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‘Ionic’ size differences from bond-valence parameters and from ionic radii

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Expectation values for size differences between pairs of ‘ions’ (atoms in oxidation states $\neq 0$) embedded into similar coordination environments are calculated from tables of bond-valence parameters and ionic radii.

1. Introduction

During the past three decades two kinds of sources have mainly been used for the simple prediction of nearest-neighbour atomic distances D_{A-X} in inorganic solid-state compounds consisting of atoms with both positive and negative oxidation states (called ‘ions’ in the following): ionic radii (IR) tables (Shannon, 1976, 1981) and bond-valence (BV) parameter tables (*e.g.* Brown & Altermatt, 1985; Brese & O’Keeffe, 1991; Adams, 2001). Both kinds of tables have been set up using bond length information extracted from large numbers of crystal structures.

With respect to the IR concept, a nearest-neighbour distance is simply estimated by forming the sum of the empirically determined IR of the ‘ions’ A^{p+}, X^{q-} (briefly A, X) in question, with $p+$ and $q-$ indicating the respective oxidation states

$$d_{A-X} = (D_{A-X})_{\rm est} = {\rm IR}_A + {\rm IR}_X. \quad (1)$$

It should be noted that the IR of an ion depends on its coordination number, CN, and, to a lesser degree, on the spin multiplicity (if relevant). With respect to unsymmetrical coordination polyhedra of A or X (*i.e.* polyhedra containing $A-X$ bonds of different lengths) d_{A-X} predicts merely the *mean* $A-X$ bond length for a *mean* degree of distortion (Δ), where the influence of Δ on, for example, the mean $A-$O bond lengths seems to be $\leq \pm 0.05$ Å (Brown & Shannon, 1973; Shannon, 1976; Baur, 1981). If the coordination polyhedron is heterogeneous (*i.e.* if it consists of, say, X and Y ligands), predicted values may differ substantially from the (mean) experimental ones if X and Y have different oxidation states.

These shortcomings are – theoretically – avoided by the BV concept (Brown, 1977, 1992; Urusov, 1995; Adams, 2001). Here, a nearest-neighbour distance between two specific atoms A_i and X_j in a crystal structure can be estimated by using (2) below (Pauling, 1947; Zachariasen, 1978)

$$d_{A_i-X_j} = (R0)_{AX} - (b)_{AX} \ln s_{A_i-X_j}, \quad (2)$$

where $R0$ (sometimes also called $R1$) and b are empirically determined parameters specific for the combination of the two atom types A^{p+}, X^{q-} ($R0$ being – theoretically – the length of an $A^{p+}-X^{q-}$ *single* bond) and $s_{A_i-X_j}$ is the ideal ‘valence’ of

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the bond in question. The ideal valence of any bond in a crystal can be calculated from just the oxidation states of the atoms of the asymmetric unit and the connectivity scheme of the structure (Brown, 1977; O'Keeffe, 1990; Orlov *et al.*, 1998). The ideal valence should not be confused with the 'experimental' bond valence $S_{A_i-X_j}$, which replaces $s_{A_i-X_j}$ in (2) when $d_{A_i-X_j}$ is replaced by the *experimental* distance $D_{A_i-X_j}$. For limits of the BV concept, see, for example, Preiser *et al.* (1999). Other relations between $d_{A_i-X_j}$ and $s_{A_i-X_j}$ have been investigated (Brown, 1977; Mohri, 2000), but (2) has been the most widely used, meaning that most tabulated BV parameters refer to this relation; the present work is therefore exclusively based on (2).

Now let us consider two isotypic structures, which differ by the replacement of a certain 'ion', say A_i, by a chemically related one of the same oxidation state, say B_i. As all other atoms and the connectivity scheme will have remained unchanged the theoretical (ideal) valences of all bonds will remain unchanged as well (but see Keller & Krämer, 2006). For any bond in which B_i participates we then find

$$d_{B_i-X_j} = (R0)_{BX} - (b)_{BX} \ln s_{B_i-X_j}. \tag{3}$$

As $s_{B_i-X_j}$ is supposed to be equal to $s_{A_i-X_j}$, the difference $(\Delta D_{AB})_X = D_{B_i-X_j} - D_{A_i-X_j}$ can be predicted by $(\Delta d_{AB})_X$ [defined in (4)] provided that $(b)_{BX} = (b)_{AX}$:

$$(\Delta d_{AB})_X = d_{B_i-X_j} - d_{A_i-X_j} = (R0)_{BX} - (R0)_{AX} = (\Delta R0_{AB})_X. \tag{4}$$

This relation is supposed to pertain to all $(A,B){-}X$ bonds (of any valence) in the structure. As most authors have used a fixed value of b in deriving BV parameters [mostly the classical 'universal' value of 0.37 Å (Brown & Altermatt, 1985)] there is a relatively high probability in finding a pair of $(R0, b)$ values with b (nearly) equal for any $(A,B)/X$ combination.

$(\Delta R0_{AB})_X$ can be seen as an 'isotypic' size difference between A and B, meaning that it can be used to predict $B{-}X$ bond lengths from $A{-}X$ bond lengths and *vice versa* for a given structure type or for a series of 'nearly isotypic' structures with identical connectivity schemes [for an unsymmetrical A environment with more than one X ligand $(\Delta R0_{AB})_X$ may predict the *average* bond length difference rather than the individual differences]. If we now assume that this size difference is mainly dependent on A and B and much less on their bonding partners we would expect that $\Delta R0_{AB}$ will not vary much if we replace X by any other anion Y. This assumption can be checked for any A/B pair by determining the standard deviation of the average of the differences $(R0)_{BY} - (R0)_{AY}$ (b approximately equal) for as many different Y as possible. As a by-product, if this standard deviation is small, the average can be used as a *general* expectation value for the isotypic A/B size difference.

The size difference determined this way may furthermore be compared with that derived analogously from the average A/B IR difference $\langle\Delta \mathrm{IR}_{AB}\rangle$, where averaging is performed over all coordination numbers for which both (A and B) IR have been tabulated. Owing to the simplicity of the IR concept, such a difference may be applicable also in cases where the two structures in question are not strictly, or even nearly, isotypic.

2. Experimental

To enable the tasks proposed in the introduction to be performed for any desired A/B pair in an economic way, the Fortran 77 program *RADDIF* has been written. This program uses two different databases: (1) the file bvparm.cif, available on the internet, which contains a collection of BV parameters extracted from 27 publications (Brown, 2003); (2) the file shannon.txt, set up by us as a computer-readable copy of the IR tables from oxide and halide structures (Shannon, 1976) and from sulfide structures (Shannon, 1981). *RADDIF* is able to:

(i) extract BV and IR parameters available from the two databases for a selected 'ion';

(ii) calculate average BV and IR size differences ($\langle\Delta R0_{AB}\rangle$ and $\langle\Delta \mathrm{IR}_{AB}\rangle$) as well as a combined average, $\langle\Delta\rho_{AB}\rangle$ (see below), for a selected pair of 'ions';

(iii) calculate Δf for A/B–Y combinations (see below).

Optionally, the program can be instructed to:

(i) use a Δb threshold above which the difference between the two $R0$ values is excluded;

(ii) downweigh or reject outliers on averaging;

(iii) exclude (parts of) IR data or (parts of) BV data;

(iv) exclude BV parameters for selected bonding partners;

(v) exclude BV parameters from selected publications;

(vi) exclude IR values for selected coordination numbers;

(vii) exclude a selected IR or $R0$ parameter range;

(viii) exclude ions with virtual oxidation state +9 (see below).

RADDIF is driven by simple typed commands. The source code, an executable for MS Windows PCs, and the IR database are available from http://www.krist.uni-freiburg.de/ki/Mitarbeiter/Keller/raddif.html.

3. Results and discussion

Initial calculations with *RADDIF* were somewhat discouraging with respect to the hypothesis that $\Delta R0_{AB}$ should be more or less independent of the bonding partner Y. For example, $\langle\Delta R0_{\mathrm{Cl\,Br}}\rangle$ (for the pair $\mathrm{Cl}^-/\mathrm{Br}^-$) calculated from averaging 60 differences $(R0)_{E\,\mathrm{Br}} - (R0)_{E\,\mathrm{Cl}}$ was 0.15 (9) Å. However, inspection of the individual differences showed that the large standard deviation was caused by four severe outliers, while all others were close to 0.15 Å (Fig. 1). The four outliers are possibly caused by erroneous $R0$ values; thus, calculation of size differences might be an appropriate method to detect errors in the BV parameter database.

Downweighing the outliers (in general defined as those values for which the absolute difference Δ_j from the mean is greater than 3σ) by applying a weight $w_j = 1/(\Delta_j/\sigma - 2)$ and using three cycles of averaging led to a new average of 0.15 (2) Å. Interestingly, $\Delta \mathrm{IR}_{\mathrm{Cl\,Br}}$ (determined from IR) is also 0.15 Å. Table 1 contains the results of the calculations for

Table 1
Individual size differences (Å) for the pair Na^+('1') /K^+('2') from BV data (top) and IR data (bottom) as printed by *RADDIF*.

Y†	Ref.1‡	Ref.2‡	*R*01	*R*02	*b*1	*b*2	Δ*R*0
O^{2-}	*a*	*a*	1.80	2.13	0.37	0.37	0.33
O^{2-}	*a*	*u*	1.80	2.11	0.37	0.37	0.31
O^{2-}	*v*	*a*	1.76	2.13	0.37	0.37	0.38
O^{2-}	*v*	*u*	1.76	2.11	0.37	0.37	0.36
O^{2-}	*c*	*o*	1.58	1.84	0.47	0.48	0.26
O^{2-}	*o*	*c*	1.66	1.95	0.44	0.43	0.29
S^{2-}	*a*	*b*	2.30	2.59	0.37	0.37	0.29
S^{2-}	*b*	*b*	2.28	2.59	0.37	0.37	0.31
Se^{2-}	*b*	*b*	2.41	2.72	0.37	0.37	0.31
Te^{2-}	*b*	*b*	2.64	2.93	0.37	0.37	0.29
F^-	*a*	*a*	1.68	1.99	0.37	0.37	0.31
Cl^-	*b*	*a*	2.15	2.52	0.37	0.37	0.37
Br^-	*b*	*b*	2.33	2.66	0.37	0.37	0.33
I^-	*b*	*b*	2.56	2.88	0.37	0.37	0.32
N^{3-}	*b*	*b*	1.93	2.26	0.37	0.37	0.33
P^{3-}	*b*	*b*	2.36	2.64	0.37	0.37	0.28
As^{3-}	*b*	*b*	2.53	2.83	0.37	0.37	0.30
H−	*b*	*b*	1.68	2.10	0.37	0.37	0.42
Mean difference $\langle \Delta R0_{\rm Na\,K} \rangle$							0.322 (37)

OF denotes oxide/fluoride data; ch denotes sulfide data. CN is the coordination number.

Set	CN1	CN2	IR1	IR2	ΔIR
OF	4	4	0.99	1.37	0.38
OF	6	6	1.02	1.38	0.36
OF	7	7	1.12	1.46	0.34
OF	8	8	1.18	1.51	0.33
OF	9	9	1.24	1.55	0.31
OF	12	12	1.39	1.64	0.25
ch	4	4	1.11	1.49	0.38
ch	6	6	1.21	1.52	0.31
Mean difference $\langle \Delta {\rm IR}_{\rm Na\,K} \rangle$					0.332 (41)
Combined mean difference $\langle \Delta \rho_{\rm Na\,K} \rangle$					0.325 (28)

† Bonding partner of Na/K. ‡ Literature reference in file bvparm.cif.

the pair Na^+/K^+. The decrease of the IR difference with increasing CN is a trend generally observable for 'cation' pairs from the upper rows of the periodic system.

3.1. Tables of 'ionic' size differences

Table 2 lists $\langle \Delta R0_{AB} \rangle$ and $\langle \Delta {\rm IR}_{AB} \rangle$ values calculated by employing the above downweighing scheme for most main-group element 'ion' pairs, one member of which sits directly underneath the other in the periodic table. Only 'ions' with identical oxidation states have been compared (see *Note added in proof*). The maximal allowed *b* difference was 0.02 Å, which corresponds to a bond-length error of 0.014 Å for $s_{A_i - X_j}$ = 0.5 valence units (v.u.). BV values assigned to the reference 'e' in bvparm.cif (flagged 'unchecked' in the database) led, in numerous cases, to severe outliers and were therefore generally excluded from the calculations. 'Ions' to which the oxidation state +9 is assigned in the database (meaning that the true oxidation state is not indicated in the publication) were accepted as bonding partners for the anions but were not included in the retrieval of BV parameters for actually existing 'cations'. The IR data from both sources (oxides/halides and sulfides) were used. Anion–anion BV parameters (O'Keeffe & Brese, 1992) have been excluded from the calculations. Their tentative inclusion led to $\langle \Delta R0_{XY} \rangle$ values for the nine anion pairs that differed by less than 0.01 Å from those in Table 2, but with enlarged standard deviations. $\langle \Delta R0_{XY} \rangle$ values calculated *exclusively* from anion–anion parameters are similar to those derived from cation–anion parameters (except for N^{3-}/P^{3-}), but have in most cases considerably larger standard deviations.

For any $\langle \Delta R0_{AB} \rangle$ (or $\langle \Delta {\rm IR}_{AB} \rangle$) value in Table 2, the number of contributions and the number of outliers (generally less than 7% of the former) are given. In most cases, the standard deviations are 0.03 Å or less. This supports the idea that $\Delta R0_{AB}$ values do not, in principle, depend much on the bonding partner *Y*. It would be interesting to compare the standard deviations in Table 2 to those of the BV and IR parameters they have been derived from; however, all corresponding figures have been published without quoting uncertainties. The largest standard deviations from BV data in Table 2 are often observed for pairs from rows 2 and 3 of the periodic table, *i.e.* pairs with a large electronegativity difference. On the other hand, some of these pairs (such as N^{3-}/P^{3-} or O^{2-}/S^{2-}) are found to replace each other in isotypic structures relatively rarely.

It should be noted in this context that O'Keeffe & Brese (1991) proposed the BV parameter $(R0)_{AX}$ to be the sum of two 'ion'-specific constant size parameters, namely r_A and r_Y, and a correction term $-f(c_A, c_Y, r_A, r_Y)$, defined in (5), where c_A and c_Y are (approximately) the electronegativities of *A* and *Y*, respectively:

$$(R0)_{AY} = r_A + r_Y - (f_A)_Y, \quad \text{with } (f_A)_Y = \frac{r_A r_Y \left[(c_A)^{1/2} - (c_Y)^{1/2} \right]^2}{c_A r_A + c_Y r_Y}. \tag{5}$$

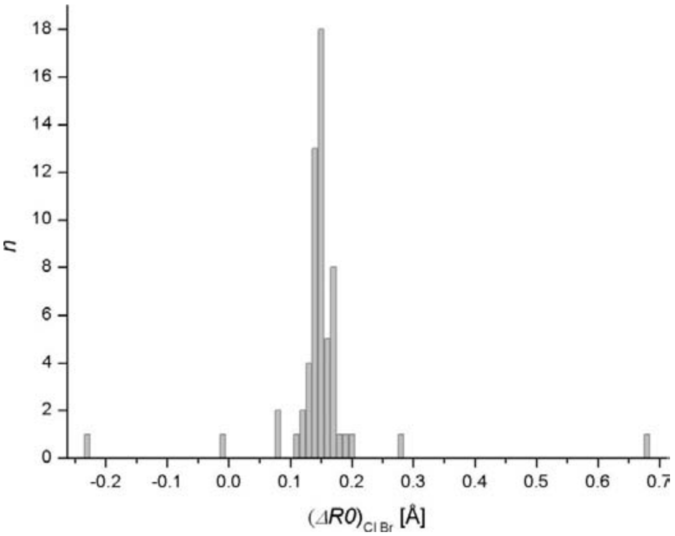

Figure 1
Histogram of $\Delta R0_{\rm Cl\,Br}$ values, rounded to the nearest 0.01 Å.

Table 2
Mean ‘ionic’ size differences (Å) for main-group element pairs.

A	B	$\langle \Delta R0 \rangle$	n_c [n_o]†	$\langle \Delta \mathrm{IR} \rangle$	n_c†	δ	$\langle \Delta \rho \rangle$	Flag‡
Li^{+}	Na^{+}	0.317 (31)	12	0.320 (57)	5	0.003	0.32 (3)	–
Na^{+}	K^{+}	0.322 (37)	18	0.332 (41)	8	0.011	0.33 (3)	–
K^{+}	Rb^{+}	0.116 (44)	16	0.104 (27)	9	−0.011	0.11 (3)	–
Rb^{+}	Cs^{+}	0.171 (20)	13	0.153 (12)	7	−0.019	0.165 (14)	–
Cs^{+}	Fr^{+}	–	–	0.13	1	–	0.130 (15)	×
Be^{2+}	Mg^{2+}	0.348 (33)	12	0.300 (24)	3	−0.048	0.33 (2)	*
Mg^{2+}	Ca^{2+}	0.261 (25)	13	0.250 (22)	3	−0.011	0.26 (2)	–
Ca^{2+}	Sr^{2+}	0.147 (28)	12	0.146 (25)	8	0.000	0.15 (2)	–
Sr^{2+}	Ba^{2+}	0.198 (27)	12	0.160 (16)	8	−0.038	0.19 (2)	*
Ba^{2+}	Ra^{2+}	–	–	0.075 (15)	2	–	0.075 (15)	×
B^{3+}	Al^{3+}	0.302 (31)	13	0.288 (23)	3	−0.014	0.30 (2)	–
Al^{3+}	Ga^{3+}	0.058 (23)	4	0.061 (24)	5	0.003	0.059 (17)	–
Ga^{3+}	In^{3+}	0.190 (18)	4	0.174 (14)	4	−0.016	0.185 (13)	–
In^{3+}	Tl^{3+}	0.076 (26)	3	0.097 (38)	4	0.021	0.08 (2)	–
C^{4+}	Si^{4+}	0.271 (30)	6	–	–	–	0.27 (3)	!
Si^{4+}	Ge^{4+}	0.103 (15)	5	0.115 (21)	3	0.012	0.107 (12)	–
Ge^{4+}	Sn^{4+}	0.164 (19)	4	0.167 (9)	3	0.002	0.165 (13)	–
Sn^{2+}	Pb^{2+}	0.138 (33)	2	–	–	–	0.14 (3)	–
Sn^{4+}	Pb^{4+}	0.129 (24)	3	0.106 (16)	4	−0.023	0.122 (17)	–
N^{3+}	P^{3+}	–	–	0.28	1	–	0.280 (15)	×
N^{5+}	P^{5+}	0.178 (6)	2	0.25	1	0.072	0.195 (30)	*
P^{3+}	As^{3+}	–	–	0.14	1	–	0.140 (15)	×
P^{5+}	As^{5+}	0.156 (6)	2	0.120 (35)	3	−0.036	0.145 (17)	*
As^{3+}	Sb^{3+}	0.192 (8)	5	0.18	1	−0.012	0.188 (7)	–
As^{5+}	Sb^{5+}	0.176 (1)	2	0.157 (17)	2	−0.019	0.170 (9)	–
Sb^{3+}	Bi^{3+}	0.109 (15)	5	–	–	–	0.109 (15)	!
Sb^{5+}	Bi^{5+}	0.144 (23)	3	0.16	1	0.016	0.149 (16)	–
S^{4+}	Se^{4+}	0.166 (29)	3	0.13	1	−0.036	0.15 (2)	*
S^{6+}	Se^{6+}	0.141 (16)	3	0.145 (15)	2	0.004	0.143 (12)	–
Se^{4+}	Te^{4+}	0.152 (11)	3	–	–	–	0.152 (11)	!
Se^{6+}	Te^{6+}	0.133 (5)	3	0.145 (5)	2	0.012	0.137 (6)	–
F^{7+}	Cl^{7+}	–	–	0.19	1	–	0.190 (15)	×
Cl^{5+}	Br^{5+}	–	–	0.19	1	–	0.190 (15)	×
Cl^{7+}	Br^{7+}	0.179 (8)	3	0.145 (25)	2	−0.034	0.168 (16)	*
Br^{5+}	I^{5+}	–	–	0.13	1	–	0.130 (15)	×
Br^{7+}	I^{7+}	0.117 (5)	3	0.155 (15)	2	0.038	0.128 (18)	*
F^{-}	Cl^{-}	0.463 (40)	140 [4]	0.48	1	0.017	0.47 (3)	–
Cl^{-}	Br^{-}	0.148 (23)	60 [4]	0.15	1	0.002	0.149 (16)	–
Br^{-}	I^{-}	0.216 (20)	89 [3]	0.24	1	0.024	0.224 (14)	–
O^{2-}	S^{2-}	0.428 (61)	97 [3]	0.44	1	0.012	0.43 (4)	–
S^{2-}	Se^{2-}	0.123 (26)	76 [5]	0.140 (0)	2	0.017	0.13 (2)	–
Se^{2-}	Te^{2-}	0.205 (30)	67	0.230 (0)	2	0.025	0.21 (2)	–
N^{3-}	P^{3-}	0.388 (55)	81 [3]	–	–	–	0.39 (5)	–
P^{3-}	As^{3-}	0.080 (15)	69 [4]	–	–	–	0.080 (15)	–

† n_c is the number of contributions; n_o is the number of outliers. ‡ Meaning of flags: * IR data downweighed; ! existing IR data omitted; × combined difference derived from only one IR difference.

Accordingly we obtain (6) for $(\Delta R0_{AB})_Y$

$$(\Delta R0_{AB})_Y = p - (\Delta f_{AB})_Y, \tag{6}$$

with $p = (r_B - r_A)$ = constant and

$$\Delta (f_{AB})_Y = \frac{r_B r_Y \left[(c_B)^{1/2} - (c_Y)^{1/2} \right]^2}{c_B r_B + c_Y r_Y} - \frac{r_A r_Y \left[(c_A)^{1/2} - (c_Y)^{1/2} \right]^2}{c_A r_A + c_Y r_Y}.$$

Equation (6) suggests that $\Delta R0_{AB}$ depends on the electronegativity and size of the bonding partner Y of A/B. On the other hand, in the comparison of 600 $R0$ values calculated from (5) with those determined empirically, the scatter of the data points (after exclusion of some outliers) corresponded to a σ of 0.037 Å (O'Keeffe & Brese, 1991), which is comparable to the σ values for $\langle \Delta R0_{AB} \rangle$ obtained in the present work. Calculation of Δf by *RADDIF* showed that it is mainly dependent on the A/B combination. For example, $\langle \Delta f \rangle$ is −0.057 (18) Å for $\mathrm{F}^-/\mathrm{Cl}^-$ (111 contributors) and −0.012 (4) Å for $\mathrm{Br}^-/\mathrm{I}^-$ (82 contributors). In Fig. 2, we have plotted $\Delta R0_{AB}$ *versus* Δf for two ‘ion’ pairs. Equations of the linear fits approximate equation (6), but the correlation is, in most cases, weak (correlation coefficient $R < 0.5$), such that a clear dependence of $\Delta R0$ on Δf cannot be stated in general.

For 34 ‘ion’ pairs in Table 2 both values $\langle \Delta R0_{AB} \rangle$ and $\langle \Delta \mathrm{IR}_{AB} \rangle$ could be determined; for 24 of these pairs, the two

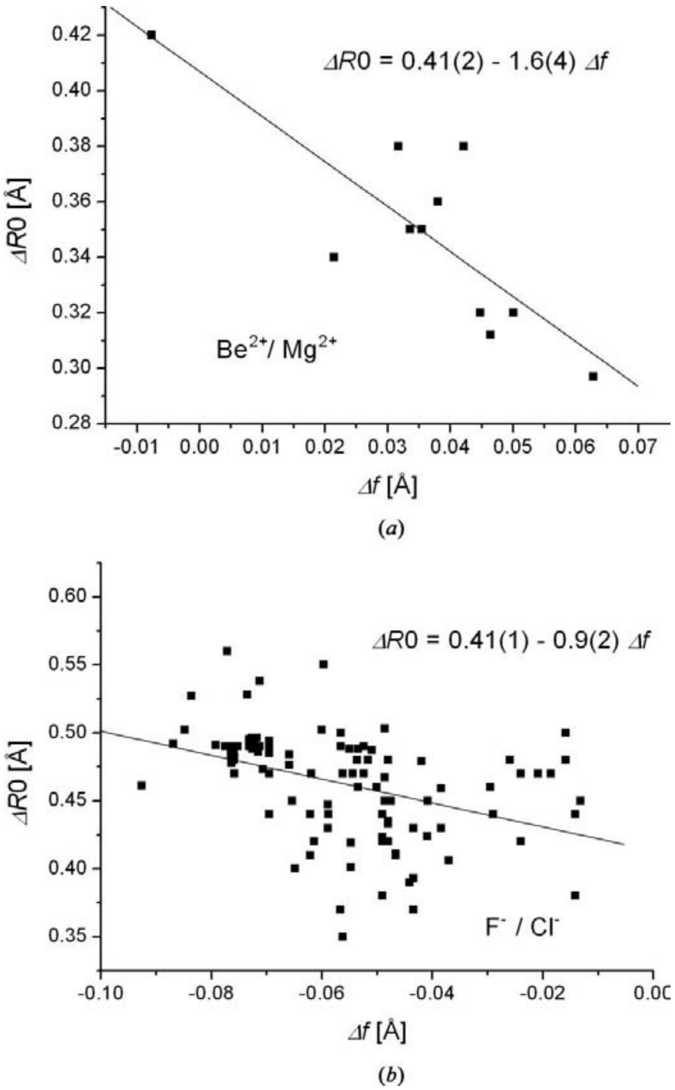

Figure 2
Plot of $\Delta R0_{AB}$ or $\Delta R0_{XY}$ against Δf for (*a*) $\mathrm{Be}^{2+}/\mathrm{Mg}^{2+}$, one of the few examples with a clearly recognizable correlation between $\Delta R0_{AB}$ and Δf (correlation coefficient R = 0.82); (*b*) $\mathrm{F}^-/\mathrm{Cl}^-$ (R = 0.44).

Table 3
Mean 'ionic' size differences (Å) for some transition metal 'ion' pairs.

A	B	$\langle\Delta R0\rangle$	n_c $[n_o]$†	$\langle\Delta\text{IR}\rangle$	n_c†	δ	$\langle\Delta\rho_{AB}\rangle$	Flag‡
Sc^{3+}	Y^{3+}	0.168 (11)	13	0.148 (6)	3	−0.020	0.162 (10)	–
Y^{3+}	La^{3+}	0.158 (17)	13	0.139 (3)	5	−0.019	0.152 (11)	–
Ti^{4+}	Zr^{4+}	0.111 (19)	5	0.124 (28)	6	0.013	0.115 (16)	–
Zr^{4+}	Hf^{4+}	−0.010 (12)	5	−0.010 (6)	6	0.000	−0.010 (8)	–
V^{5+}	Nb^{5+}	0.112 (3)	5	0.112 (12)	2	0.000	0.112 (5)	–
Nb^{5+}	Ta^{5+}	0.013 (10)	4	−0.007 (19)	4	−0.021	0.006 (10)	–
Cr^{3+}	Mo^{3+}	0.118 (8)	2	0.065 (10)	2	−0.053	0.10 (2)	*
Cr^{6+}	Mo^{6+}	0.112 (32)	4	0.150 (0)	2	0.038	0.12 (2)	*
Mo^{6+}	W^{6+}	0.010 (10)	7	0.007 (4)	5	−0.003	0.009 (7)	–
Mn^{4+}	Re^{4+}	–	–	0.10	1	–	0.100 (15)	×
Mn^{7+}	Re^{7+}	0.100 (40)	2	0.100 (30)	2	0.000	0.10 (3)	–
Fe^{3+}	Ru^{3+}	0.012 (6)	3	0.000 (35)	2	−0.012	0.008 (12)	–
Ru^{3+}	Os^{3+}	–	–	−0.015	1	–	−0.015 (15)	×
Co^{3+}	Rh^{3+}	0.115 (27)	4	0.055	1	−0.060	0.10 (3)	*
Rh^{3+}	Ir^{3+}	–	–	0.010 (5)	2	–	0.010 (5)	–
Ni^{2+}	Pd^{2+}	0.109 (46)	4	0.147 (21)	3	0.038	0.12 (3)	*
Pd^{2+}	Pt^{2+}	−0.028 (25)	3	−0.042 (14)	3	−0.014	−0.033 (17)	–
Pd^{4+}	Pt^{4+}	–	–	0.01	1	–	0.010 (15)	×
Cu^{+}	Ag^{+}	0.267 (51)	6	0.319 (76)	4	0.052	0.28 (4)	×
Ag^{3+}	Au^{3+}	–	–	0.055 (45)	2	–	0.06 (5)	–
Zn^{2+}	Cd^{2+}	0.200 (24)	13	0.203 (15)	7	0.002	0.201 (17)	–
Cd^{2+}	Hg^{2+}	0.041 (29)	6	0.072 (67)	4	0.032	0.05 (3)	*
La^{3+}	Ce^{3+}	−0.029 (26)	7	−0.021 (4)	6	0.007	−0.026 (17)	–
Ce^{3+}	Pr^{3+}	−0.017 (4)	7	−0.018 (1)	3	−0.001	−0.017 (3)	–
Pr^{3+}	Nd^{3+}	−0.014 (8)	13	−0.013 (4)	3	0.000	−0.013 (5)	–
Nd^{3+}	Pm^{3+}	−0.017 (5)	3	−0.016 (2)	3	0.001	−0.016 (3)	!
Pm^{3+}	Sm^{3+}	−0.017 (5)	3	−0.013 (1)	3	0.004	−0.015 (3)	!
Sm^{3+}	Eu^{3+}	−0.011 (2)	5	−0.013 (3)	6	−0.002	−0.011 (2)	–
Eu^{3+}	Gd^{3+}	−0.010 (1)	6	−0.011 (2)	6	−0.001	−0.010 (1)	–
Gd^{3+}	Tb^{3+}	−0.019 (6)	8	−0.013 (3)	6	0.006	−0.017 (4)	–
Tb^{3+}	Dy^{3+}	−0.019 (13)	8	−0.013 (3)	6	0.006	−0.017 (9)	–
Dy^{3+}	Ho^{3+}	−0.004 (12)	7	−0.011 (0)	3	−0.007	−0.007 (8)	–
Ho^{3+}	Er^{3+}	−0.013 (9)	8	−0.011 (0)	3	0.003	−0.012 (6)	–
Er^{3+}	Tm^{3+}	−0.014 (20)	8	−0.010 (0)	3	0.004	−0.012 (13)	–
Tm^{3+}	Yb^{3+}	−0.017 (22)	17	−0.010 (1)	3	0.006	−0.015 (14)	–
Yb^{3+}	Lu^{3+}	−0.005 (8)	17 [1]	−0.014 (9)	4	−0.009	−0.008 (6)	–
La^{3+}	Lu^{3+}	−0.20 (2)	16	−0.179 (6)	3	0.023	−0.194 (17)	–

† n_c is the number of contributions; n_o is the number of outliers. ‡ Meaning of flags: * IR data downweighed; ! one existing BV parameter omitted; × combined difference derived from only one IR difference.

values differed by 0.025 Å or less (*i.e.* mostly less than one of the two standard deviations). This result suggests that both concepts (BV and IR) should *in principle* lead to the same results (see *Note added in proof*). Large deviations between the two may then be assigned to assumed errors in the published data. The three cases in which $\delta = |\langle\Delta R0_{AB}\rangle - \langle\Delta\text{IR}_{AB}\rangle|$ exceeds 0.075 Å are discussed in the following:

(*a*) Sb^{3+}/Bi^{3+} (δ = 0.106 Å): While the IR difference for CN 5 (0.16 Å) is comparatively close to $\langle\Delta R0_{AB}\rangle$ [0.11 (2) Å], the IR difference for CN 6 (0.27 Å) is an outlier. One reason for this deviation is that in the case of Sb^{3+} the IR tabulated for CN 6 (0.76 Å) is *smaller* than that for CN 5 (0.80 Å), which is not as expected.

(*b*) C^{4+}/Si^{4+} (0.096 Å): While the IR difference for CN 6 (0.24 Å) is rather close to $\langle\Delta R0_{AB}\rangle$ [0.27 (3) Å], the IR difference for CN 4 (0.11 Å) is an outlier. A reason may be seen in the fact that the IR of C^{4+} for CN 4 is only 0.01 Å smaller than that of CN 6, which is again not as expected; for all other 'ions' with oxidation state +4 (and both IR values tabulated) the two corresponding figures differ by 0.13–0.19 Å.

(*c*) Se^{4+}/Te^{4+} (0.318 Å): The three contributions to the BV difference are very consistent and form an average of 0.15 (1) Å, which is close to the Se^{6+}/Te^{6+} value [0.13 (1) Å], as well as to the S^{4+}/Se^{4+} [0.17 (3) Å] and the S^{6+}/Se^{6+} [0.14 (2) Å] values. When looking at the corresponding IR values, the Se^{4+}/Te^{4+} value of 0.47 Å (1 contribution) is a severe outlier with respect to the other three (0.13–0.15 Å).

In all three cases (flagged by '!' in Table 2) the IR data have therefore been excluded from the final calculations. Table 2 also contains the final differences δ (column 7) as well as combined $\langle\Delta\rho_{AB}\rangle$ values (column 8). The latter have been calculated by averaging $\langle\Delta R0_{AB}\rangle$ and $\langle\Delta\text{IR}_{AB}\rangle$ and assigning a relative weight, w_{BV}, to the former (w_{IR} fixed to 1). For $\delta <$ 0.03 Å, w_{BV} was set to 2; in the other cases, w_{BV} was set to 1 + δ/0.03. This – admittedly unusual – weighing scheme was used as the BV results are believed to be more reliable, a view that is supported by the above three cases of 'ion' pairs and the Ag^{+}/Au^{+} pair discussed below. One should be aware, though, that values flagged by '*' in Table 2 (those with $\delta >$ 0.03 Å) are biased by subjective judgement.

Combined values $\langle\Delta\rho\rangle$ have been included in Table 2 because for a number of 'ion' pairs either the BV or the IR value was not available owing to a lack of appropriate parameters. Furthermore, as BV and IR databases can be thought of as two independent sources, averaging can lead to smaller standard deviations σ. As σ of a combined value we selected the *larger* one of (*a*) σ_{av} due to averaging and (*b*) σ_{ep} calculated by error propagation from the σs of the two contributors, with the contributing σ set to 0.015 Å if the 'average' had been 'calculated' from only *one* value. The standard deviations determined this way are, in most cases, 0.03 Å or less. Cases where $\langle\Delta\rho\rangle$ has been derived from a single IR difference only are flagged with '×' in Table 2.

In Table 3 we present some results for transition metal groups and for the lanthanides. The following corrections were made: One of the two $R0$ values for Pm^{3+}/Cl^{-} from reference '*p*' ($R0$ = 2.42 Å) fitted well, while the other one ($R0$ = 2.82 Å) generated two extreme outliers and was therefore excluded. The affected 'ion' pairs are flagged by '!' in Table 3. For the Ag^{+}/Au^{+} pair no suitable BV parameters were available and the two IR differences (one from the oxides/fluorides table for CN 6 and the other one from the sulfides table for CN 2) differed extremely (0.22 *versus* −0.13 Å). Thus, this pair is not listed in Table 3. Standard deviations and differences between BV and IR values are comparable to those for the main group 'ion' pairs.

3.2. Applications

Ionic size differences (derived exclusively from IR data) have recently been used for the discussion of deviations from Vegard's law in solid solutions (Keller & Krämer, 2005). The advantage of size *differences* as compared to size *ratios* is their independence from a more or less arbitrarily determined radius of reference like the O^{2-} radius (Shannon, 1976). Size differences should therefore generally be the parameters of choice if geometrical reasons for non-Vegard behaviour of mixed 'ionic' systems are to be considered.

In principle, the size differences given in Tables 2 and 3 can be used to derive special sets of 'isotypic' radii. This requires, however, the deduction or retrieval of one of the desired values from another source. For example, if in a certain environment the radius of Ca^{2+} defined in some way happens to be 1.00 Å then the radii of the other earth alkali ions in the same environment would be expected to be 0.41 (3) (Be^{2+}), 0.74 (2) (Mg^{2+}), 1.15 (2) (Sr^{2+}) and 1.33 (2) Å (Ba^{2+}). The first and the last values in this series have not been derived from Table 2 but by direct size difference calculations for the pairs Be^{2+}/Ca^{2+} and Ca^{2+}/Ba^{2+}.

It should be noted that the size differences collected in Tables 2 and 3 are of the 'overall' kind. For special problems, it may be reasonable to include only selected parts of the data for the calculations. For example, for a study of *oxides*, the restriction of the BV bonding partners to O^{2-}/F^{-} and the restriction of IR to oxide/fluoride data should be considered, as this measure will mostly lead to smaller differences between $\langle \Delta R0_{AB} \rangle$ and $\langle \Delta \mathrm{IR}_{AB} \rangle$, and to significantly reduced σ values (but, of course, at the cost of a substantial decrease of the number of contributors).

The initial aim of the present work was to obtain more reliable size difference expectation values for the halide ions to be used in a study of series of isotypic bismuth compounds. Actually, our results suggest some small corrections (maximally 0.016 Å) to halogen size differences derived merely from IR (see Table 2) and the new values could be equipped with standard deviations. The results of a comparison between expected halide ion size differences and experimentally determined bond length differences in three isotypic bismuth chalcogenide halide series will be discussed elsewhere (Keller & Krämer, 2006).

Note added in proof. The calculation of $\langle \Delta R0 \rangle$ and $\langle \Delta \mathrm{IR} \rangle$ values for pairs of *non*-isovalent 'ions', $A^{n+}/B^{n'+}$, generally also leads to σ values around 0.03 Å, but the two results differ severely. This fact can be explained as follows: $\langle \Delta \mathrm{IR}_{AB} \rangle$ *generally* should reflect the average experimental bond-length difference $\langle \Delta D_{AB} \rangle$ with respect to a large number of coordination polyhedral pairs $A^{n+}X_p$ and $B^{n'+}X_p$. $\langle \Delta R0_{AB} \rangle$ do not: the bond valences in an $A^{n+}X_p$ polyhedron and those in a corresponding $B^{n'+}X_p$ polyhedron will differ per average by a factor of n'/n, while $\Delta R0$ predicts ΔD only for two bonds of equal valences. Thus, only for a pair of *iso*valent 'ions' ($n' = n$), $\langle \Delta R0_{AB} \rangle$ can be expected to also quantify $\langle \Delta D_{AB} \rangle$ and thus to be equal to $\langle \Delta \mathrm{IR}_{AB} \rangle$.

References

Adams, S. (2001). *Acta Cryst.* B**57**, 278–287.

Baur, W. H. (1981). *Structure and Bonding in Crystals*, Vol II, edited by M. O'Keeffe & A. Navrotsky, pp. 31–52. New York: Academic Press.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Brown, I. D. (1977). *Acta Cryst.* B**33**, 1305–1310.

Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.

Brown, I. D. (2003). Accumulated table of bond-valence parameters (bvparm.cif), downloaded from http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/bond_valence_param/.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

Keller, E. & Krämer, V. (2005). *Z. Naturforsch. Teil B*, **60**, 1255–1263.

Keller, E. & Krämer, V. (2006). *Acta Cryst.* B**62**, 417–423.

Mohri, F. (2000). *Acta Cryst.* B**56**, 626–638.

O'Keeffe, M. (1990). *Acta Cryst.* A**46**, 138–142.

O'Keeffe, M. & Brese, N. E. (1991). *J. Am. Chem. Soc.* **113**, 3226–3229.

O'Keeffe, M. & Brese, N. E. (1992). *Acta Cryst.* B**48**, 152–154.

Orlov, I. P., Popov, K. A. & Urusov, V. S. (1998). *J. Struct. Chem.* **39**, 575–579.

Pauling, L. (1947). *J. Am. Chem. Soc.* **69**, 542–553.

Preiser, C., Lösel, J., Brown, I. D., Kunz, M. & Skowron, A. (1999). *Acta Cryst.* B**55**, 698–711.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Shannon, R. D. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe & A. Navrotsky, pp. 53–70. New York: Academic Press.

Urusov, V. S. (1995). *Acta Cryst.* B**51**, 641–649.

Zachariasen, W. H. (1978). *J. Less Common Met.* **62**, 1–7.