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Relationship between bond valence and bond softness of alkali halides and chalcogenides

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Established bond-valence parameter tables rely on the assumption that the bond-valence sum of a central atom is fully determined by interactions to atoms in its first coordination shell. In this work the influence of higher coordination shells is tested in detail for bonds between lithium and oxygen. It is demonstrated that the sum of the weak interactions with atoms of the second coordination shells significantly contributes to the valence sum and should therefore not be neglected. Since the independent refinement of the two parameters R_0 and b is hardly possible from the limited range of bond lengths occurring in the first coordination shell, the restriction of bond-valence sums to contributions from nearest neighbours implicated another far-reaching simplification: the postulation of a universally fixed value of the bond-valence parameter b which characterizes the shape of the bond-valence pseudopotential for the respective atom pair. However, recent more sophisticated applications of the bond-valence concept, *e.g.* to model ion-transport pathways in solid electrolytes, demand sensible estimates of the bond-valence sums for mobile ions not only at their equilibrium sites but also at interstitial sites and bottle-necks of transport pathways. Calculations of bond valences at these non-equilibrium sites require the knowledge of the actual shape of the bond-valence pseudopotential. A systematic route to a more realistic estimate of b for alkali halides and chalcogenides is developed in this work from an empirical correlation between b and the absolute softnesses of the interacting particles.

1. Introduction

The use of empirical correlations between the bond length and strength of chemical bonds in crystal chemistry dates back to the work of Byström & Wilhelmi (1951) and Zachariasen (1954), who generalized Pauling's electrostatic valence principle to extract estimates for the different bond strengths, *e.g.* in the asymmetric coordination polyhedra of transition metals. Donnay & Allmann (1970) developed these ideas into the concept of bond valence (BV). It is one of the major advantages of the BV concept that it does not require an *a priori* distinction between covalent and ionic types of bonding. Thus, the terms 'cation' and 'anion' in this context simply classify the particles according to their electronegativity and are equivalent to Lewis acids and bases. The monotonic decrease of the bond valence s_{A-X} with bond length R_{A-X} between a cation A and an anion X may be approximated as

$$s_{A-X} = \exp[(R_0 - R_{A-X})/b]. \quad (1)$$

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Some of the early investigations preferred the power law *ansatz*

$$s_{A-X} = (R_0/R_{A-X})^N \quad (2)$$

mostly because of the slightly reduced computational effort. The empirical parameters R_0 and b (or R_0 and N) are chosen to ensure that the expectancy value for the bond-valence sum $V(A)$ of the cation A for bonds to all its coordinating anions X

$$V(A) \equiv \sum_X s_{A-X} \quad (3)$$

equals the formal valence $V_{\rm ideal}(A)$. A detailed introduction into the bond-valence model as well as a stringent formal deduction from a set of axioms can be found in the work of Brown (1992, 1997). Empirical bond-valence parameters for numerous atom pairs can be found in the literature (*e.g.* Brese & O'Keeffe, 1991; Brown, 1996); for a compilation of data from earlier literature see *e.g.* Brown (1981). Over the last decades bond-valence sum calculations have become a valuable tool in crystal structure determinations for the localization of light atoms from X-ray data, the distinction of isoelectronic ions (such as Al^{III} from Si^{IV}) or as a quick check for the plausibility of a structure solution (see *e.g.* Waltersson, 1978; Adams *et al.*, 1993; Withers *et al.*, 1998) The predictive power of the bond-valence approach stimulated considerable efforts to elucidate its equivalence to the established concepts of bonding in inorganic solids, especially to the borderline cases of purely ionic (*cf.* Brown, 1992; Preiser *et al.*, 1999) or covalent bonding (*cf.* Burdett & Hawthorne, 1993; Hawthorne, 1994; Urusov, 1995; Mohri, 2000).

Nevertheless, one should be aware that the refinement of bond-valence parameters from bond lengths of reference crystal structures is based on simplifying assumptions which in some cases limit their applicability. One of these assumptions that shall be addressed in this work is the hypothesis that the bond-valence parameter b may be treated as a universal constant. As for numerous cation–anion pairs only a limited number of reliable structure determinations were available, a significant refinement of the two highly correlated BV parameters b and R_0 was generally hard to achieve and often impossible. Thus, Brown & Altermatt (1985) suggested keeping b to the universal value of 0.37 Å and to refine R_0 only.

Based on that simplification Brese & O'Keeffe (1991) could also determine R_0 values for less common cation–anion pairs in their comprehensive bond-valence parameter tables. Following a suggestion by Ray *et al.* (1979), these authors interpreted the values of $R_0(ij)$ as the sum of atomic radii of the atoms i and j modified by an electronegativity related correction term

$$R_0(ij) = R_i + R_j - [R_iR_j(\chi_i^{1/2} - \chi_j^{1/2})^2/(\chi_iR_i + \chi_jR_j)]. \quad (4)$$

Thereby it became possible to estimate R_0 even for atom pairs, where no experimental data were available. Brese and O'Keeffe employed their own electronegativity scale (O'Keeffe & Brese, 1991), which except for the charge-dependent electronegativity of hydrogen is closely related to the widely accepted scale of Allred & Rochow (1958). As will be shown further below, the question whether this simplification is justified is intimately linked to the more fundamental question what is the maximum cation–anion distance that should be assumed to contribute to a chemical bond.

2. Influence of bond softness on bond valence

In order to illustrate the consequences of the approximation of a universal parameter b, it may be helpful to rewrite the monotonic correlation between bond length R_{A-X} and bond valence s_{A-X} into a pseudopotential of bond-valence deviation Δs_{A-X}

$$\Delta s_{A-X} = |\exp[(R_{A-X} - R_0)/b] - s_{\rm ideal}|, \quad (5)$$

where $s_{\rm ideal}$ represents the bond-valence contribution from a single bond that would give rise to a total valence sum $V(A) = V_{\rm ideal}(A)$.

In Fig. 1 it is presumed that a monovalent central cation A^+ is symmetrically coordinated by four anions X^{z-}. Assuming that only nearest neighbours contribute to the valence sum the ideal bond-valence contribution from a single bond would thus be $s_{\rm ideal}(A-X) = \frac{1}{4}$. Any deviation of the bond length R_{A-X} from its ideal value $R_{\rm ideal}$ (corresponding to $s_{\rm ideal}$) leads to an increase of $|\Delta s_{A-X}| = |s_{A-X} - s_{\rm ideal}|$. The concavity of the relation between s and R ensures that the increase of $|\Delta s_{A-X}|$ is steeper in the $R < R_{\rm ideal}$ branch. For a given coordination type the postulation of a fixed value of b in this picture would mean that the shape of the pseudopotential becomes identical for all monovalent cations (*cf.* broken line in Fig. 1), irrespective of the type of bonding or the polarizability of the interacting particles. Thus, applications of the bond-valence concept to any field that might be affected by the shape of the bond-length bond-valence pseudopotential should not rely on

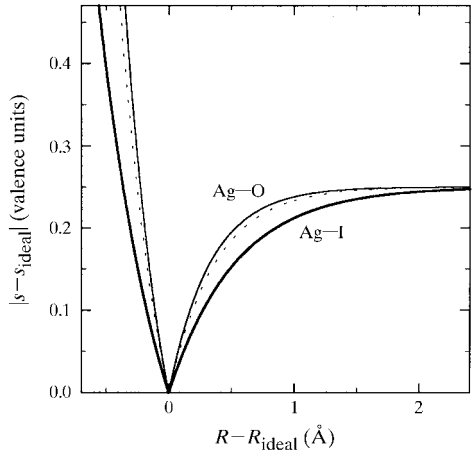

Figure 1
Pseudopotential representation of the correlation between bond-length R and bond valence s. $R_{\rm ideal}$ is the bond distance that leads to a bond valence of $s_{\rm ideal}$ = 0.25 v.u. (the bond valence for a monovalent cation in a symmetrical tetrahedral coordination). Full lines refer to bond-valence parameters of Ag—O and Ag—I with freely refined b (Radaev *et al.*, 1994; Trömel, 1994); the broken line displays the universal shape for pseudopotentials that employ a fixed b = 0.37 Å.

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bond-valence parameter sets with a fixed parameter b. It appears more natural to incorporate the effects of the polarizability by the determination of a suitable value of b instead of treating it as a correction term to the atomic radii [as had been performed implicitly in (4)].

Adjusting the value of b to the softness of a bond at first requires an independent measure of the softness of a bond. Following Parr & Pearson (1983) individual atoms, ions or radicals may be characterized by their '*electronic chemical potential*' μ and their '*absolute hardness*' η. The exact definition of these quantities as

$$\mu = (\partial E/\partial N)_v, \tag{6}$$

and

$$\eta = \tfrac{1}{2}(\partial\mu/\partial N)_v = \tfrac{1}{2}(\partial^2 E/\partial N^2)_v, \tag{7}$$

where N equals the number of electrons and v represents the potential of the nucleus and external influences, which may appear quite abstract, but for neutral particles approximate values for μ and η are experimentally accessible from the relation of these quantities to ionization energy IE and electron affinity EA

$$-\mu \simeq (IE + EA)/2 = \chi_{\rm abs}. \tag{8}$$

In this approximation $|\mu|$ becomes identical to Mulliken's definition of the *absolute electronegativity* $\chi_{\rm abs}$. It should be noted that for a system in equilibrium $\chi_{\rm abs}$ attains a constant site-independent value, whereas the value of η varies locally with a global average value of

$$\eta \simeq (IE - EA)/2 = 1/\sigma. \tag{9}$$

The 'absolute softness' σ is thereby defined as the reciprocal value of hardness η. The softness of a cation M^{z+} may be calculated in the same manner using the zth ionization energy as IE and replacing EA by the ionization energy of $M^{(z-1)+}$ (Pearson, 1985). As electron affinities of anions are generally inaccessible (and their meaningfulness in the determination of bond softnesses appears questionable), a similar extension to anions is not viable. According to Pearson (1988) the values of IE and EA for the neutral elements may serve as a rough approximation for the anions. In the first part of the paper we will follow this guideline. Later it will be outlined how an empirical correlation between the anion radius and the anion softness may be utilized to obtain a more precise estimate of the anion softness.

To derive a measure for the softness of the $A-X$ bond, the softnesses of the interacting species A^+ and X^{z-} need to be combined. In an earlier investigation on a possible connection between bond softness and bond valence, Urusov (1995) had argued that the softness of a bond should increase with the sum of the softnesses of the interacting particles. Contrasting to this assumption, the empirical HSAB (hard and soft acids and bases) concept (Pearson, 1963; Parr & Pearson, 1983; Nalewajski, 1993) suggests that reactions will occur most readily between species that match each other in hardness or softness. If the formation of strong bonds between anions and cations of equal softness is the fundamental reason for this empirical rule, then it appears straightforward to conclude that the interatomic potentials for these bonds should be steeper (and thus correspond to a smaller value of b) than those for the weaker bonds between particles of mismatched softnesses.

The diagrams in Fig. 2 compare the significance of the two suggested correlations based on those literature bond-valence parameters (for halide and chalcogenide compounds) that did not follow the assumption of a universal bond-valence parameter b. Obviously there is no strong correlation to be expected, since the comparison includes data from different sources (some of them were rather old and therefore based on the considerably smaller number of structures available at that time) using slightly different conventions for the selection of 'well determined' structures and the choice of the counterions that contribute to the bond-valence sum. In some cases it is also not evident whether the published b parameters were the results of free refinements or biased, *e.g.* by whatever the authors assumed to be 'chemical knowledge'. Some of the bond-valence parameters are intended to apply to atoms for a range of formal valences, but each valence state corresponds to a different softness. The approximative conversion formula suggested by Burdett & Hawthorne (1993) for parameter sets that employ the power law *ansatz* of (2) systematically produces lower values of b. The converted data have therefore been scaled by a constant factor of 1.25, so that the average value of b for the literature parameter sets from (1) and (2) becomes equal. Moreover, the exponent N of the power law parameters was mostly given as an integer number in the literature, which leads to noticeable rounding errors. Despite all these drawbacks Fig. 2 reveals that the difference of the softnesses $\sigma_{\rm anion} - \sigma_{\rm cation}$ should be loosely related to b in the sense predicted by the HSAB concept, whereas there seems to

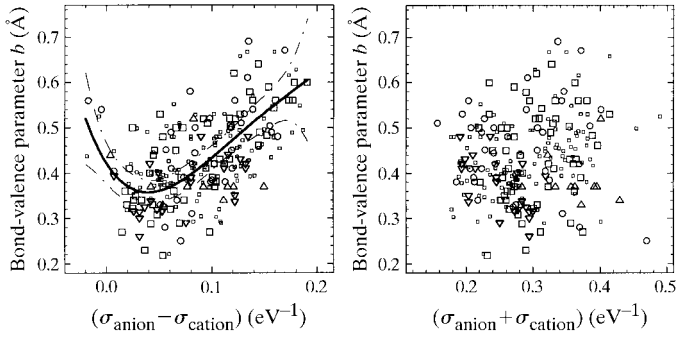

Figure 2
Comparison of the dependence of the bond-valence parameters b on the difference between the softnesses of anions (halides and chalcogenides) and cations (left-hand side) or on the sum of the softnesses as predicted by Urusov (1995) (right-hand side). Large symbols refer to b values from various literature compilations (Radaev *et al.*, 1994; Trömel, 1994; Brown, 1981, 2000), while small symbols refer to b values converted from parameters of the power law *ansatz* of (2) as described in the text. In harmony with the HSAB concept, bonds between atoms with different softnesses tend to be weaker and therefore correspond to larger values of the parameter b (solid line: fourth-order polynomial fit to all data; broken lines: 99% confidence interval). However, no correlation at all is discernible in the right-hand side diagram between b and the softness sum for the same set of data.

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be no discernible correlation between b and the sum of softnesses $\sigma_{anion} + \sigma_{cation}$. From these data it is impossible to decide whether the slopes for the two branches of the correlation between b and the softness difference ($\sigma_{anion} > \sigma_{cation}$ or $\sigma_{anion} > \sigma_{cation}$) differ, since the case $\sigma_{anion} < \sigma_{cation}$ occurs only for a low number of cation–anion pairs. The apparent shift of the minimum in the correlation to positive softness differences may serve as an indication that the rough estimate of the anion softness (by assuming equal softnesses for neutral atoms and anions) tends to overestimate the anion softness.

These findings do not preclude that a different combination of the individual softnesses might lead to a more significant correlation. In this context it may be noteworthy that Mohri (2000) recently derived an alternative formulation of the correlation between the bond distance and bond valence from a molecular orbital viewpoint. The conversion of his parameters into the conventional Brown–Altermatt formula leads to values of b that are generally lower (*ca* 2/3 of literature data), but exhibit the same rough correlation to the softness difference.

The low values of b found by Pauling (1947, 1960) in his early investigations of the analogous relationships between bond length and 'bond order' for bonds between the same type of atoms ($b \simeq 0.30$ Å for metals, $b \simeq 0.26$ Å for C—C bonds) may be tentatively interpreted as a further line of evidence that bonds between particles of equal softness are characterized by a low value of b.

3. Influence of higher coordination shells: the example Li—O

Any practical use of correlations between bond-valence parameters and the softness of a bond requires that the b values at least for some atom pairs can be determined reliably. Besides different criteria for the selection of reliable crystallographic reference data, the large deviations of literature values of b values from the general trend are mostly caused by differing and in some cases inappropriate boundary conditions. A crucial role in the process of bond-valence determinations is the decision which anions X^{z-} in the environment of a cation A^+ should be considered as interacting with A^+ and thus contribute to its valence sum. The so far common convention to include only nearest-neighbouring counterions might even provoke a fundamental indefiniteness of b, if all the reference compounds contain the same symmetric coordination polyhedron. Equivalent descriptions could then be found for any value of b by adjusting R_0. Indeed symmetric coordinations with central ions on highly symmetrical special positions tend to be preferred as reference data in literature determinations of bond-valence parameter sets, because of the (apparently) higher precision in the determination of bond lengths.

The influence of different choices of the distance $R_{cut\text{-}off}$ up to which an anion should be considered as interacting with the central cation has been investigated in detail in this work for the case of bonds between Li^I and O^{II} from 96 Li coordinations in room-temperature structures of fully ordered ternary compounds with O^{II} as the only anion. All crystal structure data were extracted from the Inorganic Crystal Structure Database (1997) using the crystallographic agreement index ($R \leq 0.04$), but not the symmetry of the coordination as the main criterion. Another *ca* 20 Li^+ coordinations with comparable agreement indices were omitted in the final refinements since they lead to strongly deviating bond-valence sums for any choice of $R_{cut\text{-}off}$. Some of these structure determinations (or at least the entries in the ICSD) were obviously wrong, but a detailed investigation of the reasons for deviations was considered to be beyond the limits of this study. The choice of this special atom pair effectively resulted from the practical need for accurate Li—O parameters in order to model the transport pathways ion conduction in fast Li^+ ion conductors (Adams & Swenson, 2001*a*). Li—O may on the other hand be regarded as a typical case with respect to *e.g.* the bond type which is intermediate between ionic and covalent. At the same time the choice of two main group elements with a clear designation of valence states avoids complications that might arise from special electronic effects in transition metal complexes (*cf.* Brown, 1997).

For the given set of Li environments the maximum interaction distance $R_{cut\text{-}off}$ was varied systematically up to 6 Å and bond-valence parameter sets (R_0, b) were determined by least-

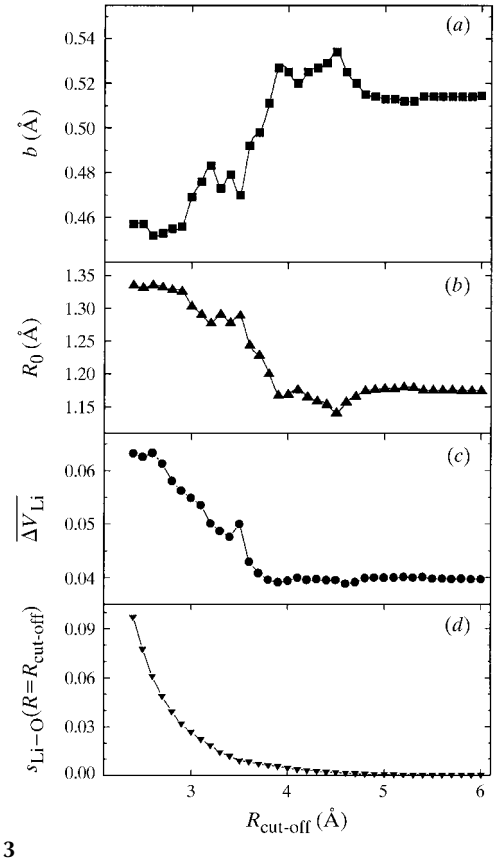

Figure 3
Consequences of different choices for the cut-off radius $R_{cut\text{-}off}$ on the refinement of bond-valence parameters for Li—O bonds for a set of 96 reference data sets: (*a*) refined BV parameter b; (*b*) BV parameter R_0; (*c*) average valence-sum mismatch for the refined structures; (*d*) bond valence for a bond distance that equals $R_{cut\text{-}off}$.

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squares refinement of the valence-sum deviation from its ideal value $V(\mathrm{Li}) = 1$ for each value of $R_{\text{cut-off}}$. The restriction to reference compounds with O^{II} as the only anion is a natural consequence of the presupposition that all anions up to a distance of $R_{\text{cut-off}}$ contribute to the valence sum of Li^{+}.

As demonstrated in Fig. 3(*a*), the choice of $R_{\text{cut-off}}$ significantly affected the refined values of b for the chosen set of Li coordinations. The refined values of $b(\mathrm{Li-O})$ significantly decrease with decreasing cut-off radius (but remain > 0.37 Å even for the lowest cut-off radii). The dependence of b on $R_{\text{cut-off}}$ slightly varies with the investigated atom pair and structural details of the selected reference compounds, but generally cut-off radii which are too small tend to produce smaller b values. This is an example of a self-fulfilling prophesy. A cut-off radius which is too small is veiled by a stronger apparent increase of bond strength with decreasing bond length, so that the missing part of the valence sum is ascribed to the short bonds within $R_{\text{cut-off}}$. While the same argument might in principle also apply *vice versa*, it is obvious that the weakness of the contributions of distant interactions will lead to a convergence of b for sufficiently high cut-off radii. The decrease of the refined value of R_0 with increasing $R_{\text{cut-off}}$ shown in Fig. 3(*b*) simply compensates the increase of b. The application of any of these parameter pairs (R_0, b) will produce reasonable estimates of the actual bond-valence sum, if the suitable cut-off convention is used. However, Fig. 3(*c*) reveals that including more atoms than the nearest neighbours also affects the accuracy of bond-valence parameters: the average deviation of the lithium valence sum from the formal valence of lithium $V_{\text{ideal}} = 1$

$$\overline{\Delta V_{\mathrm{Li}}} = \left\{ (1/n) \sum_{i=1}^{n} [V(i) - 1]^2 \right\}^{1/2} \qquad (10)$$

for our set of reference data significantly decreased with increasing cut-off radius from about 0.07 v.u. (if only the nearest neighbours were considered) down to *ca* 0.04 v.u. for $R_{\text{cut-off}} \simeq 4$ Å. For higher cut-off radii the average valence sum mismatch $\overline{\Delta V_{\mathrm{Li}}}$ remained almost constant. Thus, an underestimation of $R_{\text{cut-off}}$ significantly decreases the accuracy of the results, while an overestimation has almost no negative effect apart from the unnecessary high number of minute contributions that have to be summed up. Since it will be hardly possible to determine ideal cut-off radii from diffraction data for all atom pairs, bond-softness sensitive bond-valence tables should be built on cut-off radii which are too high rather than too small.

The decrease of the bond valence for bond distances equal to $R_{\text{cut-off}}$ is displayed in Fig. 3(*d*). This may be interpreted as a measure for the error introduced by neglecting interactions between more distant atom pairs. While these contributions for a single atom pair appear rather small at first sight, it should be kept in mind that higher coordination shells may contain numerous bonds of equal length so that the sum of these contributions may still be relevant.

As shown in Fig. 4, the increased significance in the determination of b by the use of higher cut-off radii is also evident from plots of the optimum bond-valence parameter R_0 and of the corresponding minimum average valence mismatch *versus* a range of fixed BV parameters b for two different choices of the cut-off radius. $R_{\text{cut-off}} = 2.67$ Å equals the value used by Brown & Altermatt (1985) in their determination of $R_0(L-\mathrm{O})$ assuming a fixed $b = 0.37$ Å (Brown, 2000), whereas $R_{\text{cut-off}} = 6$ Å has been chosen as it was the maximum value used in this study. While too small values for b result in a comparably low quality of the refinement ($\overline{\Delta V_{\mathrm{Li}}} \simeq 0.10$) for both cut-off radii, the improvement of the fit for the respective optimum b is more pronounced for the higher cut-off radius. Fig. 4 also demonstrates that the deterioration of $\overline{\Delta V_{\mathrm{Li}}}$ for values of b which are too high is less prominent than for values which are too low.

The distribution of bond lengths in our reference data is indicated in the upper diagram of Fig. 5, where the number of O^{II} atoms within a certain distance interval ($R \pm 0.025$ Å) from Li^{I} is plotted *versus* the centre of this distance interval (averaged over all 96 Li coordinations of the data set). Coordination shells should be perceptible as peaks in this graph. The lower end of the plateau of $\overline{\Delta V_{\mathrm{Li}}}$ at *ca* 4 Å (*cf.* Fig. 3*c*) coincides with the upper limit of the second coordination shell. A constant value of b is reached, when all the interactions to O atoms of the third coordination shell up to *ca* 5 Å are taken into consideration. Therefrom it may be deduced that the inclusion of the weak interactions with counterions of the second coordination shell is definitely required (in the case of Li—O bonds) and an inclusion of higher coordination shells

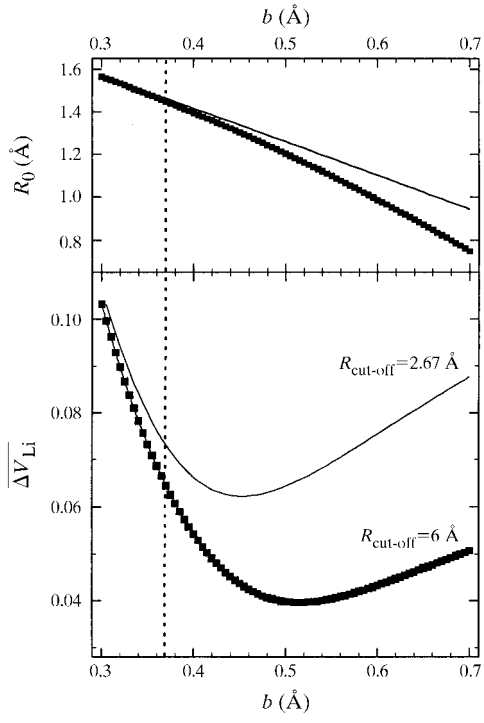

Figure 4
Dependence of the optimum bond-valence parameter R_0 (upper diagram) and of the resulting average valence mismatch (lower diagram) on the choice of the parameter b for two different cut-off radii (squares: $R_{\text{cut-off}} = 6$ Å, thin solid line: $R_{\text{cut-off}} = 2.67$ Å). The broken line indicates the value $b = 0.37$ Å.

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makes the refinement more stable. Over 11% of the Li valence sum determined with $R_{\text{cut-off}} = 6$ Å is due to Li—O interactions with $R > 2.67$ Å. Interactions with $R > 4$ Å contribute only *ca* 3% to the total valence sum and thus appear to be on the borderline of significance. At the same time the average number of individual bonds that contribute to the valence sum of a single Li increases from *ca* five nearest neighbours (since the data set contained Li^+ in both tetrahedral and octahedral coordinations) to ~15 up to the second and >30 up to the third coordination shell (*cf.* bottom part of Fig. 5).

As an additional check of the reliability of our refinement, a similar refinement has been performed for the 'coordinations' around a central O^{II}. This refinement required a different set of reference data, to ensure that the complete valence sum of O^{II} originates from bonds to Li^{I}. However, the number of ternary compounds with Li^{I} as the only cation was too small for a meaningful refinement. The only way out was the choice of structures with only a single crystallographic site for oxygen. Then at least the fraction of the oxygen valence sum that originates from bonds to lithium should be obvious from the stoichiometry. For 49 environments of O^{II} ions we found practically the same refinement results ($b = 0.52$ Å, $R_0 = 1.63$ Å for $R_{\text{cut-off}} = 6$ Å), but the refinements were less conclusive, as it was possible to shift the refined value of b in the range $0.48 < b < 0.54$ Å by the omission of a single O^{II} environment.

Applications of bond-valence parameters in our studies on ion transport pathways in solid electrolytes (*cf.* Adams & Swenson 2000, 2001*b*; Swenson & Adams, 2001) substantiate the usefulness of bond-valence parameters that have been determined using large cut-off radii. The calculation of valence sums for mobile ions at extremely asymmetrically coordinated interstitial sites and the investigation of ionic motion can only yield sensible results if the contributions from higher coordination shells are included (*e.g.* to avoid nonphysical stepwise changes of the valence sum, if the ion passes a doorway between two coordination polyhedra). In full agreement with our results, the relevance of bonds beyond the first coordination shell has also been suggested in a recent study on pathways for the anisotropic electronic conduction in cetineites (Liebau, 2000) as well as in a study on the connection between the bond-valence approach and Coulomb interactions (Preiser *et al.*, 1999).

4. Softness-sensitive bond-valence parameters for alkali halides and chalcogenides

As demonstrated in the previous sections, bond-valence parameter sets are empirically related to the softness of a bond, which may be expressed as the difference of the softnesses of interacting particles. For the advantageous case of Li—O, where a sufficient number of different Li coordinations is available from the ICSD structure database, the refinement leads to a well defined optimum parameter set, if the weak contributions of higher coordinaton shells are taken into consideration. Following the same procedure as for Li—O bonds, it should in principle be possible to establish a consistent set of (bond softness sensitive) bond-valence parameters for bonds between alkali ions and various halide or chalcogenide ions, which had been the original aim of this study.

Despite the high total number of alkali coordinations in the study (688 halide coordinations and 836 chalcogenide coordinations in the final refinements; *ca* 15% additional coordinations have been eliminated because of their strange bond-valence sums), for some of the atom pairs the number of cation coordinations were still rather low ranging from 125 for Na–O down to only 3 for Rb–Te. In most cases fully ordered room-temperature structures with agreement indices $R < 0.05$ were selected as reference data, but for some of the less frequent cation–anion pairs slightly higher agreement indices (up to $R = 0.07$) were also accepted. Cut-off radii in the range 6–8 Å have been used to ensure that the influence of the weak interactions of long 'bonds' are not overlooked. A cut-off radius x was assumed to be sufficiently high, if the sum of all contributions from interactions with $x < R < x + 1$ Å was less than 1% of the valence sum. The results of the refinements are summarized in Table 1.

The free refinement of bond-valence parameters for bromide-coordinated Na^{I} (from nine reference coordinations) completely failed, but for all other atom pairs free refinements of both b and R_0 resulted in values for b that increase with increasing softness difference in full accordance with the general trend for halides and chalcogenides discussed in §2 (*cf.* Fig. 6). Due to the lower statistical scatter of our refinements,

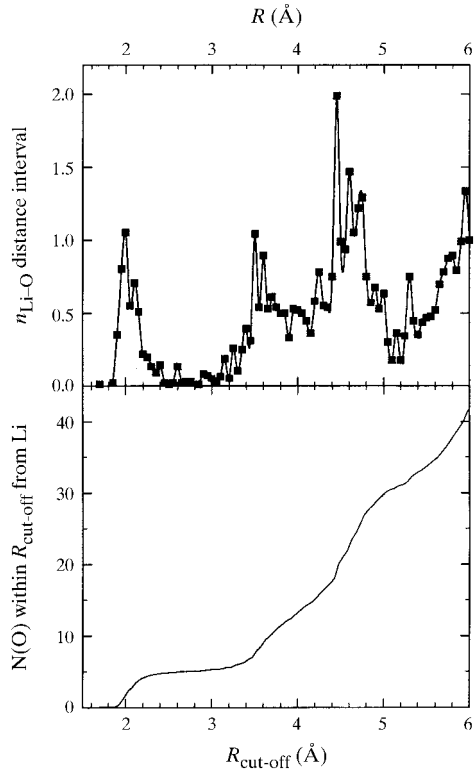

Figure 5
Number of O atoms within the distance interval $R \pm 0.025$ Å from a Li (top); bottom: number of O atoms within a sphere of radius $R_{\text{cut-off}}$ around a Li (bottom). Data are averaged over all 96 Li environments of the reference data.

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Table 1
Bond-valence parameters b, R_0 refined for alkali chalcogenides using a cut-off radius of $R_{\text{cut-off}}$.

The softnesses σ'_X of anions and σ_A of cations are calculated by the formalism described in the text. The free refinement of n cation environments leads to the BV parameters b and R_0, whereas b' is the value determined from the correlation between bond softness ($\sigma'_X - \sigma_A$) and the freely refined values of b shown in Fig. 8. R'_0 is the fit result for the same data set of n cation coordinations and the same cut-off radius $R_{\text{cut-off}}$ when fixing b to b'. ΔV (and $\Delta V'$) denote the average bond-valence sum mismatch for the chosen reference systems when R_0 and b are refined freely (or for b fixed to b').

$A-X$	$\sigma'_X - \sigma_A$ (eV^{-1})	n	b (Å)	R_0 (Å)	ΔV (v.u.)	$R_{\text{cut-off}}$ (Å)	b' (Å)	R'_0 (Å)	$\Delta V'$ (v.u.)
(*a*)									
Li—O	0.11905	96	0.515	1.1725	0.0396	6	0.514	1.1745	0.0396
Na—O	0.10007	125	0.483	1.5602	0.0871	6	0.475	1.5766	0.0871
K—O	0.07424	52	0.422	1.9729	0.0895	6	0.430	1.9548	0.0896
Rb—O	0.06099	44	0.425	2.0573	0.0563	7	0.415	2.0812	0.0564
Cs—O	0.04370	38	0.403	2.2985	0.0781	7	0.408	2.2862	0.0781
Li—S	0.19586	13	0.632	1.5070	0.0401	6	0.656	1.4607	0.0401
Na—S	0.17688	92	0.621	1.8311	0.0829	6	0.626	1.8213	0.0829
K—S	0.15105	40	0.571	2.1711	0.0630	7	0.580	2.1516	0.0630
Rb—S	0.13780	29	0.552	2.3011	0.0481	7	0.553	2.2991	0.0481
Cs—S	0.12051	41	0.522	2.5147	0.0640	7	0.517	2.5253	0.0640
Li—Se	0.21320	5	0.735	1.5296	0.1036	7	0.681	1.6272	0.1043
Na—Se	0.19422	70	0.660	1.8787	0.0526	7	0.654	1.8908	0.0526
K—Se	0.16389	53	0.624	2.2569	0.0579	7	0.612	2.2811	0.0579
Rb—Se	0.15514	19	0.581	2.4015	0.0973	7	0.587	2.3886	0.0973
Cs—Se	0.13785	37	0.546	2.6568	0.0790	7	0.553	2.6424	0.0790
Li—Te	0.23869	7	0.717	1.7340	0.0738	7	0.717	1.7340	0.0738
Na—Te	0.21970	46	0.684	2.0518	0.0666	7	0.690	2.0400	0.0666
K—Te	0.19387	20	0.662	2.3926	0.0532	7	0.653	2.4102	0.0532
Rb—Te	0.18062	3	0.615	2.4600	0.0160	8	0.633	2.4175	0.0160
Cs—Te	0.16333	6	0.617	2.7360	0.0762	8	0.603	2.7647	0.0762
(*b*)									
Li—F	0.11415	52	0.501	1.1011	0.0438	6	0.503	1.0968	0.0438
Na—F	0.09517	51	0.475	1.4262	0.0312	6	0.465	1.4485	0.0312
K—F	0.07328	104	0.422	1.8472	0.0555	6	0.429	1.8307	0.0555
Rb—F	0.05609	15	0.418	1.9572	0.0509	6	0.412	1.9718	0.0509
Cs—F	0.03880	51	0.411	2.1955	0.0558	7	0.410	2.1980	0.0558
Li—Cl	0.18542	15	0.661	1.3418	0.0535	6	0.640	1.3873	0.0536
Na—Cl	0.16640	21	0.603	1.6940	0.0295	6	0.608	1.6833	0.0295
K—Cl	0.14060	52	0.552	2.0866	0.0483	6	0.559	2.0707	0.0483
Rb—Cl	0.12735	67	0.540	2.2443	0.0560	7	0.531	2.2653	0.0561
Cs—Cl	0.11006	78	0.481	2.5046	0.0947	7	0.495	2.4715	0.0948
Li—Br	0.20822	13	0.665	1.5340	0.0519	7	0.674	1.5150	0.0519
Na—Br	0.18923	9	–	–	–	–	0.646	1.7719	0.0236
K—Br	0.16340	20	0.625	2.1001	0.0498	7	0.603	2.1529	0.0502
Rb—Br	0.15015	31	0.579	2.3272	0.0720	7	0.578	2.3296	0.0720
Cs—Br	0.13286	39	0.538	2.5152	0.0630	7	0.543	2.5035	0.0630
Li—I	0.24210	11	0.723	1.6733	0.0493	7	0.722	1.6754	0.0493
Na—I	0.22311	4	0.688	1.9694	0.0191	7	0.695	1.9555	0.0191
K—I	0.19729	16	0.641	2.3202	0.0503	7	0.658	2.2821	0.0504
Rb—I	0.18404	23	0.631	2.4667	0.0706	7	0.638	2.4509	0.0707
Cs—I	0.16674	31	0.608	2.6951	0.0406	8	0.609	2.6926	0.0406

The polynomial fit of $b(\sigma'_X - \sigma_A)$ in Fig. 8 corresponds to $b' = 0.493904 - 4.2696794x + 63.9043368x^2 - 270.8903908x^3 + 395.87511x^4$, where $x = \sigma'_X - \sigma_A$.

Fig. 6 moreover demonstrates that for the same softness difference alkali halides exhibit a slightly higher b than alkali chalcogenides. This may be interpreted as resulting from the low-level estimate of the anion softnesses by their identification with the softness of the respective neutral atoms. This approximation seems to overestimate the softness of the doubly charged chalcogenide ions slightly (or more exactly: overestimates the softness of the doubly chalcogenides slightly more than it overestimates the softness of the singly charged halides). From a simple comparison with the charging energy of spheres of different radii, it may be assumed that the anion softness should be proportional to the anion radius and independent of the charge (*cf.* Pearson, 1988). Shannon radii for the series of halide ions X^- or chalcogenide ions X^{2-} (in sixfold coordinations) indeed closely follow this relationship, but the softness of the chalcogenide ions [as estimated according to (9) for neutral chalcogen atoms] is $\sim$0.017 eV^{-1} higher than that of a halide with a comparable radius (*cf.* Fig. 7). Estimates for the softness of anions which are derived from data for the respective neutral atoms should be more

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accurate for singly charged anions than for doubly charged anions. If the apparent shift of the *softness-versus-anion radius* relationship can be interpreted as an artifact due to the imperfect approximation $\sigma_{\rm anion} \simeq \sigma_{\rm neutral\ atom}$, then a more appropriate estimate of the anion softness should result from $\sigma'_X = \sigma_X - 0.017\ {\rm eV}^{-1}$ for the doubly charged anions and $\sigma'_X = \sigma_X$ for the singly charged anions. (An analogous argument suggests that the softnesses for the monovalent anions are also slightly overestimated. Such a further correction of all anion softnesses would simply shift the whole correlation shown in Figs. 2 and 6 slightly to the left and thus bring its minimum closer to the value of zero expected from the HSAB concept.)

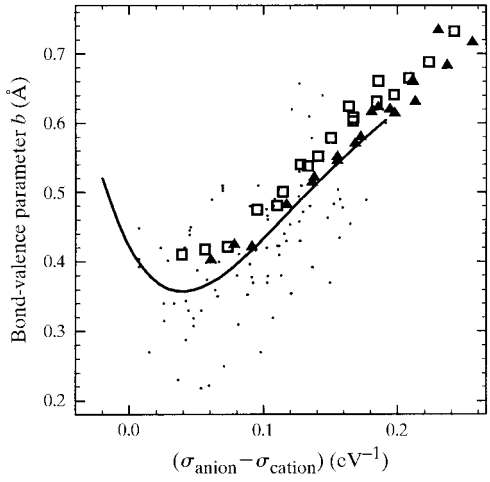

Figure 6
Variation of the bond-valence parameter b as a function of the difference between the softnesses of anions and cations for alkali halides (squares) and alkali chalcogenides (triangles) as refined in this work, taking into account anion–cation distances up to 6–8 Å depending on the atomic radii sum. The solid line represents the polynomial fit to the literature data of Fig. 2 (data shown as dots).

When the softness differences for alkali halides and chalcogenides are calculated using the modified anion softness σ'_X, the correlations between the BV parameter b and the softness differences for the two classes of compounds agree within experimental scatter (*cf.* Fig. 8). This permits the calculation of a general relationship between the softness difference $(\sigma_{\rm anion} - \sigma_{\rm cation})$ and the bond-valence parameter b, which is displayed in Fig. 8 as a fourth-order polynomial fit to all data. In this fit each data point is weighted by the square root of the number of cation coordinations that have been used in its determination.

This correlation permits a recalculation of the values of R_0 with b fixed to the value b' resulting from the polynomial fit in Fig. 8; *i.e.* with a value of b that varies systematically with the softness difference (*cf.* Table 1). The average adjustment of b amounts to only 0.010 Å, except for the worst case Li–Se, where a free refinement of (R_0, b) from only five reference data sets yielded b = 0.735 Å, whereas the polynomial fit predicts an expected value of b' = 0.681 Å. The relationship between b and the softness difference moreover permits the estimation of b for the atom pair Na–Br (where the limited number and quality of the data did not permit a free refinement of both BV parameters). Using this calculated value b'(Na–Br), a plausible value for R_0 (1.772 Å) was observed from the refinement (with an average valence-sum deviation of only 0.024 v.u. for the nine reference data sets).

An impartial criterion for judging the plausibility of bond-valence parameters is their connection to other known properties of the interacting particles. The property of the particles that is most evidently connected with R_0 is the sum of their radii. Since for most atom pairs the actual type of bonding is intermediate between purely ionic and covalent, it is not as obvious which type of radii should be used. The present approach treats the interatomic forces as localized bonds between pairs of atoms and accounts for differences in the

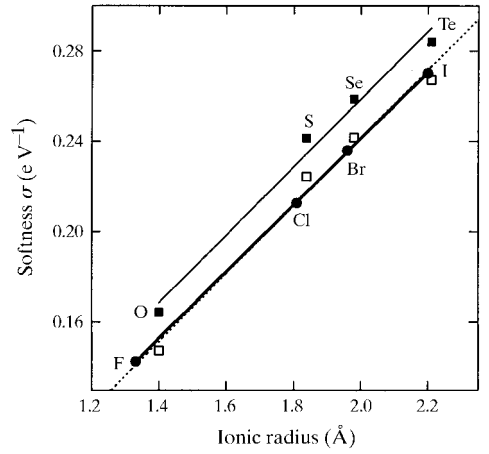

Figure 7
Correlation between the anion radius (Shannon radius for sixfold coordination) for chalcogenides X^{2-} (full squares) and halides X^- (full circles) and the estimates of anion softnesses (*i.e.* the softnesses of the respective neutral atom). The two linear relations (shown as solid lines) become congruent if the softnesses of the doubly charged chalcogenide ions are modified according to $\sigma' = \sigma - 0.017\ {\rm eV}^{-1}$.

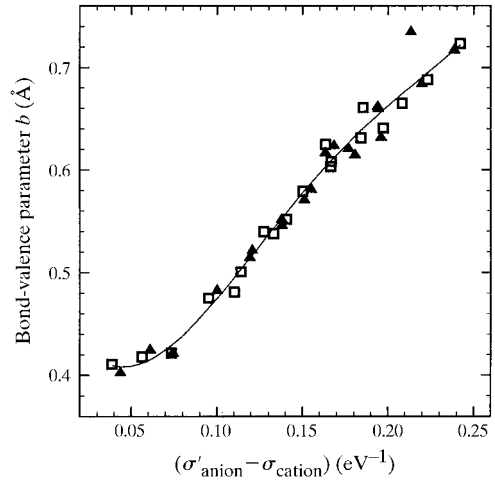

Figure 8
Variation of the bond-valence parameter b as a function of the difference between the modified anion softness $\sigma'_{\rm anion}$ = ($\sigma_{\rm anion}$ for X^- anions, $\sigma_{\rm anion}$ −0.017 eV^{-1} for X^{2-} anions) and the softness of the cation for the alkali halides (squares) and alkali chalcogenides (triangles). Same data as in Fig. 6. Solid line: weighted polynomial fit to all data.

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abilities to attract the electrons by an adjustment of the parameter b. Moreover, the treatment of interatomic interactions as covalent bonds is effectively the more general approach as the solution of the Schrödinger equation (required to describe covalent bonds) includes the special case of dominating Coulomb forces (see *e.g.* Bader, 1990). Thus, for a general correlation it might be more appropriate to relate R_0 to the sums of covalent or atomic radii rather than of ionic radii.

The left-hand side of Fig. 9 compares the values of R_0 resulting from various refinement approaches with theoretical atomic radii, as calculated by Clementi *et al.* (1963) using self-consistent-field functions. It is known that these radii are related to the radii of the maximum charge density in the outermost shell of the atom (*cf.* Winter, 2000). Empirical covalent radii were taken from the database of the Molecular Modeling program *Cerius*^{2} 2.0 (Molecular Simulations Inc., 1995). The sum of radii of the interacting atoms exhibits a pronounced correlation to the refined values of R_0 for both radii tables. In comparison to R_0 parameters determined presuming a fixed b = 0.37 Å (taken from the program *VALENCE* by Brown, 1996), the significance of the correlation between the radii sum and R_0 values from free refinements of (R_0, b) is considerably higher. A further minor increase of the statistical significance is achieved if the radii sums are related to values of R_0 refined assuming the values of b from the correlation between b and the softness difference (*cf.* Fig. 8).

5. Conclusions

For many of the elementary tasks such as checking the plausibility of structure determinations from bond length tables, it will remain more convenient to use the established bond-valence tables, which were built on the convention that only the nearest neighbours contribute to the bond valence. Therefore, it was not the aim of this work to replace these bond-valence parameter tables. Nevertheless, it is shown that using the correlations discussed in this work chemically more meaningful bond-valence pseudopotential parameters can be derived with a limited additional effort.

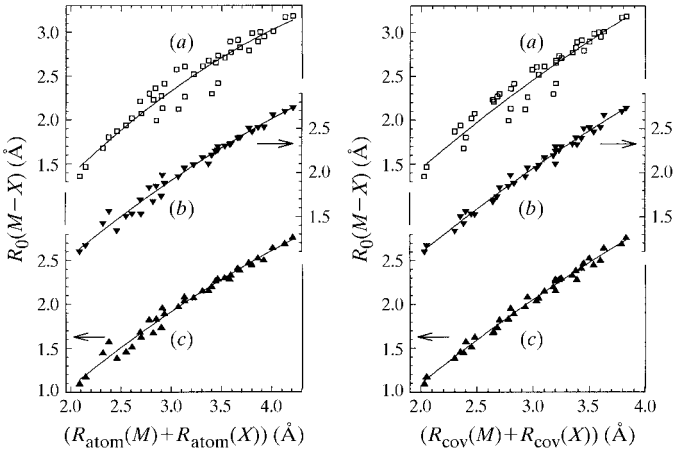

Figure 9
Comparison of the correlation between the bond-valence parameter R_0 and the sum of the radii of M and X; left: calculated 'atomic radii' after Clementi *et al.* (1963) and Winter (2000); right: empirical covalent radii as used in the *Cerius*^{2} software (Molecular Simulations Inc., 1995). The values of R_0 are taken (*a*) from the database of the program *VALENCE* (Brown, 1996) (for fixed b = 0.37 Å under the assumption that only the first coordination shell contributes to the bond-valence sum); (*b*) from the joint free refinement of R_0 and b in this work; (*c*) from a refinement of R_0 with b fixed to the value determined from the polynomial fit in Fig. 8.

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