4270 *J. Phys. Chem. A* **1999,** *103,* 4270−4274

Semiempirical Method for the Evaluation of Bond Covalency in Complex Crystals

Z. J. Wu* and S. Y. Zhang

Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun, 130022, P. R. China

Received: June 17, 1998; In Final Form: January 7, 1999

We report a semiempirical method for the evaluation of bond covalency in complex crystals. This method is the extension of the dielectric description theory delivered by Phillips, Van Vechten, Levine, and Tanaka (PVLT) which is mainly suitable for binary crystals. Our method offers the advantage of applicability to a broad class of complex materials. The simplicity of the approach allows a broader class of researchers to access the method easily and to calculate not only the bond covalency but also other useful properties such as bulk modulus. For a series study, a useful trend can be illustrated and often the prediction of the properties of the missing one(s) among the series can be possible. Finally, examples are given to show how the method is applied and the procedure is transferable to other complex crystals.

1. Introduction

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 both theoretically[1−6] and experimentally.[7] Reviews concerning bond covalency and its application had been made by Phillips,[1,2] Van Vechten,[3] Levine,[4,5] and Tanaka.[6] It is known that PV (Phillips−Van Vechten)[1−3] theory can only deal with binary crystals, especially A^NB^{8-N} type (N is the number of the valence electrons). On the other hand, although theory which can deal with complex crystals, such as AB_n and A_mB_n types of crystals, successfully had been developed by Levine,[4,5] for ABC_2, ABC_3, and ABC_4 and more complex types of crystals, an explicit expression was not given concerning how to decompose the complex multiple bond crystals into binary crystals. Whereas in Tanaka's work,[6] although similar theory has been extended to complex crystals which are anisotropic, i.e., high Tc−oxides, in practical calculations the bond covalency (ionicity) is calculated only for three types of bonds which are artificially restricted in a box. Therefore, it is worthwhile to extend these fruitful ideas. After considering these ideas in chemical bond representation, we[8−10] succeeded in generalizing Phillips−Van Vechten−Levine−Tanaka (PVLT) theory to multiple bond systems. Using this generalized theory, any complex crystal can be decomposed into the sum of binary crystals. Each binary crystal is related to the others and contains only one type of chemical bond. Furthermore, the properties for each binary crystal differ from that of real corresponding binary crystal (if it exists), although the chemical bond parameters of the determined crystal can be calculated in the similar manner. In this paper, formulas for evaluating the bond covalency in complex crystals are given and illustrated by examples.

2. Theoretical Method

Suppose A denotes cations and B anions, then any complex crystal can be written as $A^1{}_{a1}A^2{}_{a2}\cdots A^i{}_{ai}\cdot B^1{}_{b1}B^2{}_{b2}\cdots B^j{}_{bj}$, 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 and bj represent the number of the corresponding elements. Thus, together with crystallographic data, it can be decomposed into the sum of binary crystals by the following formula

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

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

Where N_{CAi} and N_{CBj} represent the nearest total coordination numbers of A^i and B^j ions in the crystal. $N(B^j-A^i)$ 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 an isotropic system, PVLT[1−6] theory can be applied to the calculation of the chemical bond parameters in complex crystals.

According to PVL[1−5] theory, the macroscopic linear susceptibility χ (the longwavelenth index of refraction) can be resolved into contributions χ^μ from the various types of bonds or from the various binary crystals and can be obtained by the following equation:[4]

$$\chi = \sum_\mu F^\mu\chi^\mu = \sum_\mu N^\mu{}_b\,\chi^\mu{}_b \qquad (3)$$

where χ^μ is the total macroscopic susceptibility of type of bond μ. F^μ is the fraction of bonds of type μ composing the actual complex crystal. $\chi^\mu{}_b$ is the susceptibility of a single bond of type μ, and $N^\mu{}_b$ is the number of bonds per cubic centimeter. According to PVL, $\chi^\mu{}_b$ can be written as

$$\chi^\mu{}_b = (4\pi)^{-1}[(h\Omega^\mu{}_p)^2/(2\pi E^\mu{}_g)^2] \qquad (4)$$

where $E^\mu{}_g$ is the average energy gap for the type μ bond. $\Omega^\mu{}_p$ is the plasma frequency obtained from the number of valence electrons of type μ per cubic centimeter $N^\mu{}_e$, using

$$(h\Omega^\mu{}_p)^2 = (4\pi N^\mu{}_e\, e^2/m)D^\mu A^\mu \qquad (5)$$

$$D^\mu(\alpha,\beta) = \Delta^\mu{}_\alpha\Delta^\mu{}_\beta - (\delta^\mu{}_\alpha\delta^\mu{}_\beta - 1)(Z^\mu{}_\alpha - Z^\mu{}_\beta)^2 \qquad (6)$$

$$A^\mu = 1 - (E^\mu{}_g/4E^\mu{}_F) + 1/3(E^\mu{}_g/4E^\mu{}_F)^2 \qquad (7)$$

10.1021/jp982674q CCC: $18.00

Δ and δ are periodic dependent constants tabulated in ref 4. $Z^{\mu}{}_{\alpha}$ and $Z^{\mu}{}_{\beta}$ are the number of valence electrons on the α and β atoms of the μ bond. $E^{\mu}{}_{F}$ is the Fermi energy, its definition is in the following (eq 12).

In analogy with the work of PV, the average energy gap $E^{\mu}{}_{g}$ appearing in eq 4 for every type of μ bond can be separated into covalent or homopolar $E^{\mu}{}_{h}$ and ionic or heteropolar C^{μ} parts as the following:

$$(E^{\mu}{}_{g})^2 = (E^{\mu}{}_{h})^2 + (C^{\mu})^2 \tag{8}$$

The bond ionicity $f^{\mu}{}_{i}$ and bond covalency $f^{\mu}{}_{c}$ of any type of μ bond are defined as

$$f^{\mu}{}_{i} = (C^{\mu})^2/(E^{\mu}{}_{g})^2$$

$$f^{\mu}{}_{c} = (E^{\mu}{}_{h})^2/(E^{\mu}{}_{g})^2 \tag{9}$$

where

$$E^{\mu}{}_{h} = 39.74/(d^{\mu})^{2.48} \tag{10}$$

For any binary crystal with $A^{i}{}_{mi}B^{j}{}_{nj}$ type, the heteropolar C^{μ} is given as

$$C^{\mu} = 14.4b^{\mu}\exp(-\kappa^{\mu}{}_{s}r^{\mu}{}_{0})[(Z^{\mu}{}_{\alpha}/r^{\mu}{}_{0}) - (nj/mi)(Z^{\mu}{}_{\beta}/r^{\mu}{}_{0})] \quad \text{if } nj > mi \tag{11a}$$

$$C^{\mu} = 14.4b^{\mu}\exp(-\kappa^{\mu}{}_{s}r^{\mu}{}_{0})[(mi/nj)(Z^{\mu}{}_{\alpha}/r^{\mu}{}_{0}) - (Z^{\mu}{}_{\beta}/r^{\mu}{}_{0})] \quad \text{if } mi > nj \tag{11b}$$

Where

$$E^{\mu}{}_{F} = (h\kappa^{\mu}{}_{F})^2/(2m)$$

$$\kappa^{\mu}{}_{s} = (4\kappa^{\mu}{}_{F}/\pi a_B)^{1/2}$$

$$\kappa^{\mu}{}_{F} = (3\pi^2 N^{\mu}{}_{e})^{1/3}$$

$$r^{\mu}{}_{0} = d^{\mu}/2 \tag{12}$$

a_B is the Bohr radius (in Å) and d^{μ} is the bond distance (in Å). The units of $E^{\mu}{}_{h}$ and C^{μ} are electronvolts. The physical interpretation of C^{μ} is that it is the difference between the screened Coulomb potentials produced by the two atoms composing the bond or, in other words, it is contributed by the interaction of point charge, while $E^{\mu}{}_{h}$ is contributed by the interaction of dipole moment and other multiple moments. exp($-\kappa^{\mu}{}_{s}r^{\mu}{}_{0}$) in eqs 11a and 11b is the Thomas−Fermi screening factor. $\kappa^{\mu}{}_{F}$ is the Fermi wave vector. b^{μ} is a correction factor and is proportional to the square of the average coordination number $N^{\mu}{}_{c}$.

$$b^{\mu} = \beta\langle N^{\mu}{}_{c}\rangle^2$$

$$\langle N^{\mu}{}_{c}\rangle = [mi/(mi+nj)]N_{CAi} + [nj/(mi+nj)]N_{CBj} \tag{13}$$

β is 0.089.[4] $N^{\mu}{}_{e}$ is expressed as follows:

$$N^{\mu}{}_{e} = n^{\mu}{}_{e}/\upsilon^{\mu}{}_{b} \tag{14}$$

$$n^{\mu}{}_{e} = Z^{\mu}{}_{A}/N^{\mu}{}_{CAi} + Z^{\mu}{}_{B}/N^{\mu}{}_{CBj} \tag{15}$$

where $n^{\mu}{}_{e}$ is the number of valence electrons per μ bond and $Z^{\mu}{}_{A}$ and $Z^{\mu}{}_{B}$ are the number of valence electrons of A and B atoms, respectively. When atoms (usually cations) have d and f electrons, the number of valence electrons $Z^{\mu}{}_{A}$ should be replaced by an effective value $(Z^{\mu}{}_{A})^*$, which is usually the sum of s, p, d, and f electrons as suggested by Tanaka.[6] $\upsilon^{\mu}{}_{b}$ is the bond volume. Since the nearest neighbor distance d^{μ} (bond distance, in Å) is expected to be proportional to the bond volume [$\upsilon^{\mu}{}_{b} \propto (d^{\mu})^3$]. We have

$$\upsilon^{\mu}{}_{b} = (d^{\mu})^3/\sum_{\nu}[(d^{\nu})^3 N^{\nu}{}_{b}] \tag{16}$$

For complex crystals, which are usually anisotropic systems, the coordination number $N^{\mu}{}_{CAi}$ in eq 15 should be written as[6]

$$N^{\mu}{}_{CAi} = V_i/s^{\mu}{}_{i} \tag{17}$$

V_i is the oxidation state of atom A_i, and $s^{\mu}{}_{i}$ is the bond valence of μ bond associated with atom i. According to bond valence sums (BVS),[11,12] V_i and $s^{\mu}{}_{i}$ can be written as

$$V_i = \sum_{\mu} s^{\mu}{}_{i} \tag{18}$$

$$s^{\mu}{}_{i} = \exp[(R^{\mu}{}_{i} - d^{\mu}{}_{i})/b] \tag{19}$$

where $R^{\mu}{}_{i}$ is the bond valence parameter. it is an empirical parameter dependent on the species of atoms and on the oxidation states. Their values have been tabulated for a wide variety of atomic pairs.[11] $d^{\mu}{}_{i}$ is the bond distance (in Å), and b is a constant equal to 0.37.

Thus, bond covalency and bond susceptibility can be calculated for isotropic systems which contain only one type of bond each. For isotropic systems, our evaluation for the coordination number is naturally reduced to PVL theory.

If d and/or f holes exist, because the transition to these d and/or f empty levels will increase the bond susceptibility, in this case according to Levine[5] the corrected average energy gap $E^{\mu}{}_{g}{}^*$ is

$$(E^{\mu}{}_{g}{}^*)^2 = (C^{\mu *})^2 + (E^{\mu}{}_{h})^2 \tag{20}$$

It can also be expressed as[5]

$$(E^{\mu}{}_{g}{}^*)^2 = (E^{\mu}{}_{g})^2/(1+\Gamma) \tag{21}$$

where Γ = number of d or f holes/number of valence electrons. The value of the effective heteropolar gap $C^{\mu *}$ is

$$(C^{\mu *})^2 = ((C^{\mu})^2 - \Gamma(E^{\mu}{}_{h})^2)/(1+\Gamma) \tag{22}$$

Thus, the corrected bond covalency $(f^{\mu}{}_{c})^*$ can be obtained via eqs 9, 21, and 22 as

$$(f^{\mu}{}_{c})^* = (1+\Gamma)f^{\mu}{}_{c} \tag{23}$$

Therefore, it is seen that d and f holes result in an increase in bond covalency and hence a decrease in bond ionicity.

3. Examples

In this section, two examples have been presented to illustrate the application of the method. The decomposition of complex crystals (R_2BaCuO_5, RMn_2O_5; R = rare earth) into the sum of binary crystals is clearly given, and the procedure of how the bond covalency is evaluated is shown. This is helpful for understanding how our method has been applied, and the procedure is transferable to other complex crystals.

TABLE 1: Bond Covalencies (%) from BVS Scheme in R_2BaCuO_5[a]

	Sm	Gd	Dy	Ho	Y	Er	Tm	Yb	Lu
Ba−O(1)	1.93	1.96	2.31	2.39	2.55	2.69	2.72	2.43	2.95
Ba−O(2)	2.87	3.07	3.43	3.81	4.10	4.05	4.28	4.44	4.76
Ba−O(3)	5.24	4.77	5.07	5.29	5.71	5.41	5.71	5.97	6.30
R(1)−O(1)	18.56	8.64	4.88	3.96	3.58	3.28	2.80	2.71	2.26
R(1)−O(2)	17.60	7.81	4.44	3.50	3.08	2.96	2.46	2.08	1.92
R(1)−O(3)	18.18	9.13	5.45	4.60	4.00	4.06	3.35	2.91	2.73
R(2)−O(1)	15.36	9.27	4.93	4.02	3.64	3.22	2.70	3.05	2.10
R(2)−O(2)	12.73	7.66	4.31	3.37	2.97	2.75	2.25	1.93	1.72
R(2)−O(3)	17.00	10.95	6.69	5.37	4.81	4.64	3.65	3.34	3.03
Cu−O(1)	22.79	20.85	20.42	20.54	20.58	20.40	20.61	21.37	20.03
Cu−O(2)	20.25	17.81	18.78	18.35	17.54	18.64	18.54	17.42	16.97
Cu−O(3)	13.71	13.55	12.24	12.51	12.44	12.59	12.99	12.34	12.44

[a] The structural data of Sm are taken from ref 13, those of Gd from ref 14, and those of Dy to Lu from ref 15.

TABLE 2: Bond Valences (v.u.) from BVS Scheme in R_2BaCuO_5

	Sm	Gd	Dy	Ho	Y	Er	Tm	Yb	Lu
Ba−O(1)	0.0944	0.0961	0.1004	0.1003	0.1004	0.1055	0.1044	0.1077	0.1071
Ba−O(2)	0.1329	0.1428	0.1521	0.1551	0.1551	0.1561	0.1643	0.1670	0.1729
Ba−O(3)	0.2951	0.2768	0.2846	0.2928	0.2983	0.2989	0.2997	0.3038	0.3070
R(1)−O(1)	0.4315	0.4567	0.4667	0.4579	0.4542	0.4469	0.4493	0.4433	0.4397
R(1)−O(2)	0.4422	0.4394	0.4292	0.4231	0.4144	0.4178	0.4150	0.4071	0.3965
R(1)−O(3)	0.4011	0.4518	0.4629	0.4679	0.4457	0.4667	0.4667	0.4604	0.4457
R(2)−O(1)	0.4766	0.4403	0.4356	0.4347	0.4262	0.4304	0.4396	0.4866	0.4231
R(2)−O(2)	0.4200	0.3873	0.3852	0.3821	0.3699	0.3800	0.3841	0.3699	0.3679
R(2)−O(3)	0.5088	0.4899	0.5256	0.5116	0.4952	0.5228	0.5130	0.5157	0.5116
Cu−O(1)	0.4033	0.4457	0.4481	0.4505	0.4567	0.4493	0.4493	0.4629	0.4592
Cu−O(2)	0.3600	0.3780	0.4066	0.4011	0.3979	0.4088	0.4033	0.4088	0.4055
Cu−O(3)	0.2137	0.2589	0.2311	0.2349	0.2362	0.2324	0.2407	0.2362	0.2368

TABLE 3: Oxidation States of the Constituent Elements from BVS Scheme in R_2BaCuO_5

	Sm	Gd	Dy	Ho	Y	Er	Tm	Yb	Lu
Ba	1.79	1.79	1.86	1.90	1.92	1.94	1.98	2.01	2.04
R(1)	3.03	3.12	3.11	3.08	3.01	3.03	3.03	2.98	2.91
R(2)	3.26	3.03	3.04	3.02	2.94	3.01	3.04	2.96	2.94
Cu	1.74	1.91	1.94	1.94	1.94	1.94	1.94	1.97	1.97
O(1)	−1.98	−1.98	−1.97	−1.98	−1.96	−1.97	−1.99	−2.09	−1.96
O(2)	−1.93	−1.93	−1.96	−1.94	−1.91	−1.94	−1.95	−1.93	−1.91
O(3)	−2.01	−2.03	−2.07	−2.09	−2.07	−2.12	−2.12	−2.12	−2.12

3.1. R_2BaCuO_5 (R = Sm, Gd, Dy, Ho, Y, Er, Tm, Yb, Lu). In this example, bond covalency has been calculated in R_2BaCuO_5 (R = Sm, Gd, Dy, Ho, Y, Er, Tm, Yb, Lu). They are isostructural, green-colored, and often found as impurities in the synthesis of high-T_c $RBa_2Cu_3O_7$ oxides. According to the method stated above (eqs 1 and 2) and crystallographic data (Sm,[13] Gd,[14] Dy to Lu[15]), R_2BaCuO_5 (RBCO) can be decomposed into the sum of binary crystals as follows:

$$\begin{aligned} R_2BaCuO_5 &= R(1)R(2)Ba(1)Cu(1)O_2(1)O_2(2)O(3) \\ &= R_{2/7}(1)O_{1/3}(1) + R_{4/7}(1)O_{2/3}(2) + \\ &\quad R_{1/7}(1)O_{1/6}(3) + R_{4/7}(2)O_{2/3}(1) + R_{2/7}(2)O_{1/3}(2) + \\ &\quad R_{1/7}(2)O_{1/6}(3) + Ba_{4/11}(1)O_{2/3}(1) + Ba_{4/11}(1)O_{2/3}(2) + \\ &\quad Ba_{3/11}(1)O_{1/2}(3) + Cu_{2/5}(1)O_{1/3}(1) + Cu_{2/5}(1)O_{1/3}(2) + \\ &\quad Cu_{1/5}(1)O_{1/6}(3) \end{aligned}$$

The coordination number of R(1) and R(2) is 7, those of Ba and O (including O(1), O(2), O(3)) are 11 and 6, respectively. From the method stated above (eq 17), it is known that the bond valence (in valence unit, v.u.) is a crucial quantity in the calculation of bond covalency and should be calculated with good accuracy. In this paper, the bond valence is calculated by the following two methods. (1) Bond valence sums (BVS), this theory has now been well recognized.[11,12] The bond valence parameters in this calculation are taken from ref 11. (2) Equal-valence of the oxidation state of cations Ba, R(1), R(2) (the oxidation states of Ba, R(1), R(2), and O are fixed to 2.0, 3.0, 3.0, and −2.0, respectively), that of Cu is obtained according to electroneutrality principle. The thus obtained oxidation state of Cu is 2.0, which coincides with its formal oxidation state (from stoichiometry). This method is only suitable for isotropic systems. The comparison of the two methods is made in the following.

The calculated bond covalencies are collected in Table 1-(from BVS) and Table 4 (from equal-valence scheme). The bond valences for constituent bonds in RBCO are shown in Table 2 (from BVS) and Table 4 (from equal-valence scheme). The oxidation state for each element from BVS is given in Table 3. It can be seen (Table 1) that for a certain RBCO the bond covalency for Ba−O type has the following order: Ba−O(3) > Ba−O(2) > Ba−O(1). For the other types of bonds, the orders are R(1,2)−O(3) > R(1,2)−O(1) > R(1,2)−O(2) (except R(1)−O type in Sm_2BaCuO_5, where R(1)−O(1) > R(1)−O(3) > R(1)−O(2)), Cu−O(1) > Cu−O(2) > Cu−O(3). It is also seen that in most cases (except R(1)−O(1,2,3) types of RBCO) the bond with larger covalency corresponds to higher bond valence (Table 2). From Table 1 it is also noticed that, with the decrease of ionic radii from Sm to Lu, the bond covalencies of Ba−O(1,2,3) increase, whereas those of R(1,2)−O(1,2,3) decrease. No obvious trend is observed for the Cu−O(1,2,3) type of bond. Table 3 gives the bond valence sums for the different RBCO oxides. With the decrease of ionic radii from Sm to Lu, the oxidation states of Ba and Cu increase, whereas those of R(1) and R(2) decrease. For anions, the oxidation states of O(1) are near to its formal valence of 2, those of O(2) are less than 2 and show a large difference from 2, whereas those of O(3) are larger than 2.

For the equal-valence scheme (Table 4), the bond covalencies for the Ba−O(1,2,3) type in a given RBCO are nearly the same, this is also observed for the R(1,2)−O(1,2,3) type of bond. For the Cu−O(1,2,3) type of bond, the bond covalencies of Cu−O(3) are larger than those of Cu−O(1,2) and the bond valences

TABLE 4: Bond Covalencies (Sm to Lu) (%) and Bond Valences (v.u.) (Last Column) from Equivalence Scheme in R_2BaCuO_5

	Sm	Gd	Dy	Ho	Y	Er	Tm	Yb	Lu	bond valence
Ba−O(1)	4.48	4.48	4.51	4.50	4.49	4.50	4.50	4.48	4.51	0.1818
Ba−O(2)	4.49	4.50	4.53	4.52	4.51	4.52	4.53	4.50	4.53	0.1818
Ba−O(3)	4.56	4.55	4.59	4.58	4.58	4.58	4.59	4.56	4.59	0.1818
R(1)−O(1)	19.75	9.59	5.26	4.15	3.57	3.36	2.78	2.32	2.08	0.4286
R(1)−O(2)	19.74	9.60	5.27	4.16	3.59	3.37	2.79	2.33	2.09	0.4286
R(1)−O(3)	19.78	9.60	5.26	4.13	3.58	3.36	2.78	2.32	2.08	0.4286
R(2)−O(1)	19.72	9.60	5.27	4.15	3.58	3.37	2.79	2.31	2.08	0.4286
R(2)−O(2)	19.77	9.65	5.28	4.17	3.60	3.38	2.80	2.34	2.10	0.4286
R(2)−O(3)	19.69	9.57	5.23	4.12	3.56	3.34	2.77	2.30	2.07	0.4286
Cu−O(1)	15.89	15.87	15.96	15.91	15.91	15.91	15.93	15.85	15.94	0.3507
Cu−O(2)	15.92	15.90	15.98	15.94	15.94	15.93	15.96	15.87	15.97	0.3507
Cu−O(3)	25.97	25.63	25.98	25.88	25.86	25.89	25.87	25.77	25.91	0.5974

TABLE 5: Bond Covalencies (%) and Bond Valences (in v.u.)from BVS Scheme in RMn_2O_5[a]

	La		Pr		Nd		Sm		Eu	
	bond covalency	bond valence	bond covalency	bond valence	bond covalency	bond valence	bond covalency	bond valence	bond covalency	bond 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

[a] The structural data are taken from ref 16.

follow this trend as well. These results are another indication that the bond covalency is mainly influenced by the bond valence in RBCO. Through Sm to Lu, although the bond covalencies of R(1,2)−O(1,2,3) show the same trend as those in BVS scheme, those of Ba−O(1,2,3) are almost the same. This suggests that, in the evaluation of bond covalency in anisotropic systems, care should be taken in the calculation of bond valence. In isotropic systems, such as some binary crystals, the BVS and equal-valence schemes may yield the same results.

3.2. RMn_2O_5 (R=La, Pr, Nd, Sm, Eu). In this example, RMn_2O_5 (R = La, Pr, Nd, Sm, Eu)[16] are investigated. They are electrical insulators and are isostructural with space group *Pbam*. In the structure, Mn^{3+} and Mn^{4+} occupy different crystallographic positions, which have a square pyramidal environment and octahedral coordination, respectively. In addition, the crystal structure contains infinite chains of $Mn^{4+}O_6$ octahedra parallel to the *c* axis and linked through $Mn^{3+}O_5$ units and bicapped RO_8 antiprisms. Based on the crystallographic data[16] and eqs 1 and 2, RMn_2O_5 can be decomposed as

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

The coordination number of R is 8, of Mn(1) is 6, Mn(2) is 5, O(1), O(2), and O(4) are 4, and O(3) is 3. As in section 3.1, two computational schemes are adopted, i.e., BVS and equal-valence schemes. In the latter case, the valences of R and O (including O(1), O(2), O(3)) are fixed to 3.0 and −2.0. The valences of Mn(1) and Mn(2) are derived from the electroneutrality principle. The obtained oxidation states of Mn(1) and Mn(2) are 4.0 and 3.0, respectively, which coincide with their values from stoichiometry as well.

TABLE 6: 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

The calculated bond covalencies and bond valences from BVS and equal-valence schemes are collected in Tables 5 and 7, respectively. The oxidation states for each element from BVS are given in Table 6. It can be seen (Table 5) that similar regularity has been observed as in section 3.1; that is, in most cases, larger bond covalencies correspond to higher bond valences. From Table 5, 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. Meanwhile, the oxidation states (Table 6) of Mn(2), O(1), and O(3) increase, those of R and O(2) decrease, and those of Mn(1) and O(4) remain relatively unchanging. We think the oxidation states of Mn(2) in $SmMn_2O_5$ and $EuMn_2O_5$ are too large compared with its formal oxidation state of 3.0. This is not surprising because from BVS theory the bond distance of Mn(2)−O(1,4) (see ref 14) is relatively short in $SmMn_2O_5$ and $EuMn_2O_5$ (this is caused by the lower coordination number of $Mn^{3+}O_5$ than that of $Mn^{4+}O_6$), and therefore results in relatively higher bond valences. This may suggest that a new bond parameter for Mn^{3+} and O^{2-} is needed.

For the equal-valence scheme (Table 7), it can be found that the same regularity has been observed for the relationship between bond valence and bond covalency as in the BVS scheme. Through La to Eu, no obvious trend is found for the magnitude of bond covalency for all considered types of bonds.

TABLE 7: Bond Covalencies (%) and Bond Valences (Last Column, in v.u.) from Equivalence Scheme in RMn_2O_5

	La	Pr	Nd	Sm	Eu	bond 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

For the two bond valence schemes, the bond covalencies of Mn−O (average value) in the $Mn^{3+}O_5$ unit are larger than those of Mn−O in the $Mn^{4+}O_6$ unit and the magnitude of bond covalency obeys the following order: Mn(2)−O > Mn(1)−O > R−O.

4. Conclusions

A semiempirical method to evaluate the bond covalency in complex crystals has been proposed. This method is the generalization of the dielectric description theory of the Phillips−Van Vechten−Levine−Tanaka scheme. In this method, an explicit expression concerning how to decompose the complex crystals which are usually anisotropic systems into the sum of binary crystals which are isotropic systems is given. The idea presented in this study can be used not only in the evaluation of bond covalency but also in other properties, such as bulk modulus,[10] and further may also be applied to compute other material's parameters. Since the ab initio calculations are complex and require significant effort, our method provides a simple but efficient tool for studying the properties of the materials and even to predict new materials, particularly in the study of series compounds. The bond valence can be treated in two ways, BVS and equal-valence scheme; which one is better depends on the materials studied. In the illustrative examples, bond covalency is mainly influenced by the bond valence for the presented materials in this paper. Larger bond valence usually corresponds to higher bond covalency; other quantities change less through the series.

Acknowledgment. The authors thank for financial support the National Natural Science Foundation of China (Grant 29871029) and Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry.

References and Notes

(1) Phillips, J. C. *Phys. Rev. Lett*. **1968**, *20*, 550.
(2) Phillips, J. C.; Van Vechten, J. A. *Phys. Rev. Lett*. **1969**, *22*, 705.
(3) Van Vechten, J. A. *Phys. Rev*. **1969**, *182*, 891.
(4) Levine, B. F. *J. Chem. Phys*. **1973**, *59*, 1463.
(5) Levine, B. F. *Phys. Rev. B* **1973**, *7*, 2591.
(6) Tanaka, S. *Physica C* **1994**, *220*, 341.
(7) Barr, T. L.; Brundle, C. R. *Phys. Rev. B* **1992**, *46*, 9199.
(8) Wu, Z. J.; Meng, Q. B.; Zhang, S. Y. *Phys. Rev. B* **1998**, *58*, 958.
(9) Meng, Q. B.; Wu, Z. J.; Zhang, S. Y. *J. Phys.:Condens. Matter* **1998**, *10*, L85.
(10) Meng, Q. B.; Xiao, C. Y.; Wu, Z. J.; Feng, Ke-an; Lin, Z. D.; Zhang, S. Y. *Solid State Commun.* **1998**, *107*, 369.
(11) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., Sect. B* **1991**, *47*, 192.
(12) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.
(13) Schiffler, S.; Müller-Buschbaum, H. K. *Z. Anorg. Allg. Chem*. **1986**, *540/541*, 243.
(14) Campá, J. A.; Gómez de Salazar, J. M.; Gutiérrez-Puebla, E.; Monge, M. A.; Rasines, I.; Ruíz-Valero, C. *Phys. Rev. B* **1988**, *37*, 529.
(15) Salinas-Sanchez, A.; Garcia-Munoz, J. L.; Rodriguez-Carvajal, J.; Saez-Puche, R.; Martinez, J. L. *J. Solid State Chem*. **1992**, *100*, 201.
(16) Alonso, J. A.; Casais, M. T.; Martínez-Lope, M. J.; Rasines, I. *J. Solid State Chem.* **1997**, *29*, 105.