

*Bond softness-sensitive bond valence parameters for crystal structure plausibility tests*Stefan Adams¹, Haomin Chen¹¹National University Of Singapore Mater. Sci. & Eng., Singapore, Singapore

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Based on a description of bond valence as functional of valence electron density a systematic bond softness sensitive approach to determine bond valence parameters and related quantities such as coordination numbers is elaborated and applied to determine consistent sets of bond valence parameters for ca. 700 cation-anion pairs under three distinct conventions regarding the variability of the bond softness parameter b and on the interactions that contribute to the bond valence sum from an identical pool of reference crystal structures:

(i) Softness sensitive variable b values adapted from the softBV parameter set [1] factoring in effects of higher coordination shells. The results can be understood as a slightly updated version of our softBV parameter set. This parameter set was mainly developed for the modeling of ion transport in solids [2,3], but has so far only been reluctantly adopted for the traditional purpose of checking the plausibility of crystal structures.

(ii) A new softCN1 parameter set is determined retaining the same softness sensitive b values as for the softBV parameter set, but refining R_0 values under the assumption that only interactions of the first coordination shell contribute to the bond valence sum. This involves introducing a systematic determination of the limits of the first coordination shell that takes into account the coordination number. While the approach used for this softCN1 parameter set is closely related to our earlier softBV parameter set, the parameters proposed here may be easier to apply in plausibility checks of crystal structures, as they follow the first coordination shell convention.

(iii) A benchmarking parameter set is determined based on the conventional choice $b = 0.37 \text{ \AA}$ again refining R_0 values under the assumption that only the first coordination shell contributes to the bond valence sum. The limits of the first coordination shell are kept the same as found for case (ii).

A comparison of the standard deviations of the bond valence sums within the reference structure sets when applying the three different conventions clearly shows the superiority of using a bond-softness adapted bond valence parameter set (case i or ii) over the classical parameters with fixed value of b , which perform well only for relatively hard anions (such as O^{2-} and F^-) and cations. The lowest standard deviation is found if the influence of the contributions from higher coordination shells is factored in, but the difference between conventions (i) and (ii) is small enough so that it may be justified to use the smaller

[1] Adams, S. (2014) in "Bond Valences" (I.D. Brown, K.R. Poeppelmeier eds.), Springer Berlin Heidelberg, Structure and Bonding 158, 91-128. (doi:10.1007/430_2013_96)

[2] Adams, S. and Prasada Rao, R. (2014) in "Bond Valences" (I.D. Brown, K.R. Poeppelmeier eds.), Springer Berlin Heidelberg, Structure and Bonding 158, 129-128. (doi:10.1007/430_2013_96)

[3] Wong, L.L., Chen, H. & Adams, S. (2017) Phys. Chem. Chem. Phys. (2017) in press (doi: 10.1039/C7CP00037E)

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