

The Influence of Bond Valence on Bond Covalency in RMn_2O_5 (R=La, Pr, Nd, Sm, Eu)

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Abstract The relationship between bond valence and bond covalency in RMn_2O_5 (R = La, Pr, Nd, Sm, Eu) has been investigated by a semiempirical method. This method is the generalization of the dielectric description theory of Phillips, Van Vechten, Levine and Tanaka scheme. The results indicate that larger valences usually result in higher bond covalencies, in good agreement with the point that the excess charge in the bonding region is the origin of formation of bond covalency. Other factors, such as oxidation state of elements, only make a small contribution to bond covalency.

Keywords: Bond valence; bond covalency; semiempirical method; RMn_2O_5 .

It is now well established that the concept of bond covalency is very important for explaining and classifying many basic properties in diverse areas including chemistry and condensed matter physics. Reviews concerning bond covalency and its application have been made by Phillips^{1,2}, Van Vechten³, Levine^{4,5} and Tanaka⁶. It is known that PV (Phillips - Van Vechten) ¹⁻³ theory can only deal with binary crystals, especially A^NB^{8-N} type. On the other hand, although theory which can deal with more complex crystals, such as AB_n , A_mB_n types of crystals, had been successfully developed by Levine^{4,5}, for ABC_2 , ABC_3 and ABC_4 types of crystals, an explicit expression was not given concerning how to decompose the complex multibond crystals into the sum of binary crystals. Whereas in Tanaka's work⁶, although similar idea has been extended to complex crystals which are anisotropic, i.e., high T_c - oxides, in actual calculations the bond ionicity (covalency) were calculated only for three types of bonds and artificially restricted in a box. Therefore, it is worthwhile to extend these fruitful ideas. After considering these ideas in chemical bond representation, we^{7,8} succeeded in generalizing Phillips-Van Vechten-Levine-Tanaka (PVL) theory for multibond systems. Using this generalized theory, any complex crystal can be decomposed into the sum of binary crystals. These obtained binary crystals are related to each other and every binary crystal includes only one type of chemical bond, but the properties of these binary crystals are different from those of corresponding real binary crystals (if existent), although the chemical bond parameters can be calculated in the same way. In this paper, formulas of calculating the bond covalencies in complex crystals are presented and the relationship between bond valences and bond covalencies in RMn_2O_5 (R=La, Pr, Nd, Sm, Eu) is investigated. They are electrical insulators and isostructural with space group *Pbam*. In the structure, Mn^{3+}

and Mn^{4+} occupy different crystallographic positions, which have square pyramidal environment and octahedral coordination respectively. In addition, the crystal structure contains infinite chains of $Mn^{4+}O_6$ octahedra parallel to *c* axis, linked through $Mn^{3+}O_5$ units and bicapped RO_8 antiprisms.

Theoretical Method

Suppose A denote cations, B anions, any multibond complex crystal can be written as $A^1_{a1} A^2_{a2} \cdots A^i_{ai} \cdots B^1_{b1} B^2_{b2} \cdots B^j_{bj}$, where A^i and B^j represent the different elements or the different sites of a given element of cations and anions respectively, and ai , bj represent the number of the corresponding elements. Thus, together with crystal structure data, it can be decomposed into the sum of binary crystals by the following formula,

$$A^1_{a1} A^2_{a2} \cdots A^i_{ai} \cdots B^1_{b1} B^2_{b2} \cdots B^j_{bj} = \sum_{i,j} A^i_{mi} B^j_{nj} \quad (1)$$

$$mi = N(B^i-A^i) ai / N_{CAi} \quad \text{and} \quad nj = N(A^i-B^j) bj / N_{CBj} \quad (2)$$

Where N_{CAi} and N_{CBj} represent the nearest total coordination numbers of A^i and B^j ions in the crystal. $N(B^i-A^i)$ represents the nearest coordination number contributed by A^i ion, and $N(A^i-B^j)$ represents the nearest coordination number contributed by B^j ion. After decomposing the complex crystal into the sum of different kinds of binary crystals, which are isotropic systems, PVL^T¹⁻⁶ theory can be directly applied to the calculation of the chemical bond parameters in complex crystals. The detailed theory can be seen in refs. 7, 8.

If *d* and *f* holes exist, the corrected bond covalency f^u_c should be replaced by an effective one, $(f^u_c)^*$,

$$(f^u_c)^* = (1+\Gamma) f^u_c \quad (3)$$

where Γ = number of *d* or *f* holes / number of valence electrons

Results and Discussion

Based on the crystallographic data⁹ and method mentioned above, RMn_2O_5 can be decomposed into the sum of binary crystals of the following,

$$\begin{aligned} RMn_2O_5 &= R(1) Mn(1) Mn(2) O(1) O(2) O(3) O_2(4) \\ &= R_{2/8}(1) O_{2/4}(1) + R_{2/8}(1) O_{2/4}(2) + R_{4/8}(1) O(4) \\ &+ Mn_{2/6}(1) O_{2/4}(2) + Mn_{2/6}(1) O_{2/3}(3) + Mn_{2/6}(1) O_{2/4}(4) \\ &+ Mn_{2/5}(2) O_{2/4}(1) + Mn_{1/5}(2) O_{1/3}(3) + Mn_{2/5}(2) O_{2/4}(4) \end{aligned}$$

It is known that the bond valence (in valence unit, v.u.) is an important quantity in the calculation of bond covalency (and in fact, the existence of bond valence is the origin of bond covalency), therefore, it should be calculated with good accuracy. In this paper, the bond valence is treated by the following two methods, (1) Bond Valence Sums (BVS), this theory has been now well recognized^{10,11}. The bond valence parameters in this calculation are taken from ref. 10. (2) Equi-valence of the oxidation state (valence) of cations R and O (3) (the valence of R and O (including O (1), O (2), O (3), O (4)) is fixed to be 3.0 and -2.0, respectively), the valences of Mn (1) and Mn (2) are obtained

according to electro-neutral principle. The thus obtained oxidation states of Mn (1) and Mn (2) are 4.0 and 3.0 respectively, coincide with their oxidation state from stoichiometry. The reason why the above two methods are chosen is that BVS is a more general method which is suitable for both anisotropic systems and isotropic systems, whereas equi-valence method is only suitable for isotropic systems (some binary crystals). The comparison of the two methods are made in the following.

The calculated bond covalencies and bond valences from BVS and equi-valence schemes are collected in **Table 1** and **Table 3** respectively. The oxidation states for each element from BVS are given in **Table 2**. It can be seen (**Table 1**) that in most cases, larger

Table 1. Bond covalencies f_c (%) and bond valences (in v. u.) from BVS scheme in RMn_2O_5

	La		Pr		Nd		Sm		Eu	
	f_c	valence	f_c	valence	f_c	valence	f_c	valence	f_c	valence
R-O (1)	4.72	0.4385	4.34	0.4011	4.19	0.3894	3.89	0.3485	3.66	0.3205
R-O (2)	4.98	0.4650	4.85	0.4505	5.08	0.4513	5.35	0.4478	5.49	0.4482
R-O (4)	4.09	0.3628	4.11	0.3673	4.19	0.3641	3.93	0.3345	3.89	0.3275
Mn (1) -O (2)	14.15	0.6049	14.56	0.6350	13.91	0.5700	13.40	0.5158	13.29	0.5033
Mn (1) -O (3)	18.38	0.7468	18.41	0.7529	17.52	0.7152	18.65	0.8165	19.51	0.8903
Mn (1) -O (4)	15.24	0.6489	14.45	0.6181	16.30	0.7018	15.73	0.6794	14.92	0.6350
Mn (2) -O (1)	28.31	0.6385	29.37	0.6981	30.21	0.7388	31.26	0.7883	32.03	0.8209
Mn (2) -O (3)	19.30	0.3552	19.05	0.3552	22.93	0.4654	20.10	0.4099	17.59	0.3514
Mn (2) -O (4)	30.48	0.6962	31.75	0.7673	28.28	0.6215	31.44	0.7509	33.24	0.8254

Table 2. Oxidation states of the constituent elements for BVS scheme in RMn_2O_5

	La	Pr	Nd	Sm	Eu
R	3.26	3.17	3.14	2.93	2.85
Mn (1)	4.00	4.01	3.97	4.03	4.06
Mn (2)	3.02	3.29	3.19	3.49	3.64
O (1)	-2.15	-2.20	-2.26	-2.27	-2.28
O (2)	-2.14	-2.17	-2.04	-1.93	-1.90
O (3)	-1.85	-1.86	-1.90	-2.04	-2.13
O (4)	-2.07	-2.12	-2.05	-2.10	-2.12

Table 3. Bond covalencies (%) and bond valences (last column, in v. u.) from equi-valence scheme in RMn_2O_5

	La	Pr	Nd	Sm	Eu	valence
R-O (1)	4.41	4.40	4.42	4.44	4.46	0.3750
R-O (2)	4.42	4.43	4.45	4.50	4.54	0.3750
R-O (4)	4.37	4.39	4.40	4.43	4.46	0.3750
Mn (1) -O (2)	15.07	15.11	15.00	14.97	15.03	0.6250
Mn (1) -O (3)	17.61	17.60	17.55	17.83	18.06	0.7500
Mn (1) -O (4)	15.16	15.08	15.26	15.30	15.30	0.6250
Mn (2) -O (1)	28.96	29.11	29.25	29.52	29.76	0.6250
Mn (2) -O (3)	23.10	23.07	23.51	23.42	23.33	0.5000
Mn (2) -O (4)	29.13	29.31	28.90	29.41	29.78	0.6250

covalencies correspond to higher bond valences, in good agreement with the viewpoint that the excess charge in the bonding region (bond valence or bond charge) is the origin of formation of bond covalency⁴. However, the violation in which the bond with higher bond valence does not produce larger bond covalency in R-O (1, 4) type of bond in

NdMn₂O₅ and SmMn₂O₅ and Mn (2) -O (1, 4) in SmMn₂O₅ tells us that besides the bond valence, there are also other factors, such as the oxidation states of elements (**Table 2**), which may influence the magnitude of bond covalency. From **Table 1**, it is also noticed that with the decrease of ionic radii from La to Eu, the bond covalencies of Mn (2) -O (1) increase, whereas those of R-O (1) decrease. No obvious trend is observed for the other types of bonds. **Table 2** gives the bond valence sums for the RMn₂O₅ oxides. With the decrease of ionic radii from La to Eu, the oxidation states of Mn (2), O (1) and O (3) increase, those of R and O (2) decrease, whereas those of Mn (1) and O (4) remain relatively unchanging. We think the oxidation states of Mn (2) in SmMn₂O₅ and EuMn₂O₅ are too large compared with its normal oxidation state 3.0. This is not surprising from BVS theory, because the bond distances of Mn (2) -O (1, 4) (see ref. 9) are relatively short in SmMn₂O₅ and EuMn₂O₅ (this is caused by lower coordination number of Mn³⁺O₅ than that of Mn⁴⁺O₆), and therefore result in relatively higher bond valences. This may suggest that new bond parameters for Mn³⁺ and O²⁻ are needed.

For the equi-valence scheme (**Table 3**), it can be found that the same regularity has been observed for the relationship between bond valence and bond covalency as in BVS scheme. This also demonstrates that the bond covalency is mainly influenced by bond valence. From La to Eu, obvious trend is not found for the magnitude of bond covalency. This suggests that in the evaluation of bond covalency in anisotropic systems like RMn₂O₅, care should be taken in the calculation of bond valence. In isotropic systems, such as some binary crystals, the BVS and equi-valence may yield the same results.

It is also seen that for the two schemes (BVS and equi-valence) the bond covalencies in Mn (2) -O of Mn³⁺O₅ unit are larger (on the average) than those in Mn (1) -O of Mn⁴⁺O₆ unit, and the magnitude of bond covalency obey the following order, Mn (2) -O > Mn (1) -O > R-O.

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