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Some applications of the bond valence model to transition metal chalcogenides

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ABSTRACT

The analysis of interatomic distances in complex transition metal chalcogenides of type $A_m[T_nS_p]$ (A, alkali or alkaline earth metal; T, mainly Fe, Cu) can furnish interesting information on the oxidation state of the metal and also of sulfur. The charge distribution in complex anions can be estimated. Structural problems of the accommodation of the cations in framework structures leading to disorder can be detected.

1. Introduction

Although the empirical bond valence model [1–3], relating a bond length to its bond valence (bond order) has been mainly used successfully for interpreting crystal structures of ionic compounds or minerals, there have been some earlier applications to transition metal chalkogenides [4–6]. In this paper some experiences with complex transition metal chalcogenides with partially salt-like structure with respect to the electropositive *A* element will be presented.

Bond valences v_{ij} of a pair of bonded atoms *ij* were calculated from the corresponding interatomic distances d_{ij} by the relation

$$v_{ij} = \exp\left[\frac{(R0_{ij} - d_{ij})}{b}\right]$$

The individual parameters $R0_{ij}$ and $b = 0.37$ as 'universal' constant were taken from [7] with the exception of $R0_{Fe} = 1.125$, which appeared more appropriate for the thioferrates. Calculations were done with the computer programs EUTAX1 [8] and DISTV3 [9]. The structural data were taken from the ICSD data file (FIZ, Karlsruhe).

2. Oxidation state of iron and copper

The sum of the bond valences V_i arriving at an atom should correspond to its oxidations state (valency). In Table 1 the results for some thioferrates with chains formed by $[FeS_4]$ tetrahedra are presented. The bond valence sums of iron are close to 3 for the valence-precise compounds and between 2 and 3 for the mixed-valent ones. $BaFe_3S_2$ is also mixed-valent, although its chemical formula suggests two-valent iron. The mixed-valent state has also been corroborated by Moessbauer spectroscopy [4,10], as well as for KFe_3S_2 [11]. In the continuous solid solution $Ba_{1-x}K_xFe_3S_2$ the oxidation state of iron does not seem to vary much in spite of the changing cation charge [12].

There are isolated $[FeS_4]$ tetrahedra in the high pressure phase Ba_3FeS_5. In accordance with the chemical formula Fe(IV) was postulated [13]. The oxidation state of Fe(IV) is not feasible together with sulfur from chemical arguments. The bond valence sum $V_{Fe} = 2.9$ (Table 1) indicates Fe(III) indeed. This was also suggested by [4] on the base of Moessbauer and magnetic measurements.

In the thiocuprates the bond valence sums are always close to 1 indicating the absence of two-valent copper (Table 2).

An interesting example is CuS (*Covellite*), which is sometimes termed *cupric* sulfide. The crystal structure, however, shows an alternating stacking of layers composed of single sulfur atoms (S1) and of disulfide groups ($S2_2$) along the c axis of the hexagonal unit cell. This would suggest a valence-precise formulation as $Cu1^{2+}(Cu2^{+})_2(S2_2)^{2-}S1^{2-}$. The bond valence sums of Cu1 and

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Table 1
Bond valence sums of some thioferrates.

Compound	Bond valence sum (*V*)			Remarks
	A	Fe	S	
$KFeS_2$	0.99	2.98	1.99	
$RbFeS_2$	0.97	2.93	1.95	Fe(III) from formula
$CsFeS_2$	0.77	3.05	2.09	
$Na_3Fe_2S_4$	1.11, 0.86	2.49	1.86, 1.97, 2.11	
$K_3Fe_2S_4$	1.31, 0.90	2.44	1.91, 1.97, 2.19	Mixed-valent
KFe_2S_3	0.62	2.78	2.35, 1.92	
$BaFe_2S_3$	1.72	2.65	2.90, 2.06	
Ba_3FeS_5	1.72, 2.71	2.91	1.97, 1.95, 1.97, 1.17	Fe(IV) from formula

Table 2
Bond valence sums of some thiocuprates.

Compound	Bond valence sum (*V*)			Remarks
	A	Cu	S	
α-$BaCu_4S_3$	2.20	0.94, 0.80, 0.84, 0.92	2.02, 1.94, 1.64	
β-$BaCu_4S_3$	2.16	0.91, 0.75	1.98, 1.68	Valence-precise
β-$BaCu_2S_2$	2.08 (2.30)[a]	0.90 (1.0)	1.94 (2.15)	
$CsCu_2S_3$	0.92 (1.03)	0.88 (1.0)	1.78 (2.01)	
KCu_4S_3	1.03	1.00	1.62, 1.70	Not valence-precise
$Na_3Cu_4S_4$	0.94, 1.03	1.0, 0.92	1.96, 1,73	
CuS	–	1.22 (1.01), 1.16 (0.96)	1.78 (1.48), 1.95 (1.61)	Cu(II) from formula

[a] Numbers in parenthesis after normalisation to V_{Cu} ≈1.0.

Cu2, however, clearly indicate oxidation state +1 in correspondence with their trigonal planar and tetrahedral coordination by sulfur, respectively, typical for Cu(I) (Table 2).

3. Oxidation state of sulfur

The bond valence sum of sulfur should be close to 2. It is generally agreed that in not valence-precise thiocuprates copper is in oxidation state +1 and the sulfur sublattice is oxidized. This can be seen from the bond valence sums of sulfur in not valence-precise KCu_4S_3 and $Na_3Cu_4S_4$, and also in CuS, where V_S is smaller than 2 (Table 2). One must be cautious, however, because often also in valence-precise compounds, e.g. KCu_3S_2, $V_S < 2$. But this is a consequence of accompanying $V_{Cu} < 1$. By scaling all bond valence sums with a constant factor so that $V_{Cu} \approx 1$, V_S comes close to 2.

In Ba_3FeS_5 the bond valence sums of atoms S1–S3 taking part of the $[FeS_4]$ tetrahedra are normal, while that of S4 has the low value of 1.17 (Table 1). This sulfide species which is coordinated by 5 barium atoms only, appears to be oxidized. Thus it is suggested to describe the bonding in this compound as $Ba_3{}^{2+}$ Fe^{3+} $S_4{}^{2-}$ S^-.

4. Charge distribution in complex anions

In complex anions or anionic partial structures (*Bauzusammenhänge*) the difference between the theoretical valence of a closed shell electronegative atom like O, S or halogen and its bond valence sum disregarding bond valences to the counter ions can be interpreted as its residual charge (bond valence charge q_i) [14]. Since usually the total charge *Q* of the anion is known, there is an independent check of consistency, because the bond valence charges of the anion should sum up to its total charge:

$$q_i = V_{i,\text{theor.}} - V_i, \quad Q \approx \Sigma q_i$$

In Fig. 1 selected examples are shown. In some cases the results become nicer, when all the bond valence sums are normalized by a constant factor to the theoretical oxidation state of a metal in the anion. In complex anions where the electronegative atoms are differently bound, e.g. two-fold coordinated and terminal sulfur in $[Cu_2S_3]^{4-}$, or if there are different kinds of atoms the resulting unequal charge distribution on the anionic entity can be estimated.

5. Bond valence sums of the cations

Since the charge of the alkali or alkaline earth ions is known for sure, the deviations of the bond valence sums must have structural origins. If there are cations in different crystallographic positions, the average value comes often close to the theoretical one. In

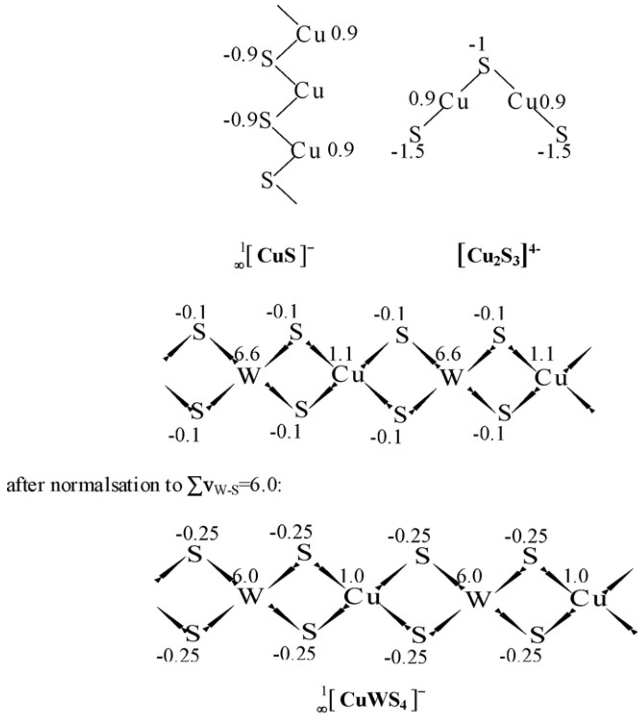

Fig. 1. Bond valence sums of metals and bond valence charges of sulfur in complex anions in KCuS, $Na_4Cu_2S_3$, and $KCuWS_4$.

cases of more rigid frameworks strong deviations may indicate a squeezed condition as in $NaFeS_2$ with $V_{Na} = 1.83$. This phase is metastable [15]. Too small bond valence sums indicate a rattling condition (the cation is too small to fill the cavity), which may be accompanied by some disorder, as it is the case in $K[CuMoS_4]$ and α- or β-$K[CuWS_4]$ [16] with $V_K \approx 0.8$.

6. Conclusion

The bond valence model can thus give valuable additional information, if used with chemical common sense because of the interplay of bonding and structural exigencies that influences the interatomic distances in a crystal structure. Its advantage is its simplicity. All calculations can be done with a pocket ruler using the generally well known interatomic distances in a crystal structure.

References

[1] I.D. Brown, D. Altermatt, Acta Crystallogr. B31 (1985) 244.
[2] I.D. Brown, Acta Crystallogr. B48 (1992) 553.
[3] M. O'Keefe, Acta Crystallogr. A46 (1990) 138.
[4] J.T. Hoggins, H. Steinfink, Inorg. Chem. 15 (1976) 1682.
[5] J.C.J. Bart, V. Ragaini, Phosphorus Sulfur 8 (1980) 161.
[6] R.D. Shannon, Structure and Bonding in Crystals, vol. II, Academic, New York, 1981, pp. 53–69.
[7] N.E. Brese, M. O'Keefe, Acta Crystallogr. B47 (1991) 192.
[8] M. O'Keefe, N.E. Brese, Acta Crystallogr. B48 (1992) 152.
[9] H. Boller, unpublished.
[10] M. Reissner, W. Steiner, H. Boller, Hyperfine Interact. (C) 5 (2002) 197.
[11] G. Amthauer, K. Bente, Naturwissenschaften 70 (1983) 146.
[12] M. Reissner, W. Steiner, J. Wernisch, H. Boller, Hyperfine Interact. 169 (2006) 1301.
[13] J.T. Lemley, J.M. Jenks, J.T. Hoggins, Z. Eliezer, H. Steinfink, J. Solid State Chem. 16 (1976) 117.
[14] H. Boller, Appl. Crystallogr.,vol. 18, World Scientific Publishing Co., 2001, pp. 27–29.
[15] H. Boller, H. Blaha, Monatsh. für Chem. 114 (1983) 145.
[16] H. Boller, K.O. Klepp, G. Gutenbrunner, C. Spindler, Solid State Phenom. 90–91 (2003) 285.