a}$$

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[6] Values of r_{0i} that were considered to deviate greatly from the mean value of r_{0i} were 'rejected from the calculation of the mean value of r_0' (Skowron & Brown, 1990).

[7] The parameter $\boldsymbol{\Phi}_i$ had been called the asphericity parameter (Liebau & Wang, 2004). However, $\boldsymbol{\Phi}_i$ describes the deviation of the central ion from the geometrical point of gravity of the peripheral ions rather than the deviation from spherical shape of a CP. Therefore, it is suggested to call, henceforth, $\boldsymbol{\Phi}_i$ the eccentricity parameter.

The $\boldsymbol{\varphi}_{ij}$ terms are the vectors pointing from the nucleus of an atom $\mathbf{L}_i$ to its ligands $\mathbf{X}_j$ (Fig. 1). Their lengths were scaled using

$$|\boldsymbol{\varphi}_{ij}| = \exp(-D_{ij}/g), \qquad (16b)$$

where an average value of $g = 0.2$ Å had been chosen.

The eccentricity parameter $\boldsymbol{\Phi}_i$ seems to be particularly suitable to describe the polyhedron eccentricity caused by LEPs, which is a special kind of polyhedron distortion.

Reasonable correlations of the form

$$r_{0i} = E|\boldsymbol{\Phi}_i| + F \qquad (17)$$

were obtained for most of the 22 data sets. Numerical details of the preliminary analysis (number N of polyhedra used, E, F and R^2 values obtained) were given in Wang & Liebau (1996*b*) without further discussion. The corresponding correlation diagrams can be obtained from the second author on request.

For all 22 data sets, the r_{0i} values are inversely correlated with the absolute value $|\boldsymbol{\Phi}_i|$ of the eccentricity parameter. According to the R^2 values, between 23% ([$\mathrm{Tl^I\ S}_n$] polyhedra) and 90% ([$\mathrm{Sn^{II}\ O}_n$] polyhedra) of the variation in r_{0i} was attributed to $|\boldsymbol{\Phi}_i|$, *i.e.* to the degree of distortion of the CPs.

In these statistical analyses from 1996 only those [$\mathbf{LX}_n$] polyhedra were included that were derived from structure analyses that were considered to be sufficiently accurate. Nevertheless, for several of the correlation diagrams the data points scattered considerably and corresponding R^2 values were rather low.

To make sure that these shortcomings are not caused by inaccuracies in the structure analyses, statistical analyses for the [$\mathbf{LX}_n$] polyhedra have now been repeated using structure data retrieved from the 2004/2 version of ICSD with the following more stringent selection criteria:

(i) all structures are ordered and all the structure sites are fully occupied,

(ii) the value of the reliability factor R of the structure refinement is less than 0.0751,

(iii) there is no mixed stoichiometric valence for any atom in the structure,

(iv) only one kind of anion is found within 4 Å from the **L** cation,

(v) no warning comments are given that could indicate that atomic coordinates are incorrect,

(vi) all bonds up to a maximum value of n are considered that have a bond valence larger than $0.04 \times {}^{\mathrm{stoich}}V_{\mathbf{L}}$ v.u., calculated using the Brese & O'Keeffe bond-valence parameters (Brown, 2002, page 43, Rule 4.1). In particular for [$\mathbf{LX}_n$] polyhedra, this procedure seems to be superior to the

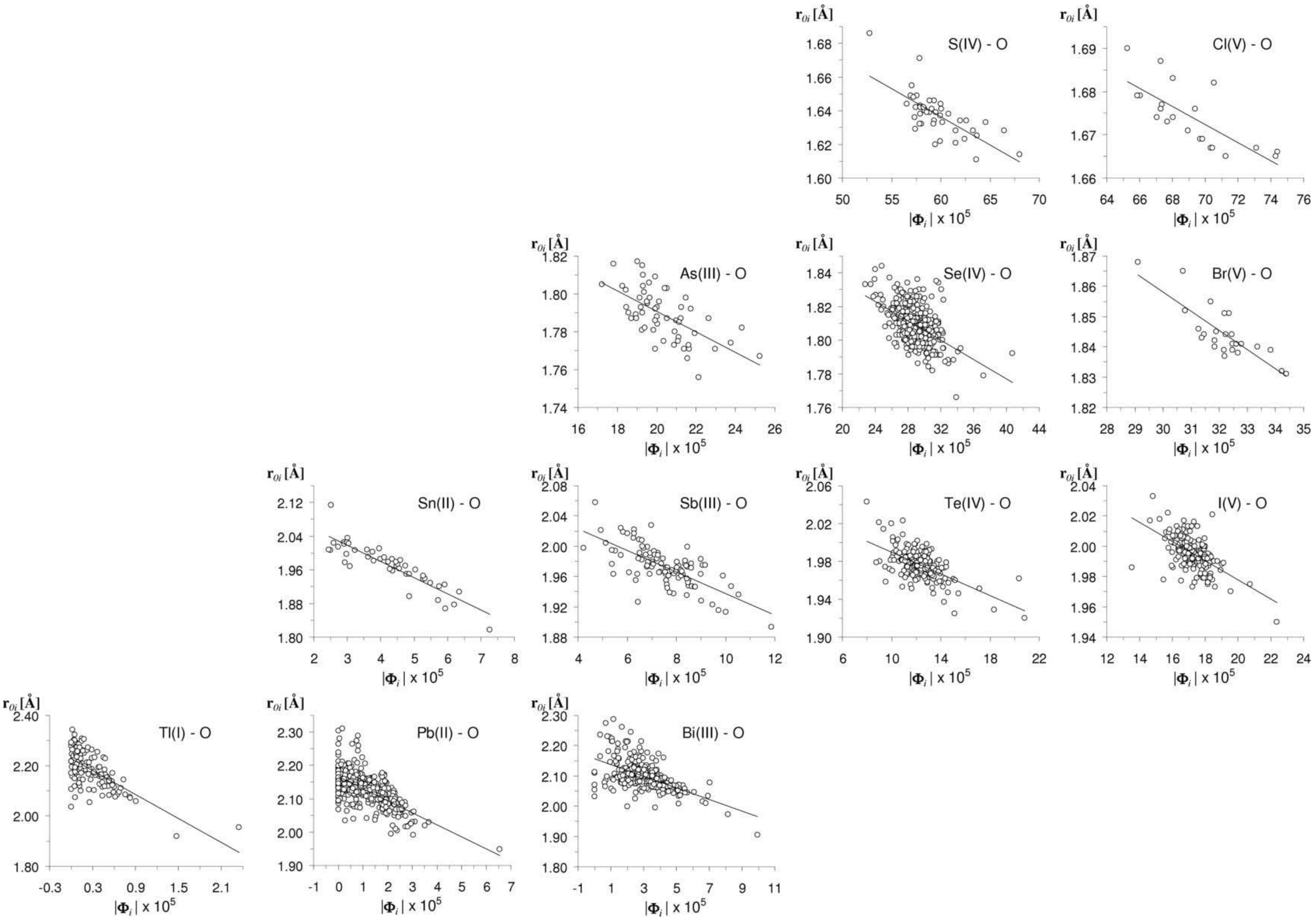

Figure 2
Linear correlation diagrams r_{0i} *versus* $|\boldsymbol{\Phi}_i|$ for 2061 individual [$\mathbf{LO}_n$] polyhedra drawn with different scales and arranged according to the position of the **L** cation in the PSE.

Table 2
Results of linear correlations $r_{0i} = E|\mathbf{\Phi}_i| + F$ for $[\mathbf{L}\mathrm{O}_n]$ polyhedra.

First line: 2061 polyhedra retrieved from the ICSD release 2004/2, analyses carried out in 2005; second line (italics): 1414 polyhedra, analyses carried out in 1996. N = number of polyhedra; R^2 = percentage of total variation of r_{0i} that is explained by the regression; $\Delta|\mathbf{\Phi}_i|$ = experimental range $|\mathbf{\Phi}_i|_{\max} - |\mathbf{\Phi}_i|_{\min}$.

$\mathbf{L}$—O	N	R^2	$\Delta\lvert\mathbf{\Phi}_i\rvert \times 10^5$	$E \times 10^{-2}$	F
$\mathrm{S^{IV}}$—O	45	0.51	16	−3.3 (5)	1.84 (3)
	52	*0.56*	*13*	*−2.4 (3)*	*1.78 (2)*
$\mathrm{Cl^{V}}$—O	21	0.55	10	−2.1 (4)	1.82 (3)
	10	*0.64*	*10*	*−1.7 (4)*	*1.78 (3)*
$\mathrm{As^{III}}$—O	57	0.39	8	−5.5 (9)	1.90 (2)
	56	*0.45*	*10*	*−3.2 (5)*	*1.84 (1)*
$\mathrm{Se^{IV}}$—O	427	0.24	19	−2.9 (2)	1.892 (7)
	171	*0.27*	*16*	*−2.4 (3)*	*1.871 (9)*
$\mathrm{Br^{V}}$—O	26	0.68	5	−6.3 (9)	2.05 (3)
	19	*0.88*	*14*	*−4.7 (4)*	*1.99 (1)*
$\mathrm{Sn^{II}}$—O	46	0.80	5	−39 (3)	2.14 (1)
	38	*0.90*	*6*	*−36 (2)*	*2.102 (8)*
$\mathrm{Sb^{III}}$—O	101	0.50	8	−14 (1)	2.08 (1)
	93	*0.55*	*8*	*−11 (1)*	*2.038 (8)*
$\mathrm{Te^{IV}}$—O	203	0.35	13	−5.7 (6)	2.047 (7)
	138	*0.54*	*14*	*−5.9 (5)*	*2.035 (6)*
$\mathrm{I^{V}}$—O	204	0.32	9	−6.3 (6)	2.10 (1)
	164	*0.67*	*14*	*−8.9 (5)*	*2.128 (9)*
$\mathrm{Tl^{I}}$—O	156	0.42	2.4	−160 (25)	2.229 (6)
	108	*0.54*	*2.4*	*−144 (10)*	*2.192 (6)*
$\mathrm{Pb^{II}}$—O	412	0.41	7	−36.0 (2)	2.166 (3)
	377	*0.54*	*8*	*−36 (20)*	*2.149 (3)*
$\mathrm{Bi^{III}}$—O	363	0.32	10	−19.3 (10)	2.157 (5)
	188	*0.28*	*8*	*−10 (1)*	*2.103 (4)*

application of distinct coordination numbers CN, which become more and more ill-defined if the size of the cation $\mathbf{L}$ increases and its stoichiometric valence decreases.

Altogether 2061 $[\mathbf{L}\mathrm{O}_n]$ + 415 $[\mathbf{L}\mathrm{S}_n]$ + 115 $[\mathbf{L}\mathrm{Se}_n]$ = 2591 $[\mathbf{L}\mathbf{X}_n^{-\mathrm{II}}]$ polyhedra from 1156, 207 and 59 structure determinations, respectively, were used for this new statistical analysis. In Figs. 2, 3 and 4 the correlation diagrams r_{0i} *versus* $|\mathbf{\Phi}_i|$ are arranged in the order of the positions of the $\mathbf{L}$ cations in the PSE. In Tables 2, 3 and 4 details of the analyses are compared with those of the preliminary analysis (Wang & Liebau, 1996*b*).

At first glance, one would expect that the application of more stringent selection rules leads to higher R^2 values of the correlation equations, because less accurate data are omitted from the analysis. However, inspection of column 3 of Table 2 shows that this is true only for $[\mathrm{BiO}_n]$ polyhedra. At second glance, it can be seen that the experimental ranges $\Delta|\mathbf{\Phi}_i| = ||\mathbf{\Phi}_i|_{\max} - |\mathbf{\Phi}_i|_{\min}|$ are, again with the exception of the $[\mathrm{BiO}_n]$ polyhedra, narrower for the present analysis than for that of 1996. This is caused by the increased stringency of the selection criteria. $(\mathrm{BVS})_i$ values for only weakly distorted polyhedra are rather insensitive to small errors of modern structure determinations, since these errors widely compensate each other. Therefore, R^2 values of the correlations depend more on the width $\Delta|\mathbf{\Phi}_i|$ than on the R values of the structure determination. Consequently, the narrower $\Delta|\mathbf{\Phi}_i|$ ranges should lead to lower R^2 values. This effect is, with the exception of the set of the $[\mathrm{SO}_n]$ polyhedra, not compensated by the large number of $[\mathbf{L}\mathrm{O}_n]$ polyhedra added to the ICSD since 1995. Inspection of Table 3 shows that the lower R^2 values of the new analysis, compared with those of the 1996 analysis, can be explained mainly by the reduction of the $\Delta|\mathbf{\Phi}_i|$ ranges.

A corresponding comparison of analysis results for the $[\mathbf{L}\mathrm{S}_n]$ and $[\mathbf{L}\mathrm{Se}_n]$ polyhedra listed in Tables 3 and 4, respectively, is inconclusive, probably due to the very narrow ranges of $\Delta|\mathbf{\Phi}_i|$ in both analyses.

The data listed in Tables 2, 3 and 4 and shown in Figs. 2, 3 and 4 of the present analysis and a comparison of these figures with the unpublished figures of the earlier analysis (available on request from the second author) confirm that these results and those of the analysis of 1996 are qualitatively the same. In particular, the kind and degree of scatter of data points in corre-

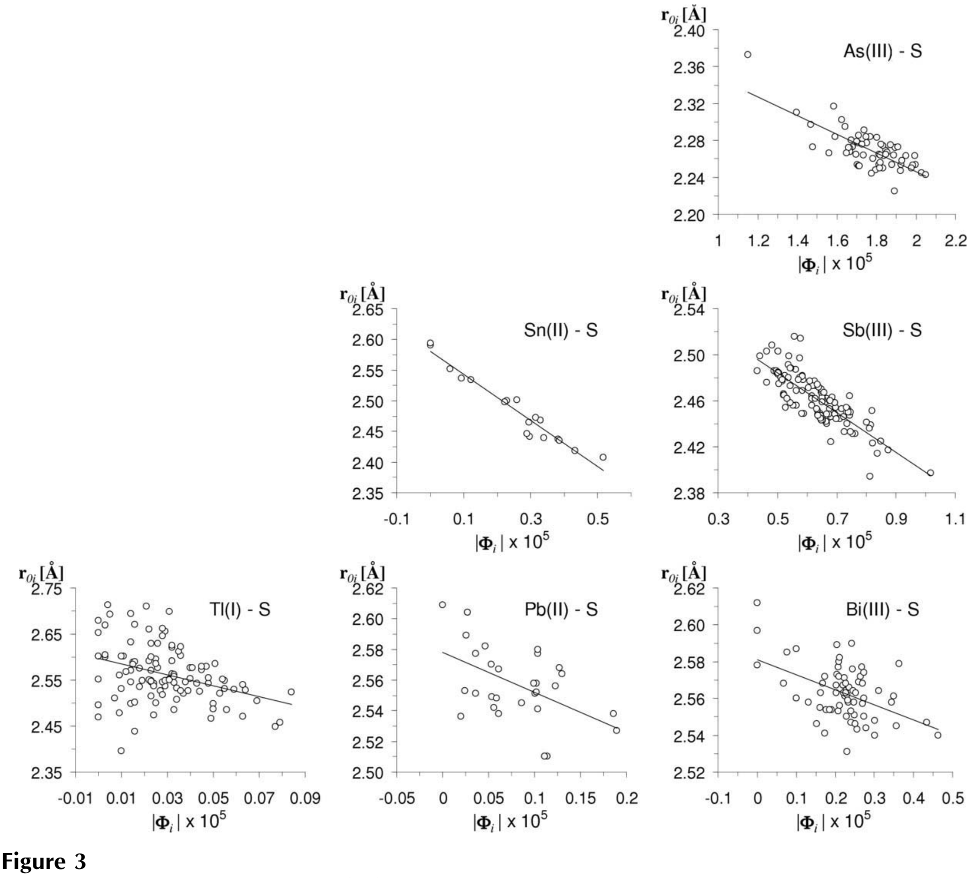

Figure 3
Linear correlation diagrams r_{0i} *versus* $|\mathbf{\Phi}_i|$ for 415 individual $[\mathbf{L}\mathrm{S}_n]$ polyhedra drawn with different scales and arranged according to the position of the $\mathbf{L}$ cation in the PSE.

Table 3
Results of linear correlations $r_{0i} = E|\mathbf{\Phi}_i| + F$ for $[\mathbf{L}\mathrm{S}_n]$ polyhedra.

First line: 415 polyhedra, analyses carried out in 2005; second line (italics): 432 polyhedra, analyses carried out in 1996. For further details see Table 2.

L—S	*N*	R^2	$\Delta|\mathbf{\Phi}_i| \times 10^5$	$E \times 10^{-3}$	*F*
$\mathrm{As^{III}}$—S	61	0.56	0.9	−10 (1)	2.45 (2)
	74	*0.64*	*2*	*−8 (1)*	*2.40 (1)*
$\mathrm{Sn^{II}}$—S	18	0.94	0.5	−37 (2)	2.58 (1)
	19	*0.86*	*0.6*	*−44 (4)*	*2.58 (2)*
$\mathrm{Sb^{III}}$—S	127	0.66	0.6	−17 (1)	2.57 (1)
	124	*0.79*	*0.9*	*−25 (1)*	*2.61 (1)*
$\mathrm{Tl^{I}}$—S	107	0.13	0.08	−118 (30)	2.60 (1)
	116	*0.23*	*0.1*	*−130 (20)*	*2.59 (1)*
$\mathrm{Pb^{II}}$—S	33	0.23	0.17	−26 (9)	2.58 (1)
	68	*0.45*	*0.3*	*−37 (5)*	*2.57 (1)*
$\mathrm{Bi^{III}}$—S	69	0.23	0.45	−8.2 (1.9)	2.58 (1)
	31	*0.32*	*0.5*	*−8.2 (2)*	*2.58 (1)*

Table 4
Results of linear correlations $r_{0i} = E|\mathbf{\Phi}_i| + F$ for $[\mathbf{L}\mathrm{Se}_n]$ polyhedra.

First line: 115 polyhedra, analyses carried out in 2005; second line (italics): 87 polyhedra, analyses carried out in 1996.

L—Se	*N*	R^2	$\Delta|\mathbf{\Phi}_i| \times 10^5$	$E \times 10^{-4}$	*F*
$\mathrm{As^{III}}$—Se	31	0.72	0.45	−1.5 (2)	2.54 (2)
	13	*0.71*	*0.23*	*−1.2 (2)*	*2.51 (2)*
$\mathrm{Sb^{III}}$—Se	26	0.69	0.24	−3.4 (5)	2.70 (2)
	16	*0.88*	*0.45*	*−3.3 (3)*	*2.68 (1)*
$\mathrm{Tl^{I}}$—Se	24	0.09	0.03	5 (12)	2.61 (2)
	32	*0.34*	*0.05*	*−19 (5)*	*2.67 (1)*
$\mathrm{Bi^{III}}$—Se	34	0.57	0.20	−2.0 (3)	2.703 (4)
	17	*0.38*	*0.12*	*−1.3 (4)*	*2.69 (1)*

sponding correlation diagrams are similar for both analyses.

Although in most of the diagrams the data points scatter considerably and, consequently, the corresponding R^2 values are rather low, the tables and the diagrams show clearly that in the case of the $[\mathbf{L}\mathrm{O}_n]$ polyhedra between 24 and 80% and of the $[\mathbf{L}\mathrm{S}_n]$ polyhedra between 13 and 90% of the scatter can be explained by (17). This means that, at least for $[\mathbf{LX}_n]$ polyhedron types for which $R^2 > 0.50$, the r_{0i} values are correlated with polyhedron eccentricity, in contradiction to the assumption r_0 = const of the present BVM. Reasons why, *e.g.* for nearly half of the $[\mathbf{L}\mathrm{O}_n]$ data sets, the correlation between the values of r_{0i} and $|\mathbf{\Phi}_i|$ is poorer than $R^2 = 0.50$, will be discussed in §4.2.3.

4.2.2. Correlations between BVS and polyhedron eccentricity. The same 2591 $[\mathbf{LX}_n^{-\mathrm{II}}]$ polyhedra retrieved from ICSD 2004/2, from which (17) was derived, were used to calculate the BVS of their **L** cations, $(\mathrm{BVS})_i$, using (5) and the bond-valence parameter values $b = 0.37$ Å and r_0 tabulated by Brese & O'Keeffe. For these $(\mathrm{BVS})_i$ values regression analyses were performed in the same way as described in the previous section for the r_{0i} values. It can be shown that corresponding BVS and $|\mathbf{\Phi}_i|$ values are linearly correlated following

$$(\mathrm{BVS})_i = E'|\mathbf{\Phi}_i| + F'. \tag{18}$$

Results of the analyses are given in Tables 5–7 and the regression diagrams are shown in Figs. 5–7.

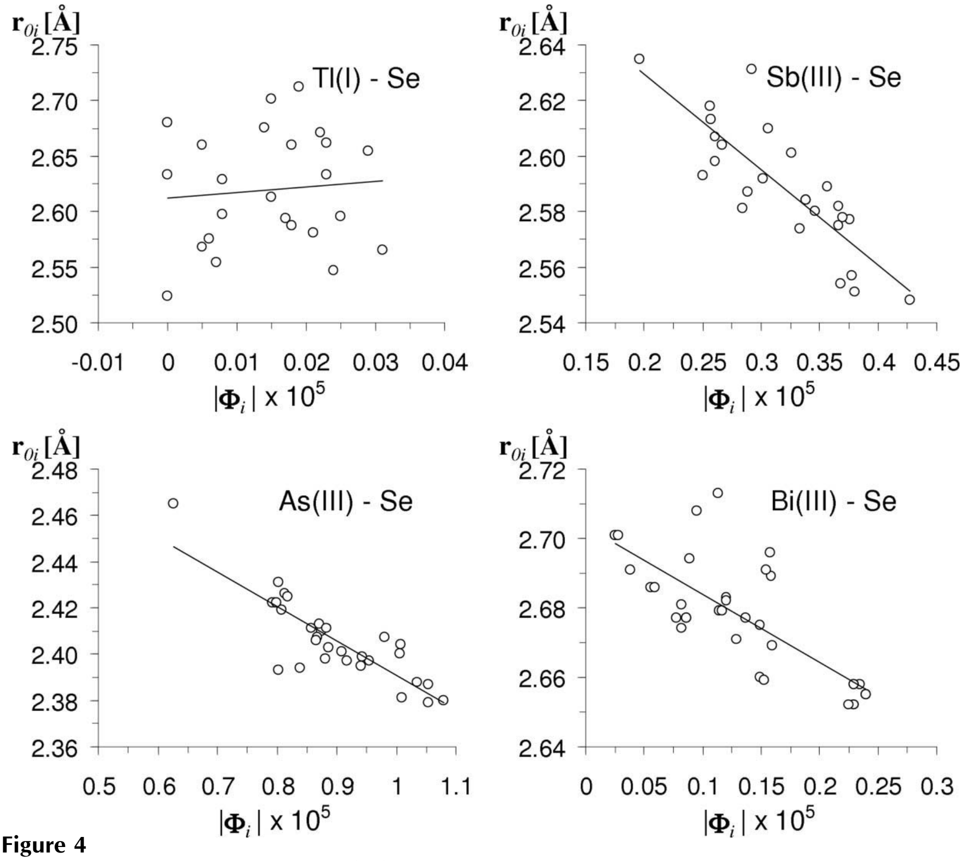

Figure 4
Linear correlation diagrams r_{0i} *versus* $|\mathbf{\Phi}_i|$ for 115 individual $[\mathbf{L}\mathrm{Se}_n]$ polyhedra drawn with different scales.

As expected from (5), the scatter of the data points and R^2 values for the correlations $(\mathrm{BVS})_i$ *versus* $|\mathbf{\Phi}_i|$ are very similar to those for the corresponding correlations r_{0i} *versus* $|\mathbf{\Phi}_i|$. It can clearly be seen that the calculated BVSs increase with increasing $|\mathbf{\Phi}_i|$, *i.e.* the more distorted the polyhedra.

4.2.3. Consideration of R^2 values and the scatter of data points in the correlations. Following (5), r_0 and $(\mathrm{BVS})_i$ are intimately linked with each other. Therefore, with regard to the accuracies of their correlations with $|\mathbf{\Phi}_i|$, it is sufficient to consider the correlations $(\mathrm{BVS})_i$ *versus* $|\mathbf{\Phi}_i|$. According to Tables 5–7, the R^2 values range between 13–94% for the individual sets of $[\mathbf{LX}_n^{-\mathrm{II}}]$ polyhedra. This means that between 13 and 94 percent of the variation of $(\mathrm{BVS})_i$ can be explained by the influence of $|\mathbf{\Phi}_i|$ on $(\mathrm{BVS})_i$, where all the correla-

Table 5
Results of linear correlations $(\mathrm{BVS})_i = E'|\boldsymbol{\Phi}_i| + F'$ derived for 2061 $[\mathbf{L}\mathrm{O}_n]$ polyhedra retrieved from the ICSD release 2004/2.

N = number of polyhedra; R^2 = percentage of total variation of $(\mathrm{BVS})_i$ that is explained by the regression.

L—O	N	R^2	$E' \times 10^{-2}$	F'
$\mathrm{S^{IV}}$—O	45	0.52	36 (5)	1.9 (3)
$\mathrm{Cl^{V}}$—O	21	0.56	28 (6)	3.05 (4)
$\mathrm{As^{III}}$—O	57	0.39	45 (7)	2.1 (2)
$\mathrm{Se^{IV}}$—O	427	0.25	31.7 (3)	3.11 (2)
$\mathrm{Br^{V}}$—O	26	0.68	84 (12)	2.3 (4)
$\mathrm{Sn^{II}}$—O	46	0.79	228 (17)	1.13 (8)
$\mathrm{Sb^{III}}$—O	101	0.50	117 (12)	2.13 (9)
$\mathrm{Te^{IV}}$—O	203	0.36	63 (6)	3.24 (7)
$\mathrm{I^{V}}$—O	204	0.32	87 (9)	3.6 (2)
$\mathrm{Tl^{I}}$—O	156	0.49	487 (40)	0.85 (2)
$\mathrm{Pb^{II}}$—O	412	0.44	196 (11)	1.72 (2)
$\mathrm{Bi^{III}}$—O	363	0.35	154 (11)	2.48 (4)

tions were for simplicity assumed to be linear. Higher-order functions do not give a significantly better fit, despite a larger number of variables. Inspection of Figs. 5–7 indicates that the type and amount of scatter of data points, and therefore the R^2 values, depend on the position of the **L** cations within the PSE. This suggests that they are caused by the nature of the electron configurations of the *p*-block atoms.

(i) Fig. 5 shows that in the correlation diagrams for the $[\mathbf{L}\mathrm{O}_n]$ polyhedra of the sixth period, $[\mathrm{Tl^{I}O}_n]$, $[\mathrm{Pb^{II}O}_n]$ and $[\mathrm{Bi^{III}O}_n]$, scatter increases strongly if $|\boldsymbol{\Phi}_i|$ approaches zero. This can be explained, at least partly, by a specific kind of inaccuracy of the experimentally determined atomic positions of these **L** cations. Diffraction methods average atomic positions over space and time and, therefore, do not give distances between atoms but, instead, distances between their averaged positions (see footnote 5). In many of the structure analyses, the atomic displacement parameters of the stereoactive $\mathrm{Tl^{I}}$, $\mathrm{Pb^{II}}$ and $\mathrm{Bi^{III}}$ cations are found to be unusually high, indicating that these cations actually deviate statically or dynamically considerably from their averaged positions. This is particularly true for those polyhedra in which the 'averaged cations' have been located at special Wyckoff positions, thus leading to 'averaged $[\mathbf{L}\mathrm{O}_n]$ polyhedra' with rather low apparent $|\boldsymbol{\Phi}_i|$ values. In fact, in a non-averaged $[\mathbf{L}\mathrm{O}_n]$ polyhedron, the **L** cation would deviate from its averaged position such that some of the experimental **L**—O bond lengths are shorter and others are longer than the D_{ij} distances derived in the crystal-structure determination and used in the correlation analyses. As a result, the actual $|\boldsymbol{\Phi}_i|$ value for the non-averaged polyhedron should be higher and, because of the mathematical form of (7), its r_{0i} value lower than that of the averaged polyhedron. Correspondingly, the actual $(\mathrm{BVS})_i$ value should

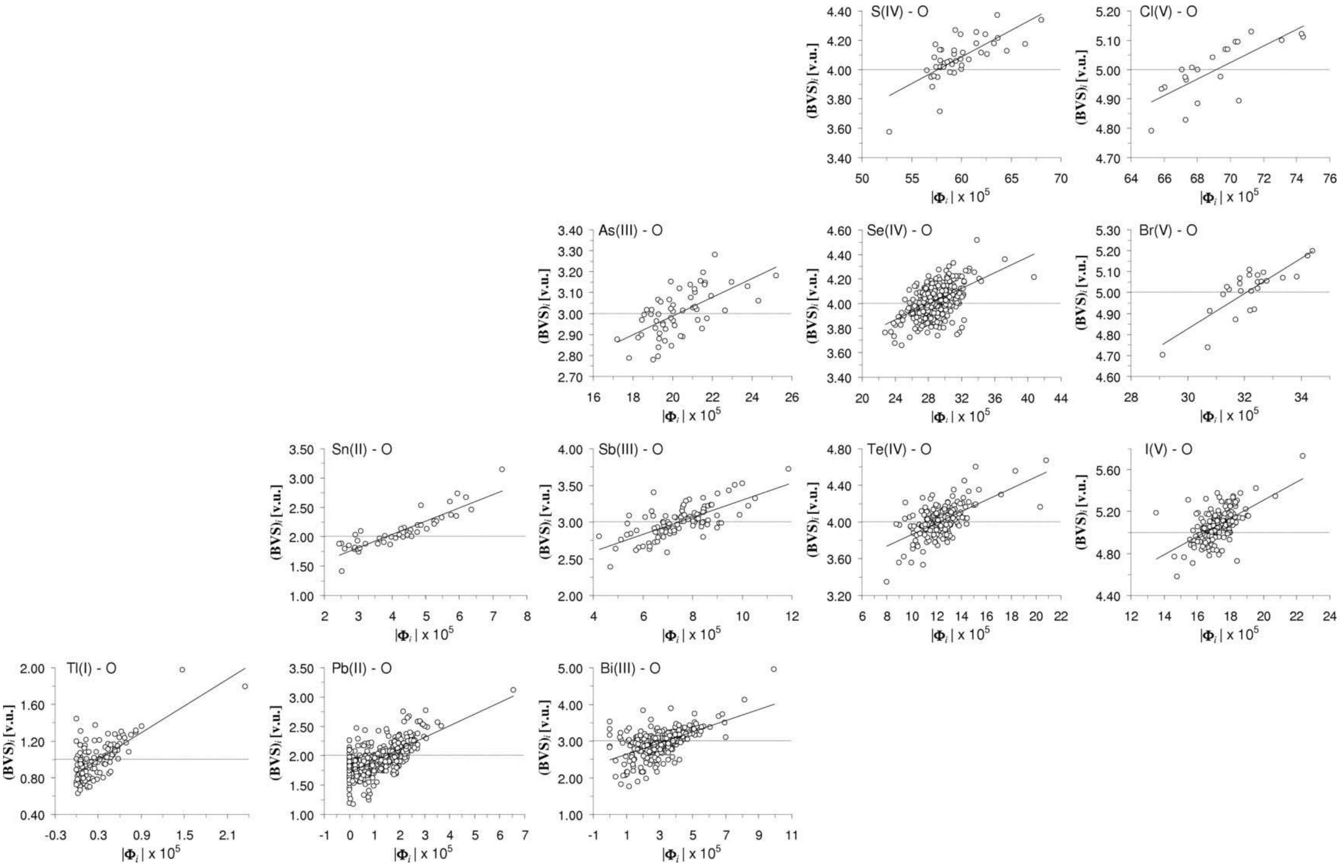

Figure 5
Linear correlation diagrams $(\mathrm{BVS})_i$ *versus* $|\boldsymbol{\Phi}_i|$ for 2061 individual $[\mathbf{L}\mathrm{O}_n]$ polyhedra drawn with different scales and arranged according to the position of the **L** cation in the PSE. The horizontal lines indicate the whole-number values of ${}^{\mathrm{stoich}}V_i$.

Table 6
Results of linear correlations $(\mathrm{BVS})_i = E'|\mathbf{\Phi}_i| + F'$ derived for 415 $[\mathbf{L}\mathrm{S}_n]$ polyhedra retrieved from the ICSD release 2004/2.

For further details see Table 5.

L—S	N	R^2	$E' \times 10^{-3}$	F'
$\mathrm{As^{III}}$—S	61	0.55	76 (9)	1.6 (2)
$\mathrm{Sn^{II}}$—S	18	0.95	178 (11)	1.39 (3)
$\mathrm{Sb^{III}}$—S	127	0.67	147 (9)	2.18 (6)
$\mathrm{Tl^{I}}$—S	107	0.11	364 (99)	1.11 (3)
$\mathrm{Pb^{II}}$—S	33	0.22	136 (46)	1.86 (4)
$\mathrm{Bi^{III}}$—S	69	0.22	62 (14)	2.76 (3)

be higher than that for the 'averaged' polyhedron used for the correlations of Fig. 5. It is presumed that, for this kind of $[\mathbf{L}\mathrm{O}_n]$ polyhedra, D_{ij} values derived from spectroscopic (*e.g.* IR and NMR) methods, if available, would lead to less scatter of data points and higher R^2 values than D_{ij} values derived with diffraction methods. $[\mathrm{CuO_6}]$ octahedra dynamically distorted by Jahn–Teller effects were previously discussed by Burns & Hawthorne (1996).

(ii) Figs. 5 and 6, in addition, show that in the correlation diagrams of $[\mathbf{LX}_n]$ polyhedra with large, low-valent **L** cations such as $\mathrm{Sn^{II}}$ and $\mathrm{Sb^{III}}$, there is little scatter in the data around the regression line. The degree of scatter is almost independent of $|\mathbf{\Phi}_i|$. This is probably related to the higher flexibility in the bond configurations of these polyhedra. In contrast, for $[\mathbf{L}\mathrm{O}_n]$ polyhedra with high-valent **L** cations such as $\mathrm{Se^{IV}}$, $\mathrm{Te^{IV}}$ and $\mathrm{I^{V}}$, the data points tend to be concentrated in a small range of $|\mathbf{\Phi}_i|$ values and scatter strongly in this range, which is dominated by $[\mathbf{L}\mathrm{O}_3]$ pyramids. As a consequence, R^2 values of the corresponding correlations are particularly low for the latter and relatively high for the former. The fact that this effect is obviously restricted to certain regions of the PSE indicates that this effect has a chemical reason just as does the scatter described in the previous paragraph.

Table 7
Results of linear correlations $(\mathrm{BVS})_i = E'|\mathbf{\Phi}_i| + F'$ derived for 115 $[\mathbf{L}\mathrm{Se}_n]$ polyhedra retrieved from the ICSD release 2004/2.

For further details see Table 5.

L—Se	N	R^2	$E' \times 10^{-5}$	F'
$\mathrm{As^{III}}$—Se	31	0.73	1.1 (1)	1.9 (1)
$\mathrm{Sb^{III}}$—Se	26	0.70	2.7 (4)	2.0 (1)
$\mathrm{Tl^{I}}$—Se	24	0.01	−2 (4)	1.28 (7)
$\mathrm{Bi^{III}}$—Se	34	0.59	1.8 (3)	3.13 (4)

5. Results

The statistical analyses presented in §4 show that for $[\mathbf{LX}_n^{-\mathrm{II}}]$ polyhedra, where **L** are cations with one LEP, the r_{0i} values are inversely correlated with the absolute value $|\mathbf{\Phi}_i|$ of the eccentricity parameter, *i.e.* with the distortion of the CPs. This disagrees with the assumption made in the present BVM that r_0 can be considered to be constant. In addition, because of (5), BVSs calculated with b = 0.37 Å and the tabulated r_0 values of Brown & Altermatt (1985) or Brese & O'Keeffe (1991) are also correlated with $|\mathbf{\Phi}_i|$ rather than being constant and, in particular, equal to the integer values of ${}^{\mathrm{stoich}}V_i$.

It is, of course, possible to adjust the calculated BVSs to the ${}^{\mathrm{stoich}}V$ values by mathematical treatment. In fact, there are a number of recent publications in which, for various **A**—**X** bond types in strongly distorted $[\mathbf{AX}_n]$ polyhedra, new r_0 values (*e.g.* Trzesowska *et al.*, 2004) or r_0 and $b \neq 0.37$ Å values (*e.g.* Lösel *et al.*, 1993; Burns *et al.*, 1997; Krivovichev & Brown, 2001; Locock & Burns, 2004; Sidey, 2006) are determined in order to minimize discrepancies between $(\mathrm{BVS})_i$ and ${}^{\mathrm{stoich}}V$. Such attempts may improve the agreement between ${}^{\mathrm{calc}}(\mathrm{BVS})_i$ and ${}^{\mathrm{stoich}}V_i$ for the ions for which the r_0 and b parameters were specifically refined. However, as pointed out

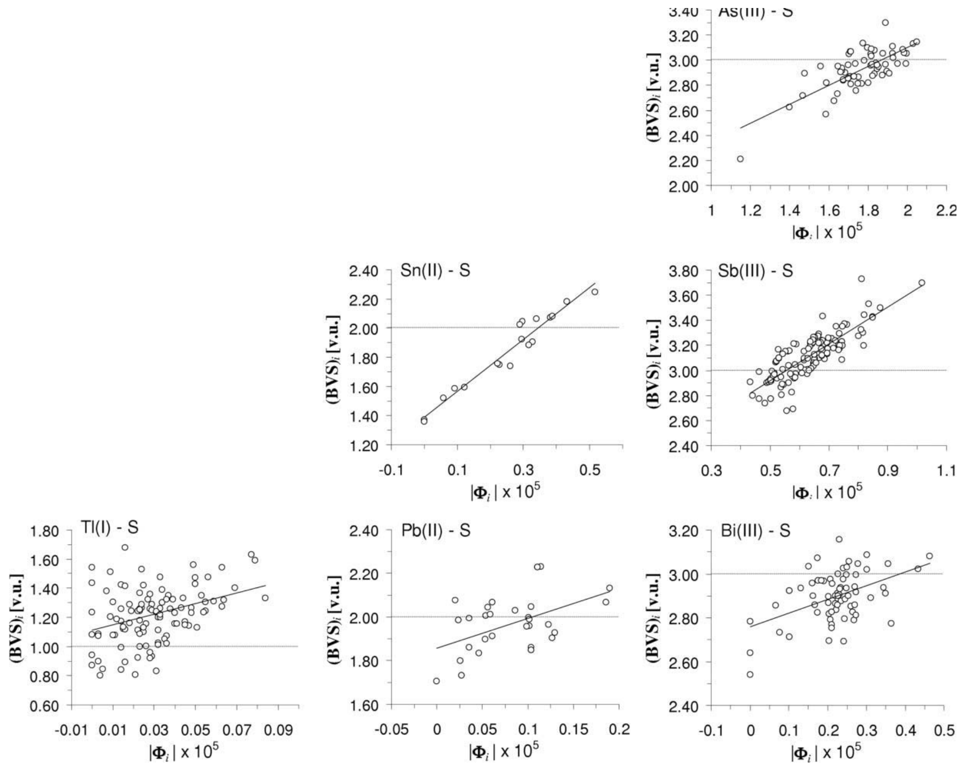

Figure 6
Linear correlation diagrams $(\mathrm{BVS})_i$ *versus* $|\mathbf{\Phi}_i|$ for 415 individual $[\mathbf{L}\mathrm{S}_n]$ polyhedra drawn with different scales and arranged according to the position of the **L** cation in the PSE. The horizontal lines indicate the whole-number values of ${}^{\mathrm{stoich}}V_i$.

by Wang & Liebau (2005), this may simply shift the discrepancy to other atoms of the structure.

In some cases, substantial deviations of the calculated BVSs from ${}^{\rm stoich}V$, particularly in transition metal oxides, have been attributed to physical reasons such as lattice-induced strain and cation–cation repulsions (Brown, 1992, 2002). However, at least in compounds containing $[\mathbf{LX}_n]$ polyhedra, the correlation (18) between $(\mathrm{BVS})_i$ and $|\boldsymbol{\Phi}_i|$ reflects the influence of the stereoactive lone electron pair on the geometry of the polyhedra. This is a chemical effect and not an artefact of the bond-valence parameters. It is, therefore, concluded that the BVSs reflect a chemical property of an atom that is different from its stoichiometric valence. For this property the term *structural valence* is suggested (Liebau & Wang, 2005). This structural valence will be defined and its properties described in a separate paper (Liebau & Wang, 2007).

6. Discussion and future prospects

In §4.2.3, two reasons are given, which give rise to rather low R^2 values of correlations (17) and (18) between r_{0i} and $(\mathrm{BVS})_i$, on the one hand, and $|\boldsymbol{\Phi}_i|$ on the other. There are other reasons that also contribute to low R^2 values that should in the future be considered in order to better describe the correlations between $(\mathrm{BVS})_i$ and the polyhedron distortion.

(i) *Distortion index*: It is obvious that, at least for centrosymmetric CPs such as the centrosymmetric Jahn–Teller distorted polyhedra of transition element cations, the eccentricity parameter $\boldsymbol{\Phi}_i$ is not suitable to describe polyhedron distortion. For these polyhedra, $|\boldsymbol{\Phi}_i| = 0$, because for each $\mathbf{A}-\mathbf{X}$ bond with $\boldsymbol{\varphi}_{ij}$ there is another one with $-\boldsymbol{\varphi}_{ij}$, no matter how different the experimental bond lengths D_{ij} within a polyhedron may be. This does not necessarily mean that the r_{0i} and $(\mathrm{BVS})_i$ values calculated for $[\mathbf{AX}_n]$ polyhedra of general shape are not correlated with the distortion of their CPs. It only shows that $\boldsymbol{\Phi}_i$ is not a universal distortion index that fully describes the distortion of a CP. Therefore, the scatter of data points in Figs. 2–7 and the relatively low R^2 values of part of the correlations r_{0i} and $(\mathrm{BVS})_i$ *versus* $|\boldsymbol{\Phi}_i|$ listed in Tables 2–7 are probably partly due to the fact that $\boldsymbol{\Phi}_i$ does not fully cover all kinds of polyhedron distortion.

If $\boldsymbol{\Phi}_i$ does not describe all kinds of CP distortions, what should a 'universal distortion index' look like? Also, is the construction of an universal distortion index possible?

Several distortion indexes have been described in the literature (Robinson *et al.*, 1971; Dollase, 1974; Gaite, 1980; Makovicky & Balić-Žunić, 1998). All of them take into account both experimental bond lengths D_{ij} and, although only indirectly, experimental bond angles α_i. However, all of them are based solely on the geometrical arrangement of the atoms of the polyhedron. Consequently, they ignore that the strength of the interaction between the atoms depends on the distances between them. Therefore, distortion indexes that are only based on geometry are not well suited to reflect crystal-chemical and energetical interrelationships between structures.

In contrast to these distortion indexes, the eccentricity parameter $\boldsymbol{\Phi}_i$ is defined such that the experimental bond lengths D_{ij} are weighted with an exponential function (16*b*), which makes allowance for the fact that the strength of a bond decreases with increasing bond length. This is the reason why correlations r_{0i} and $(\mathrm{BVS})_i$ *versus* $|\boldsymbol{\Phi}_i|$ reflect chemical relationships. Wang & Liebau (1996*b*) have reported that for different $\mathbf{L}-\mathbf{X}$ types the optimal value of the constant g in (16*b*), which led to highest R^2 values for (17), varies between 0.10 Å for $\mathrm{S^{IV}-O}$ and 0.25 Å for $\mathrm{As^{III}-O}$, and that for simplicity an average value of g = 0.20 Å has been used in the statistical analyses. Therefore, the eccentricity parameter $\boldsymbol{\Phi}_i$ can be improved if g is allowed to vary.

While the eccentricity parameter of Wang & Liebau (1996*b*) takes into account the chemical strength of the bonds directly *via* the exponential function (16*b*), similar considerations of bond strengths are found in the distortion indices ΔH and ΔR recently proposed

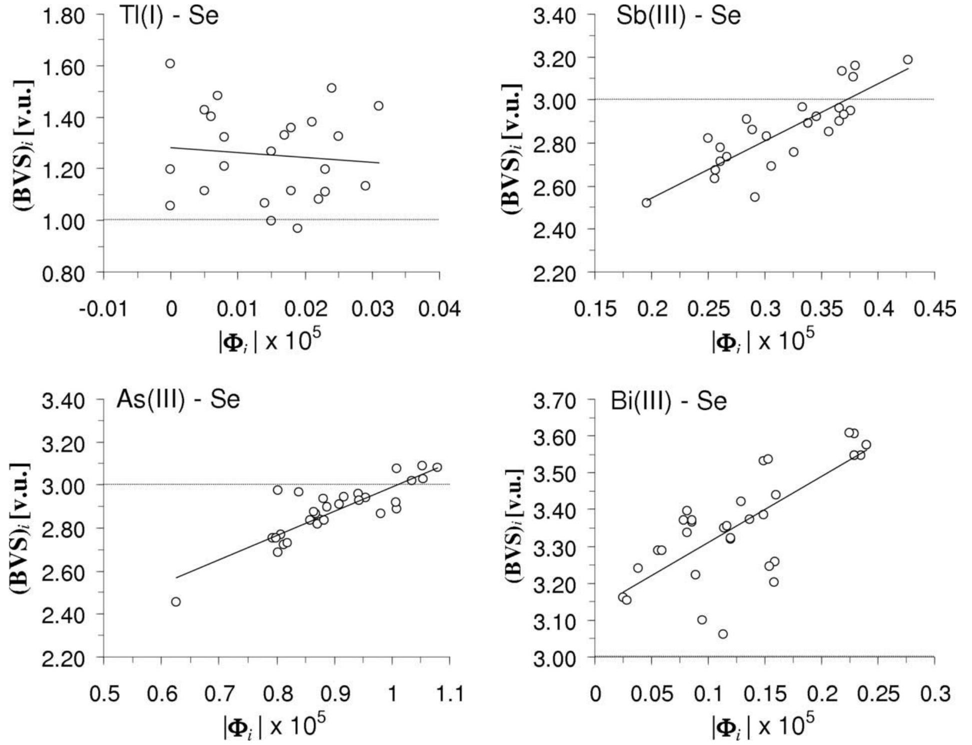

Figure 7
Linear correlation diagrams $(\mathrm{BVS})_i$ *versus* $|\boldsymbol{\Phi}_i|$ for 115 individual $[\mathbf{L}\mathrm{Se}_n]$ polyhedra drawn with different scales. The horizontal lines indicate the whole-number values of ${}^{\rm stoich}V_i$.

by Lalik (2005) and Brown (2006), respectively. However, both ΔH and ΔR ignore the spatial distribution of bonds in a coordination polyhedron since neither of them includes bond angles, and both indices are sensitive to how the bond length cut-off is chosen.

If, even for $\mathbf{L}-\mathbf{X}$ bonds, the eccentricity parameter contains, in addition to the experimental bond lengths D_{ij} and, indirectly, experimental bond angles α_i, an additional variable g, it is obvious that for other ionically, covalently or metallically bonded $[\mathbf{AX}_n]$ polyhedra further adjustments of the distortion index are necessary. These adjustments will perhaps not only involve the variable g of the exponential function of $\mathbf{\Phi}_i$, but most likely also the mathematical form of the distortion index. A 'universal distortion index' would, therefore, probably have so many variables that its practical use would be questionable.

(ii) *Bond-valence parameter b*: The bond-valence parameters r_0 and b are strongly correlated when using (5) and ${}^{\rm stoich}V$ to calculate them. By fixing b = 0.37 Å different r_0 values have been derived for bonds between cations with different stoichiometric valences of the same element and the same anion type (Brown & Altermatt, 1985). It was shown for alkali halides that the correlation between r_0 and b may be weakened and both can be refined freely by including secondary and higher coordination spheres up to 6 Å (Adams, 2001). However, the r_0 and b values derived by this approach lead to mismatches between BVS and ${}^{\rm stoich}V$ that are comparable to those calculated with r_0 and b values tabulated by Brown & Altermatt (1985). Recently, b values other than 0.37 Å and the corresponding r_0 values have been derived which are believed to be independent of the valence state of the ions involved (Zocchi, 2000, 2001, 2006; Hu & Zhou, 2004).

During our statistical analyses, which led to (17) with variable r_{0i}, the individual r_0 values were calculated with (7) under the assumption that b = 0.37 Å is constant. However, while r_{0i} and b are mutually dependent variables, it seems reasonable to assume that they are, in addition, both independently variable. Therefore, future analyses of $b = f(|\mathbf{\Phi}_i|, ...)$ will probably improve the R^2 values of correlations (17) and (18). Preliminary results show that r_{0i} values calculated with b values other than 0.37 Å can have substantially higher correlations with $|\mathbf{\Phi}_i|$ than those shown in Fig. 2. For instance, R^2 values derived with b = 0.37 Å (Tables 5 and 6) improved for $\mathrm{Sn^{II}-O}$ from 0.79 to 0.96 with b = 0.10 Å, for $\mathrm{As^{III}-O}$ from 0.39 to 0.64 with b = 0.64 Å and for $\mathrm{Tl^{I}-S}$ from 0.11 to 0.73 for b = 0.10 Å.[8]

(iii) *General* $[\mathbf{AX}_n]$ *polyhedra*: So far, the correlations (17) and (18) between r_{0i} and $(\mathrm{BVS})_i$, respectively, and $|\mathbf{\Phi}_i|$ have only been derived for the coordination polyhedra $[\mathbf{LX}_n]$ that are centred by p-block cations with one lone electron pair. The question arises whether for CPs that are centred by p-block cations with more than one lone electron pair, r_{0i} and $(\mathrm{BVS})_i$ are also correlated with the distortion of their coordination polyhedra. Furthermore, can (17) and (18) been extended to general $[\mathbf{AX}_n]$ polyhedra, for which $\mathbf{A}$ is a *s*-, *d*- or *f*-block element?

(iv) *Anion-centred polyhedra* $[\mathbf{XA}_m]$: So far, only cation-centred polyhedra have been analysed. It will have to be shown whether r_{0i} values and BVSs are also correlated with the distortion of anion-centred coordination polyhedra or not.

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[8] The corresponding diagrams r_{0i} *versus b* and R, R^2 *versus b* for each of the three data sets are available from the IUCr electronic archives (Reference: SN5045). Services for accessing these data are described at the back of the journal.

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