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New and refined bond valence parameters for $\text{Te}^{4+}\text{-F}^-$, $\text{Te}^{4+}\text{-S}^{2-}$ and $\text{Te}^{4+}\text{-Se}^{2-}$ ion pairs

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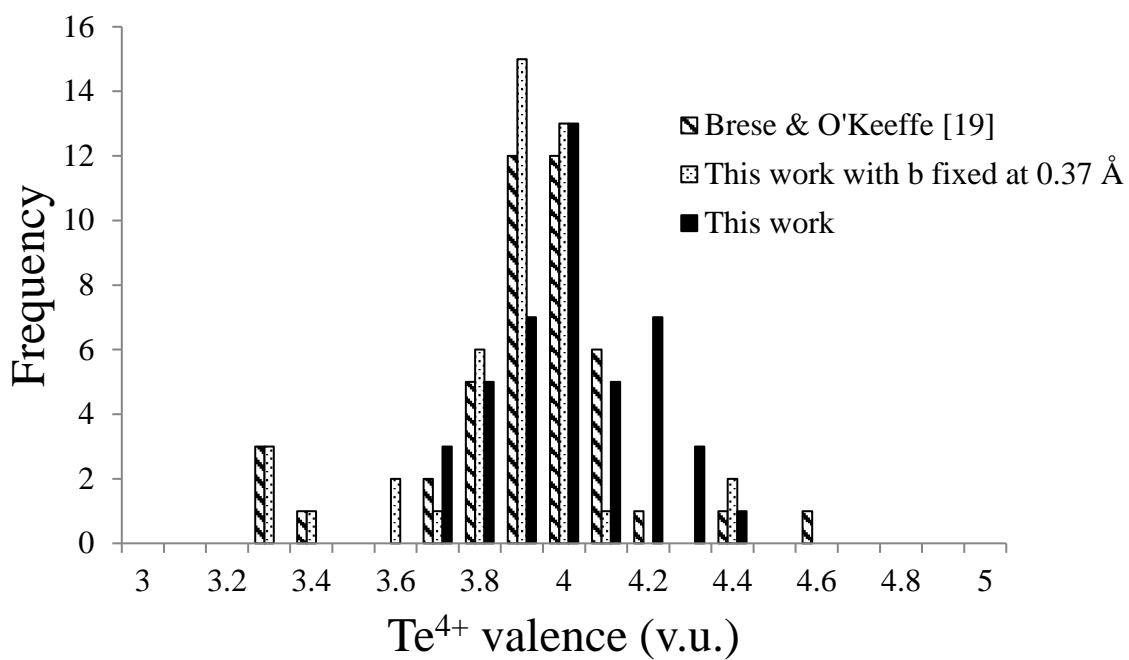
Abstract.

New and refined bond valence parameters related to ion pairs constituted of the tellurium Te^{4+} cation and non-oxide X^{n-} anions ($\text{X} = \text{F}, \text{S}$ or Se) are proposed. After a selection of specific crystalline structures, the optimization of the bond valence parameters R and b with a cutoff distance is carried out by minimizing the root mean square deviation of the Te^{4+} cation valence. The results are $R = 1.728 \text{ \AA}$ and $b = 0.622 \text{ \AA}$ with *cutoff* = 5.3 \AA for the $\text{Te}^{4+}\text{-F}^-$ pair and $R = 2.444 \text{ \AA}$ and $b = 0.387 \text{ \AA}$ with *cutoff* = 4.5 \AA for the $\text{Te}^{4+}\text{-S}^{2-}$ pair. These parameters lead to a lower dispersion of the calculated valences around the formal valence compared to that obtained with the parameters available in the literature. As for the new set related to the $\text{Te}^{4+}\text{-Se}^{2-}$ pair, we find $R = 2.578 \text{ \AA}$ and $b = 0.296 \text{ \AA}$ with *cutoff* = 3.7 \AA .

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Short summary of max. 250 characters and a figure for the Table of Contents.

New and refined bond valence parameters for $\text{Te}^{4+}\text{-X}^{n-}$ ion pairs are proposed ($X = \text{F}, \text{S}$ or Se). The results are $R = 1.728 \text{ \AA}$ and $b = 0.622 \text{ \AA}$ with $\text{cutoff} = 5.3 \text{ \AA}$ for the $\text{Te}^{4+}\text{-F}^-$ pair ; $R = 2.444 \text{ \AA}$ and $b = 0.387 \text{ \AA}$ with $\text{cutoff} = 4.5 \text{ \AA}$ for the $\text{Te}^{4+}\text{-S}^{2-}$ pair ; $R = 2.578 \text{ \AA}$ and $b = 0.296 \text{ \AA}$ with $\text{cutoff} = 3.7 \text{ \AA}$ for the $\text{Te}^{4+}\text{-Se}^{2-}$ pair.



1 Introduction

The bond valence sum rule is widely used in crystal chemistry as a verification and predictive tool for crystalline structures [1]. The valence of an ion i is calculated by adding up the bond valences S_{ij} between i and its neighbouring ions j of opposite charge, by applying the Brown and Altermatt [2, 3] relation given by:

$$S_{ij} = \exp\left(\frac{R_{ij} - d_{ij}}{b}\right)$$

Where d_{ij} is the bond length and R_{ij} is a parameter specific to the i - j pair whose value is the bond length corresponding to one valence unit. The parameter b is often considered as a universal constant equal to 0.37 Å so that R_{ij} is expressed as follows:

$$R_{ij} = b \times \ln\left(\frac{V_i}{\sum_j \exp\left(-\frac{d_{ij}}{b}\right)}\right)$$

Where V_i is the valence of the ion i , *i.e.* its formal oxidation state. R_{ij} is generally determined and used by dealing with a cutoff distance beyond which an anion is no longer considered to be bonded to a cation; in practice a *cutoff* value of about 3 Å is often used [1, 4].

Several authors recommended to use different values for the parameter b [5-9]. Adams [5] has shown that the value of b depends on the chosen cutoff distance. In particular, the parameters determined relying on the first and second coordination shells can differ significantly from those determined using only the first coordination shell while adding the third and fourth coordination shells does not modify the parameters. Chen and Adams [10] emphasized that the first coordination shell can be an effective quantity to improve the bond valence parameters of a cation-anion pair by revising the parameter R while keeping the same parameter b value from Adams [5, 6]. Other studies notably focused on structures that contain cations carrying lone electron pairs (see [11-17]). The Te^{4+} cation belongs to this category and the determination of accurate bond valence parameters mainly focused on the most common Te^{4+} - O^{2-} linkages [2, 6, 7, 9, 10, 18] in addition to linkages with other anion types such as Cl^- [6, 10, 18, 19], Br^- [6, 10, 20] or I^- [6, 10, 21]. As outlined below, handling R , b and *cutoff* allows us to tend towards valences closer to those theoretically expected and to ensure the validity of structures previously considered questionable.

In this paper, we propose bond valence parameters for the Te^{4+} - F^- , Te^{4+} - S^{2-} and Te^{4+} - Se^{2-} ion pairs. For Te^{4+} - F^- , we aim at improving the parameters with respect to the only set established by Brese & O'Keeffe back in 1991 [19]. For Te^{4+} - S^{2-} , the unique parameter set available to us is from a private communication from Brown that should be used with caution according to the author himself [20]. For Te^{4+} - Se^{2-} , to the best of our knowledge no valence parameters exist in the literature.

In section 2, we present the method used to determine these three parameter sets. In section 3, we discuss the results following the application of these new parameters to structures of inventoried crystalline phases.

2 Methodology

The crystalline structures were selected from the Inorganic Crystal Structure Database (ICSD [22]) using the following criteria:

- Entry from experimental inorganic structures;
- Data of high quality according to the ICSD, *i.e.* temperature factors given, standard deviation given for cell parameters, R-value specified, no unusual difference between calculated and measured densities;
- No hydrogen element;
- Only one anion type per structure so that the Te^{4+} valence is only influenced by the bonds with one anion type (F^- , Se^{2-} or S^{2-});
- Only one ion type per site with full occupation;
- Crystal structure determined at temperature in between 278 and 308 K and at ambient pressure;
- No interatomic distances shorter than 70% of the sum of the ionic radii (using the Shannon effective ionic radii [23]). Cation-cation, cation-anion and anion-anion distances were checked.

The bond valence parameters were determined by minimising the root mean square deviation (*RMSD*) of the valence (see [1, 9, 12, 15]):

$$RMSD = \sqrt{\frac{\sum_m (\sum_j S_{ij} - V_i)^2}{m}}$$

With m the number of non-equivalent positions of cation i in the whole selected structures. In the present work, given the very small number of structures containing only one cation type and one anion type, the bond valence sum rule is applied on Te^{4+} only, not on the anion. Thereby, the obtained bond valence parameters remain independent of other bond valence parameters involving the anion type considered and another cation type different from Te^{4+} .

3 Results and discussion

We present below the results of the bond valence parameters obtained for the three $\text{Te}^{4+}\text{-F}^-$, $\text{Te}^{4+}\text{-S}^{2-}$ and $\text{Te}^{4+}\text{-Se}^{2-}$ pairs. The details for the anion valences are gathered in the Appendix.

3.1 The case of $\text{Te}^{4+}\text{-F}^-$

The bond valence parameters were adjusted using 13 non-equivalent Te^{4+} positions from 11 structures and 2448 $\text{Te}^{4+}\text{-F}^-$ distances up to 10 Å (see Table 1, Table 2 and Figure 1). The application of the procedure reaches a minimal *RMSD* value of 0.086 for $R = 1.724$ Å, $b = 0.625$ Å and *cutoff* = 5.6 Å. These parameters lead to an average valence of 3.998 v.u. for Te^{4+} . As reported by Adams [5], the parameters R and b depend on each other, *i.e.* for a short *cutoff* (2.6 Å), a minimal R value is found so the b value increases in order to maintain valences close to 4 v.u. (see Figure 2). The optimized parameters are found when their values converge beyond a cutoff distance of 5.6 Å in that case, this value encompassing the first and second coordination shells (see Figure 1).

Table 1: Comparison of the Te^{4+} and F^- valences obtained from different parameter sets for the $\text{Te}^{4+}\text{-F}^-$ pair.

			Brese & O'Keeffe [19]	This work with b fixed at 0.37 Å	This work
			R, b, cutoff (Å)		
			1.87, 0.37, 3.7	1.861, 0.37, 3.3	1.724, 0.625, 5.6
Number of structures with one anion type	Ion type	Number of non- equivalent positions	Valence (<i>RMSD</i>)		
11	Te^{4+}	13	4.108 (0.229)	3.991 (0.198)	3.998 (0.086)
	F^-	62	1.018 (0.108)	0.998 (0.101)	1.001 (0.062)
Number of structures with one or several anion types					
33	Te^{4+}	44	3.970 (0.245)	3.920 (0.243)	4.064 (0.181)

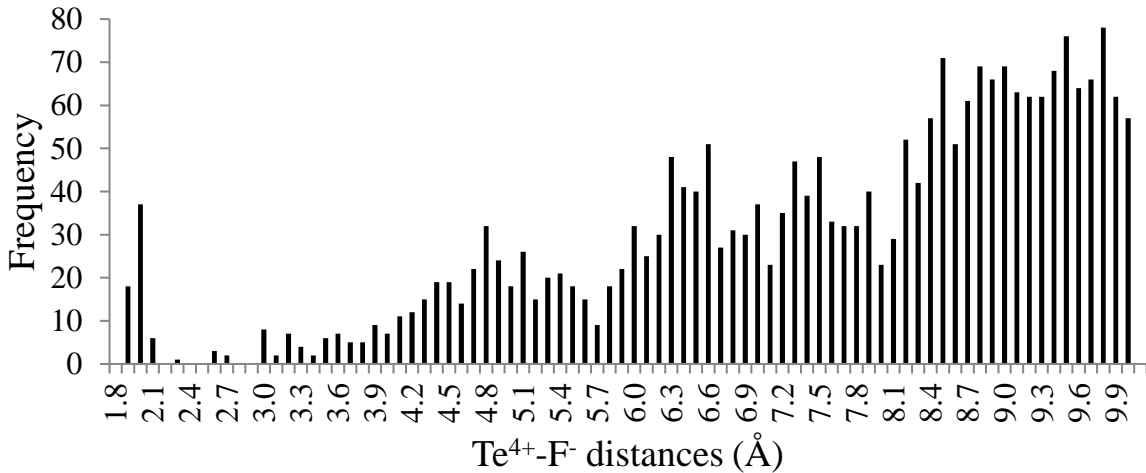


Figure 1: Distribution of the $\text{Te}^{4+}\text{-F}^-$ distances from 11 structures containing one anion type, F^- .

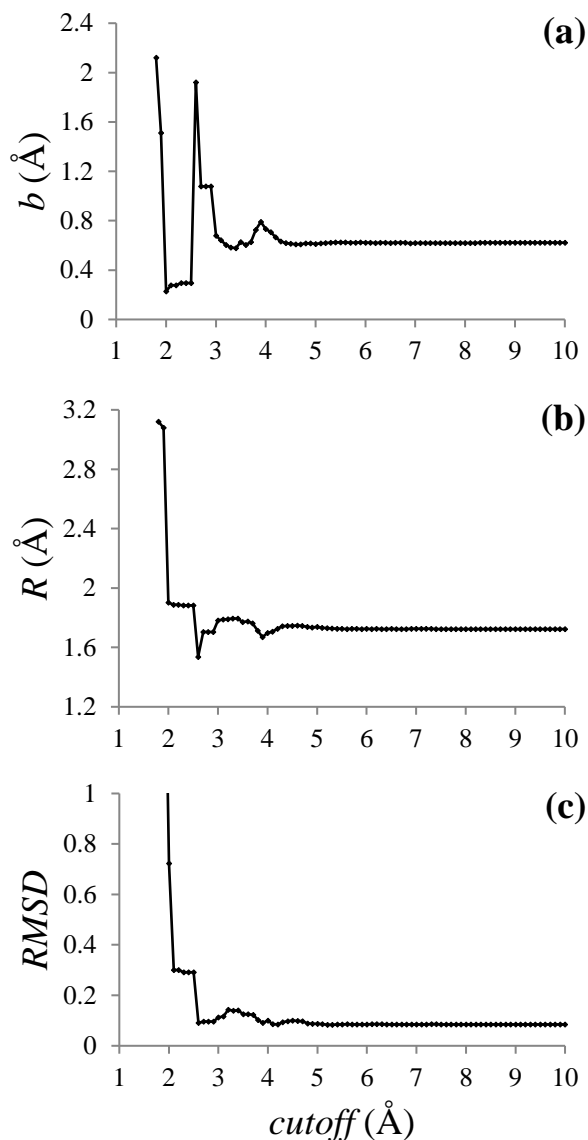


Figure 2: Influence of the *cutoff* value (a, b) on the bond valence parameters b and R and (c) on the root mean square deviation ($RMSD$) for 11 structures containing one anion type, F^- .

The parameters R , b and *cutoff* were also used to check the bond valence sums for all the anions F^- , corresponding to 62 non-equivalent positions in the 11 structures. Note that for those calculations, the bond valence parameters associated to the M^{x+} - F^- pairs (M^{x+} = cation different from Te^{4+}) were extracted from the Adams' database [6]. The average F^- valence is equal to 1.001 v.u. ($RMSD = 0.062$), very close to the formal value of 1 v.u..

Then we extended the application of this refined parameter set to structures containing more than one anion type, still considering the above selection criteria (except point d)). This corresponds to 31 additional non-equivalent Te^{4+} positions from 22 structures. The average calculated Te^{4+} valence is equal to 4.064 v.u. (with $RMSD = 0.181$) in the overall 44 positions from 33 structures.

Table 2: Comparison of the Te^{4+} valences obtained from different parameter sets for the Te^{4+} - F^- pair for 11 structures containing one anion type, F^- (colourless) and 22 structures containing several anion types (in grey).

ICSD #	Structure	Non-equivalent Te^{4+} position #	Te^{4+} valence (v.u.)		
			Brese & O'Keeffe [19]	This work with b fixed at 0.37 Å	This work
16108	Sb_2TeF_{14}	1	3.794	3.692	3.882
81862	$BaTe_2F_{10}$	1	4.136	4.020	4.141
81865	$PbTeF_6$	1	3.750	3.660	3.980
84364	KTe_2F_9	1	4.032	3.935	4.004
84364	$KTeF_5$	1	4.230	4.128	3.933
		2	4.118	4.003	3.965

85452	TeF ₄	1	4.063	3.965	4.090
88416	BaTeF ₆	1	4.100	3.935	4.095
90619	TlTeF ₅	1	4.134	4.035	3.941
200252	CsTeF ₅	1	4.618	4.499	4.103
202879	NaTeF ₅	1	4.199	4.049	4.015
203140	RbTeF ₅	1	4.195	4.085	3.979
		2	4.037	3.882	3.847
3345	BaWTeO ₅ F ₂	1	4.098	4.097	4.282
3346	BaMoTeO ₅ F ₂	1	4.094	4.093	4.279
82162	Te ₂ O ₃ F ₂	1	3.979	3.949	4.223
		2	3.936	3.895	4.165
88415	TeOF ₂	1	3.897	3.835	4.336
		2	3.362	3.319	3.897
95727	KTe ₃ O ₆ F	1	3.905	3.901	4.065
141869	Co ₁₅ Te ₁₄ O ₄₂ F ₂	1	3.841	3.841	3.841
		2	4.049	4.049	4.077
		3	3.853	3.843	3.895
200689	AsTeBr ₃ F ₆	1	3.488	3.467	4.004
200883	AsTeI ₃ F ₆	1	3.332	3.315	3.763
201603	K ₂ TeClF ₅	1	3.888	3.781	3.711
202505	SbTeI ₃ F ₆	1	3.324	3.320	3.727
241140	GaTeO ₃ F	1	4.059	4.056	4.348
241141	FeTeO ₃ F	1	4.034	4.031	4.309
254737	Li ₇ Te ₃ O ₉ F	1	3.906	3.906	3.953
260008	ScTeO ₃ F	1	4.035	4.028	4.197
260009	InTeO ₃ F	1	3.964	3.953	4.275
264323	NaPb ₄ Te ₄ O ₁₂ F	1	3.936	3.936	3.953
290265	InTe ₂ O ₅ F	1	4.088	4.077	4.243
		2	4.091	4.061	4.239
291308	Cu ₇ Te ₆ O ₁₈ F ₂	1	3.968	3.967	4.037
		2	3.945	3.935	4.091
		3	3.895	3.882	4.098
411068	KTeO ₂ F	1	3.949	3.936	4.020
		2	3.942	3.915	4.128
		3	3.976	3.962	4.026
411626	Cs ₂ TeOF ₄	1	3.972	3.914	4.030
411806	KTeOF ₃	1	4.007	3.932	4.205
412955	K ₂ TeOF ₄	1	4.478	4.410	4.442

Comparison with former bond valence parameters

Our results are compared to those calculated with two other parameter sets. The unique set identified in the literature for the Te⁴⁺-F⁻ pair was proposed by Brese and O’Keeffe [19] with $R = 1.87 \text{ \AA}$ and $b = 0.37 \text{ \AA}$ but for which the cutoff distance was not specified. First, we optimized this set following our methodology so that the results are compared in the most relevant way possible with results from other sets. For that, we carried out the optimization of the cutoff distance by reaching a minimal *RMSD* of 0.245 for the 11 structures with only one anion type. In that case, a *cutoff* of 3.7 Å is obtained. These parameters entail average Te⁴⁺ and F⁻ valences of 4.108 v.u. (*RMSD* = 0.229) and 1.018 v.u. (*RMSD* = 0.108), respectively. For the overall 33 structures, the average Te⁴⁺ valence is 3.970 v.u. (*RMSD* = 0.245).

For comparison, we also used another parameter set in which R and *cutoff* were optimized while b was fixed at 0.37 Å. This led to $R = 1.861 \text{ \AA}$ and *cutoff* = 3.3 Å for an optimization carried out from the 11 structures with one anion type. In that case the average Te⁴⁺ and F⁻ valences are equal to 3.991 v.u. (*RMSD* = 0.198) and 0.998 v.u. (*RMSD* = 0.101), respectively, expressing that the latter set is of lower quality than the set with optimized R , b and *cutoff* but of better quality than that with the parameters from Brese and O’Keeffe. However, the results diverge from the ideal valence when considering the structures with more than one anion type, leading to an average Te⁴⁺ valence of 3.920 v.u. for the overall 33 structures.

The distributions of the Te⁴⁺ valences are gathered in Figure 3 and one can notice the smaller dispersion for the proposed set with optimized R , b and *cutoff*, the sidelined valences (assuming values inferior or superior to 0.5 v.u. from the ideal valence) being found for sets in which b is fixed at 0.37 Å.

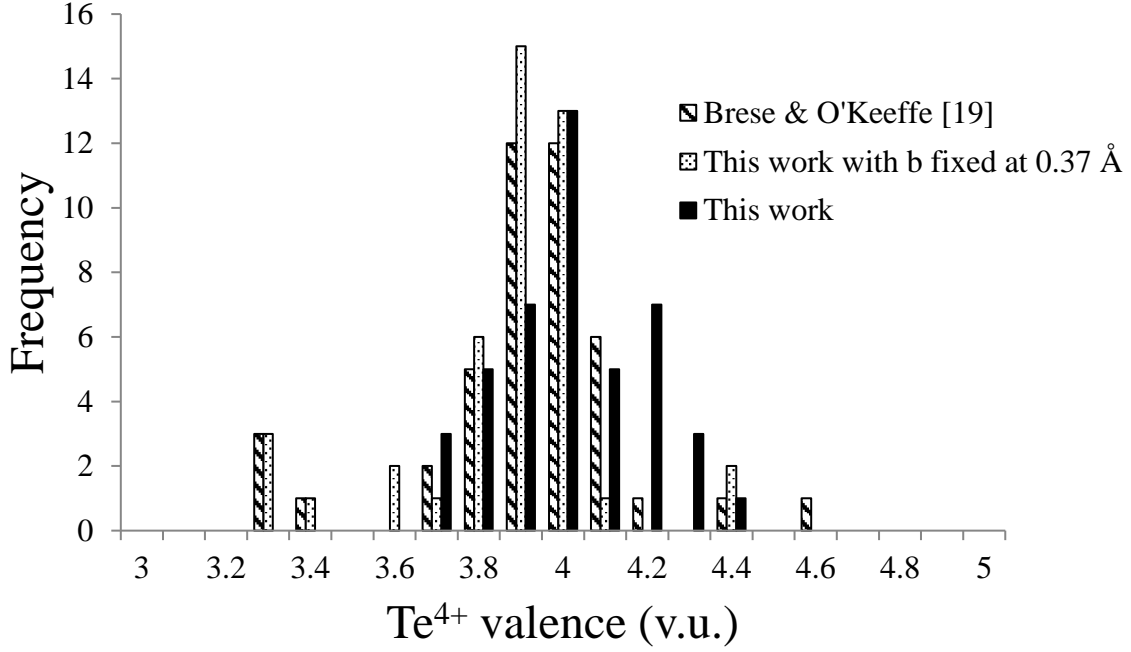


Figure 3: Distribution of the Te^{4+} valence calculated with different bond valence parameter sets of the $\text{Te}^{4+}\text{-F}^-$ pair for 33 structures.

3.2 The case of $\text{Te}^{4+}\text{-S}^{2-}$

Considering the methodology described above, the refinement of the bond valence parameters was carried out for the $\text{Te}^{4+}\text{-S}^{2-}$ pair dealing with 7 non-equivalent Te^{4+} positions in 6 structures with one anion type and 561 $\text{Te}^{4+}\text{-S}^{2-}$ distances up to 10 Å (see Table 3 and Table 4). This led to a minimal *RMSD* value of 0.070 for $R = 2.444$ Å, $b = 0.387$ Å and *cutoff* = 4.6 Å. The corresponding average Te^{4+} and S^{2-} valences are equal to 3.998 v.u. and 2.056 v.u. respectively. This set applied to a unique additional structure with more than one anion type led to a Te^{4+} valence equal to 3.962 v.u. for the overall 7 structures.

Table 3: Comparison of the average Te^{4+} and S^{2-} valences obtained from different parameter sets for the $\text{Te}^{4+}\text{-S}^{2-}$ pair.

		Brown [20]	This work with b fixed at 0.37 Å	This work	
		R, b, cutoff (Å)			
		2.44, 0.37, 4.5	2.442, 0.37, 4.5	2.444, 0.387, 4.6	
Number of structures with one anion type	Ion type	Number of non-equivalent positions	Valence (<i>RMSD</i>)		
6	Te^{4+}	7	3.977 (0.076)	3.998 (0.073)	3.998 (0.070)
	S^{2-}	18	2.043 (0.216)	2.051 (0.219)	2.056 (0.234)
Number of structures with one or several anion types					
7	Te^{4+}	8	3.940 (0.133)	3.961 (0.126)	3.962 (0.123)

Brown [20] proposed a parameter set with $R = 2.44$ Å and $b = 0.37$ Å for which, as above, we optimized the *cutoff* value and obtained 4.5 Å. We also determined a parameter set by fixing b at 0.37 Å and found values close to those of Brown with $R = 2.442$ Å and *cutoff* = 4.5 Å. The values of R , b and *cutoff* for these three sets are alike, the set proposed in the present work slightly improving the Te^{4+} valence only mostly because of a procedure with a precision of three decimal digits.

Table 4: Comparison of the Te^{4+} valences obtained from different parameter sets for the $\text{Te}^{4+}\text{-S}^{2-}$ pair for 6 structures containing one anion type, S^{2-} (colourless) and 1 structure containing several anion types (in grey).

ICSD #	Structure	Non-equivalent Te^{4+} position #	Te^{4+} valence (v.u.)		
			Brown [20]	This work with b fixed at 0.37 Å	This work

8	BaTeS ₃	1	3.976	3.998	4.008
85135	Ag ₂ TeS ₃	1	3.877	3.898	3.918
165378	Cs ₂ MnTe ₂ S ₆	1	3.885	3.906	3.898
415120	Li ₂ TeS ₃	1	4.058	4.080	4.111
424890	Cs ₂ TeS ₃	1	4.001	4.023	3.997
		2	4.081	4.103	4.071
430311	Na ₂ TeS ₃	1	3.958	3.979	3.985
85789	Cu ₃ TeClS ₃	1	3.681	3.700	3.706

3.3 The case of Te⁴⁺-Se²⁻

Following the same procedure, the bond valence parameters for the Te⁴⁺-Se²⁻ pair are $R = 2.579$ Å and $b = 0.304$ Å with a cutoff distance of 4.6 Å (see Table 5 and Table 6). A minimal *RMSD* value of 0.029 was reached by considering 4 non-equivalent Te⁴⁺ positions within 4 structures containing 301 Te⁴⁺-Se²⁻ distances up to 10 Å. An additional parameter set with b fixed at 0.37 Å was also determined but the resulting *RMSD* is larger with a value of 0.070. One can note that no additional structure with more than one anion type fulfils the above selection criteria in that case.

Table 5: Comparison of the average Te⁴⁺ and Se²⁻ valences obtained from different parameter sets for the Te⁴⁺-Se²⁻ pair.

Number of structures with one anion type	Ion type	Number of non-equivalent positions	This work with b fixed at 0.37 Å	This work
			<i>R, b, cutoff</i> (Å)	
			2.587, 0.37, 4.7	2.579, 0.304, 4.6
			Valence (<i>RMSD</i>)	
4	Te ⁴⁺	4	4.004 (0.070)	4.000 (0.029)
	Se ²⁻	12	2.059 (0.088)	2.063 (0.108)

Table 6: Comparison of the Te⁴⁺ valences obtained from different parameter sets for the Te⁴⁺-Se²⁻ pair for 4 structures containing one anion type, Se²⁻ (no structure containing several anion types).

ICSD #	Structure	Non-equivalent Te ⁴⁺ position #	Te ⁴⁺ valence (v.u.)	
			This work with b fixed at 0.37 Å	This work
63011	Na ₂ TeSe ₃ (mC48)	1	3.957	3.955
63012	K ₂ TeSe ₃	1	3.945	4.026
415121	Li ₂ TeSe ₃	1	4.121	4.025
430313	Na ₂ TeSe ₃ (mP24)	1	3.992	3.995

4 Conclusion

The bond valence parameters R and b with a cutoff distance are revised from a procedure using the root mean square deviation of the Te⁴⁺ valence for the Te⁴⁺-F⁻ ($R = 1.728$ Å and $b = 0.622$ Å with *cutoff* = 5.3 Å) and Te⁴⁺-S²⁻ ($R = 2.444$ Å and $b = 0.387$ Å with *cutoff* = 4.5 Å) ion pairs. The new parameters lead to a lower dispersion of the calculated valences compared to that obtained with the parameters of the literature. The new ones also remove the ambiguity related to the validity of some crystalline structures that apparently do not present structural singularities. Following the same procedure, new parameter set is proposed for the Te⁴⁺-Se²⁻ ion pair ($R = 2.578$ Å and $b = 0.296$ Å with *cutoff* = 3.7 Å).

Appendix

Comparison of the F⁻, S²⁻ and Se²⁻ valences obtained from different bond valence parameter sets for structures containing one anion type (11 structures containing F⁻, 6 structures containing S²⁻ and 4 structures containing Se²⁻).

ICSD #	Structure	Non-equivalent F ⁻ position #	F ⁻ valence (v.u.)		
			Breese & O'Keeffe [19]	This work with <i>b</i> fixed at 0.37 Å	This work
16108	Sb ₂ TeF ₁₄	1	1.156	1.129	0.905
		2	1.092	1.055	0.911
		3	1.146	1.119	0.886
		4	0.972	0.968	1.102
		5	0.951	0.948	1.069
		6	0.936	0.932	1.069
		7	0.905	0.905	0.942
		8	0.888	0.887	0.987
		9	0.920	0.920	0.951
		10	1.204	1.204	1.237
		11	0.822	0.822	0.869
		12	1.008	1.008	1.051
		13	0.960	0.959	1.043
		14	0.823	0.823	0.850
81862	BaTe ₃ F ₁₀	1	1.021	1.005	1.046
		2	0.907	0.872	0.990
		3	1.161	1.138	1.062
		4	1.077	1.057	1.050
		5	0.963	0.940	0.985
81865	PbTeF ₆	1	0.962	0.961	1.072
		2	0.908	0.892	0.926
		3	0.961	0.944	0.951
		4	0.865	0.850	0.964
		5	0.957	0.940	1.043
		6	1.130	1.105	1.057
84364	KTe ₂ F ₉	1	1.188	1.163	1.029
84364	KTeF ₅	1	1.030	1.011	0.986
		2	1.159	1.133	1.020
		2	1.011	0.991	0.971
		3	1.147	1.114	1.016
		3	1.195	1.170	1.065
		4	0.993	0.974	0.956
		5	1.029	1.009	0.953
		6	0.927	0.907	1.016
		7	0.865	0.837	0.978
		8	0.943	0.923	0.965
		9	0.888	0.867	1.027
85452	TeF ₄	1	1.043	1.018	1.020
		2	0.983	0.959	0.985
		3	1.140	1.113	1.037
		4	0.897	0.875	1.050
88416	BaTeF ₆	1	1.008	0.979	0.980
		2	1.092	1.051	1.066
		3	1.097	1.062	1.068
		4	0.849	0.833	0.941
		5	0.997	0.968	1.005
		6	1.065	1.048	1.043
90619	TlTeF ₅	1	1.144	1.122	1.018
		2	1.015	0.997	0.974
		3	0.984	0.963	0.990
200252	CsTeF ₅	1	1.029	1.009	1.018
		2	1.092	1.070	0.973
		3	1.305	1.268	1.049
202879	NaTeF ₅	1	1.141	1.094	1.045
		2	1.043	1.022	0.987
		3	0.988	0.957	0.999
203140	RbTeF ₅	1	1.148	1.114	1.017
		2	0.982	0.954	0.961
		3	0.971	0.938	0.939
		4	1.123	1.089	0.976
		5	1.000	0.983	0.960
		6	0.907	0.888	0.937

ICSD #	Structure	Non-equivalent S ²⁻ position #	S ²⁻ valence (v.u.)		
			Brown [20]	This work with <i>b</i> fixed at 0.37 Å	This work

8	BaTeS ₃	1	1.868	1.876	1.878
		2	1.962	1.970	1.974
85135	Ag ₂ TeS ₃	1	2.664	2.678	2.718
		2	2.084	2.092	2.108
		3	1.998	2.005	2.010
165378	Cs ₂ MnTe ₂ S ₆	1	1.922	1.929	1.926
415120	Li ₂ TeS ₃	1	2.521	2.533	2.585
		2	2.026	2.033	2.047
		3	1.974	1.982	2.003
424890	Cs ₂ TeS ₃	1	2.069	2.076	2.065
		2	2.044	2.051	2.042
		3	1.866	1.874	1.867
		4	1.952	1.959	1.947
		5	1.922	1.930	1.917
		6	1.775	1.782	1.777
430311	Na ₂ TeS ₃	1	2.007	2.015	2.016
		2	2.025	2.031	2.027
		3	2.101	2.108	2.099

ICSD #	Structure	Non-equivalent Se ²⁻ position #	Se ²⁻ valence (v.u.)	
			This work with b fixed at 0.37 Å	This work
63011	Na ₂ TeSe ₃ (mC48)	1	2.020	2.007
		2	1.982	1.956
		3	2.122	2.158
63012	K ₂ TeSe ₃	1	2.143	2.175
		2	2.048	2.073
		3	1.966	1.992
415121	Li ₂ TeSe ₃	1	2.004	2.017
		2	2.156	2.190
		3	2.065	1.986
430313	Na ₂ TeSe ₃ (mP24)	1	2.003	1.975
		2	2.043	2.031
		3	2.151	2.194

References

1. Brown I. D. *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*, 2nd ed.; Oxford University Press, Oxford, 2016.
2. Brown I. D., Altermatt D. Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallogr.* 1985, *B41*, 244–247.
3. Altermatt D., Brown I. D. The automatic searching for chemical bonds in inorganic crystal structures. *Acta Crystallogr.* 1985, *B41*, 240–244.
4. Brown I. D. Recent developments in the methods and applications of the bond valence model. *Chem. Rev.* 2009, *109*, 6858–6919.
5. Adams S. Relationship between bond valence and bond softness of alkali halides and chalcogenides. *Acta Crystallogr.* 2001, *B57*, 278–287.
6. Adams S. soft BV (version 0.96), 2004, www.softBV.net
7. Sidey V. Alternative presentation of the Brown–Wu bond-valence parameters for some s^2 cation/ O^{2-} ion pairs. *Acta Crystallogr.* 2009, *B65*, 99–101.
8. Krivovichev S. V. Derivation of bond-valence parameters for some cation-oxygen pairs on the basis of empirical relationships between r_0 and b . *Z. Kristallogr. Cryst. Mater.* 2012, *227*, 575–579.
9. Gagné O. C., Hawthorne F. C. Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallogr.* 2015, *B71*, 562–578.
10. Chen H., Adams S. Bond softness sensitive bond-valence parameters for crystal structure plausibility tests. *IUCrJ.* 2017, *4*, 614–625.
11. Krivovichev S. V., Brown I. D. Are the compressive effects of encapsulation an artifact of the bond valence parameters? *Z. Kristallogr.* 2001, *216*, 245–247.
12. Locock A. J., Burns P. C. Revised Tl(I)–O bond valence parameters and the structures of thallos dichromate and thallos uranyl phosphate hydrate. *Z. Kristallogr.* 2004, *219*, 259–266.
13. Sidey V. Accurate bond-valence parameters for the Bi^{3+}/Br^- ion pair. *Acta Crystallogr.* 2006, *B62*, 949–951.
14. Hu S.-Z. A new approach to bond valence parameters for Pb(II)—halide bonds. *Acta Phys. -Chim. Sin.* 2007, *23*, 786–789.
15. Mills S. J., Christy A. G., Chen E. C.-C., Raudsepp M. Revised values of the bond valence parameters for $^{[6]}Sb(V)$ –O and $^{[3-11]}Sb(III)$ –O. *Z. Kristallogr.* 2009, *224*, 423–431.
16. Christy A. G., Mills S. J. Effect of lone-pair stereoactivity on polyhedral volume and structural flexibility: application to $Te^{IV}O_6$ octahedra. *Acta Crystallogr.* 2013, *B69*, 446–456.
17. Hamani D., Masson O., Thomas P. Localization and steric effect of the lone electron pair of the tellurium Te^{4+} cation and other cations of the p -block elements. A systematic study. *J. Appl. Crystallogr.* 2020, *53*, 1243–1251.
18. Mills S. J., Christy A. G. Revised values of the bond-valence parameters for Te^{IV} –O, Te^{VI} –O and Te^{IV} –Cl. *Acta Crystallogr.* 2013, *B69*, 145–149.
19. Brese N. E., O’Keeffe M. Bond-valence parameters for solids. *Acta Crystallogr.* 1991, *B47*, 192–197.
20. Brown I. D. Private communication, 2001, <https://www.iucr.org/resources/data/datasets/bond-valence-parameters>
21. Sidey V. I., Zubaka O. V., Stercho I. P., Peresh E. Yu. X-ray Rietveld structure refinement and bond-valence analysis of Cs_2TeI_6 . *Chem. Met. Alloys.* 2010, *3*, 108–114.
22. Inorganic Crystal Structure Database (ICSD), <https://icsd.fiz-karlsruhe.de/>
23. Shannon R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* 1976, *A32*, 751–767.