Semiempirical study on the valences of Cu and bond covalency in $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$

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The valences of Cu and bond covalencies in $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$ have been investigated using complex chemical bond theory. This theory is the generalization of Phillips, Van Vechten, Levine, and Tanaka's scheme. The results indicate that the valences of Cu(1) and Cu(2) in our calculation agree well with those obtained by the bond valence sum method. The valences of Cu(1) and Cu(2) in our calculation also suggest that the holes introduced by Ca substitution only reside in CuO_2 planes and there is a competing mechanism for the hole density in CuO_2 planes between Ca doping and oxygen depletion. These conclusions are in satisfactory agreement with experiments. The calculated ordering of covalencies is Cu(1)-O(4)>Cu(1)-O(1) >Cu(2)-O(2,3)>Cu(2)-O(1)>Ca-O>Y-O~Ba-O, regardless of the Ca doping level and oxygen content. [S0163-1829(98)03325-6]

It is known that a common feature in high-T_c copper oxide superconductors is that the electrical conductivity can be controlled by varying doping levels through ion substitution or oxygen stoichiometry variation. A range of phases, such as high-T_c superconductors, nonsuperconducting (overdoped) metals, and antiferromagnetic insulators can thus be obtained in some oxides. In order to shed light on the mechanism of superconductivity, numerous studies related to cation substitution in $YBa_2Cu_3O_{6+y}$ (YBCO) and their effect on the critical temperature T_c have been performed. Among them, the partial replacement of Y^{3+} by Ca^{2+} has been found to be especially interesting.[1–14] It is now common knowledge that $YBa_2Cu_3O_6$ is a semiconductor, whereas the superconductivity can be restored with the substitution of Y^{3+} by Ca^{2+}.[3–5,12,14] To date, research on $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$ (YCBCO) can be classified into three groups: In the first group, the Ca doping level remains constant and the oxygen content varies from $y=0$ to 1;[2] in the second group, both Ca doping levels and oxygen content change with the former increasing and the latter decreasing;[3,6,10] finally, in the third group, Ca doping levels increase while the oxygen content remains relatively constant.[3,4,7] The experimental results of these studies are the following. (i) In the first group, materials such as $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6+y}$,[2] three distinct superconducting regions have been observed and the superconductivity disappears for $y<0.4$. Contrary to the result that YCBCO is a superconductor in an oxygen-poor region as well,[3–5,12,14] the disappearance of superconductivity was ascribed to surface oxidation of crystal grains in quenched samples.[2] T_c in the first two plateaus ($0.89\geqslant y\geqslant 0.75$, $T_c=80$ K and $0.75\geqslant y\geqslant 0.50$, $T_c=50$ K) was explained to be associated with the infinite CuO chains, whereas in the third plateau ($0.50\geqslant y\geqslant 0.40$, $T_c=25$ K), T_c was related to the formation of Cu-O-Cu dimers.[2] (ii) In the second group, two regions can be recognized in the light of oxygen content; they are fully oxygenated[3,10] and partially oxygenated or oxygen deficient.[3,6] In the fully oxygenated region, T_c decreases with the increasing Ca doping levels and decreasing oxygen content; this was explained as an overdoping effect[3] or the creation of disorder in CuO_2 planes and Ca preferring sixfold coordination.[10] In the oxygen-deficient region, T_c increases, which was ascribed to the underdoping effect, the increasing number of holes in CuO_2 planes,[3] or Ca preferring eightfold coordination.[6] (iii) In the third group, the oxygen content is either fully oxygenated or fully reduced (oxygen-poor) region and, unlike the above two groups in which the samples are all orthorhombic, the samples in this group are orthorhombic for a fully oxygenated sample and tetragonal for a fully reduced sample. For the Ca-free fully reduced sample in the third group, YBCO is a nonsuperconductor, while the superconductivity was observed by introducing divalent Ca at the Y site, and the appearance of T_c was thought to be due to a small increase of the hole density in CuO_2 planes.[3]

Research also indicates that divalent Ca substitution in YBCO does not dope holes uniformly for all values of y (Ref. 11) and the hole density in CuO_2 planes depends on the competition between Ca substitution and oxygen content variation.[6,13] In this paper, from a different point of view, YCBCO was investigated by complex chemical bond theory (CCBT). This theory is the generalization of the dielectric description theory developed by Phillips,[15,16] Van Vechten,[17,18] and Levine[19,20] and has been applied to nonlinear optics,[21,22] superconductivity,[23] lattice energy,[24] etc. The similar work was also carried out on high-T_c oxides by Tanaka,[25] but in the actual calculations only three types of bonds were considered and they were artificially restricted in a box in order to evaluate the bond covalency (ionicity). In this paper, an explicit expression concerning the decomposing of complex crystals that are usually anisotropic systems into the sum of binary crystals that are isotropic systems is given. With the method presented, YCBCO is investigated by considering all types of bonds (13 in total). We hope our work will provide some insight into the superconducting mechanism in YCBCO. The detailed theory concerning CCBT can be found in Ref. 22 and will be only briefly outlined in this paper.

It is known that Phillips–Van Vechten[15–18] theory can deal only with the binary crystals, especially $A^N B^{8-N}$ type. Although the theory had been developed by Levine,[19,20] which can deal with more complex crystals, such as AB_n and $A_{n1}B_n$ types of crystals, successfully, for ABC_2, ABC_3, and ABC_4 types of crystals, however, an explicit expression was not given about how to decompose the complex multibond crystals into binary crystals. Therefore, it is worthwhile to extend these fruitful ideas. After considering these ideas in chemical bond representation, we[22,23] succeeded in generalizing Phillips–Van Vechten–Levine[15–20] (PVL) theory for multibond systems. Using this generalized theory, any complex crystal can be decomposed into a sum of binary crystals. These binary crystals obtained are related to each other and every binary crystal includes only one type of chemical bond, but the properties of these binary crystal are different from those of a real corresponding binary crystal (if any), although its chemical bond parameters can be calculated in a similar way.

Suppose A denotes cations and B anions. Any multibond complex crystal can be written as $A^1_{a1}A^2_{a2}\cdots A^i_{a1}\cdots B^1_{b1}B^2_{b2}\cdots B^j_{bj}$, 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 and bj represent the numbers of the corresponding elements. Thus, together with crystal structure data, it can be decomposed into binary crystals by the formula

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

$$mi=N(B^j-A^i)ai/N_{CA^i},\quad nj=N(A^i-B^j)bj/N_{CB^j},$$

where N_{CA^i} and N_{CB^j} 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 fraction contributed by the A^i ion and $N(A^i-B^j)$ represents the nearest coordination fraction contributed by the B^j ion. After decomposing the complex crystal into different kinds of binary crystals, which is an isotropic system, and introducing the concept of effective valence electron, PVL theory[15–20] can be directly applied to the calculation of the chemical bond parameters in complex crystals.

Based on CCBT and crystallographic data,[2–4,6,7] $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$ can be decomposed into binary crystals as

$$\begin{aligned}Y_{1-x}Ca_xBa_2Cu_3O_{6+y}&=Y_{1-x}Ca_xBa_2Cu(1)(Cu)(2)_2O(1)_2O(2)_2O(3)_2O(4)_y\\&=Ba_{4/5}O(1)_{4/3}+Ba_{2/5}O(2)_{2/3}+Ba_{2/5}O(3)_{2/3}+Ba_{2/5}O(4)_{2y/3}+Y_{(1-x)/2}O(2)_{2(1-x)/3}+Y_{1-x/2}O(3)_{2(1-x)/3}\\&\quad+Ca_{x/2}O(2)_{2x/3}+Ca_{x/2}O(3)_{2x/3}+Cu(1)_{1/2}O(1)_{1/3}+Cu(1)_{1/2}O(4)_{y/3}\\&\quad+Cu(2)_{2/5}O(1)_{1/3}+Cu(2)_{4/5}O(2)_{2/3}+Cu(2)_{4/5}O(3)_{2/3}.\end{aligned}$$

In our calculation, the label for oxygen is that O(1) is in an apex, O(2) and O(3) are in CuO_2 planes, and O(4) is in a CuO chain. Since the oxygen content in O(5) is relatively small, it was omitted and its oxygen content was added in O(4). The covalency difference thus created is very small (within 0.02%; see Table III). The valences of Ba, Y, Ca, and O were kept fixed; they are $+2$, $+3$, $+2$, and -2, respectively. In this case, the hole density in the CuO_2 plane $V-$, as introduced by Tallon,[26] should be $V_-=V_{Cu(2)}-2$. In our calculation, the structural data were taken from Refs. 2, 3, 6, 4, and 7 and can be classified into three groups, as mentioned above. The calculated valences of Cu(1) and Cu(2) and bond covalencies based on these structures are shown in Tables I–V. The first group is in Table I, the second in Tables II (sets A and B) and III, and the third in Tables II (set C), IV, and V.

In the first group (Table I) we see that with a constant Ca doping level and decreasing oxygen content, the valences of Cu(1) and Cu(2) diminish and Cu(1) changes more rapidly than Cu(2), indicating that the valences of Cu(1) are more influenced by oxygen content than those of Cu(2). This trend was observed in the valences of bond valence sum (BVS) calculations as well.[2] Comparing the valences of Cu(1) and Cu(2) of the BVS (Ref. 2) and our calculations, we found that the average deviation is less that 10%, demonstrating that our method is reasonable. The deviation can be ascribed to the fixed valences of Y, Ca, Ba, and O in our calculation, whereas in the BVS calculation it is bond length dependent. With increasing oxygen content, the bond covalencies of Cu(2)-O(1,2,3) increase, whereas those of Cu(1)-O(1,4) decrease at small oxygen content y, reach their minimum at approximately $y=0.4$ (extrapolated value), and then increase. Since it is experimentally known that T_c appears when $y\geqslant 0.4$, from our calculation, we can deduce that for covalencies of Cu(1)-O(1,4), the superconductivity occurs when $df_c/dy\geqslant 0$ (f_c denotes covalency) and larger covalency differences between Cu(1)-O(4) (CuO chain) and Cu(2)-O(2,3) (CuO_2 plane) correspond to higher T_c.

For the second group shown in Tables II (sets A and B) and III, it is seen that with increasing Ca doping level and decreasing oxygen content, the valences of Cu(1) decrease (but only slightly in Table III until $x=0.1$ because of the relatively constant oxygen content), while those of Cu(2) slightly increase (Table II, sets A and B). The slight drop for the valence of Cu(2) in Table III when $x=0.15$ can be ascribed to the sudden decrease in oxygen content. This indicates that the holes introduced by Ca substitution are compensated by oxygen depletion, in accordance with

TABLE I. Valences of Cu(1) and Cu(2) and bond covalencies (in %) of chemical bonds in $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$. The structural data were taken from Ref. 2.

x	0.20	0.20	0.20	0.20	0.20
y	0.89	0.52	0.50	0.33	0.13
Valence					
Cu(1)	2.234	1.695	1.667	1.431	1.166
Cu(1)[a]	2.45	1.91	1.76	1.51	1.36
Cu(2)	2.373	2.273	2.267	2.214	2.147
Cu(2)[a]	2.27	2.18	2.16	2.11	2.05
Bond covalency					
Cu(1)-O(1)	19.75	17.33	17.31	17.35	18.44
Cu(1)-O(4)	19.92	17.53	17.49	17.55	18.74
Cu(2)-O(1)	14.28	12.64	12.52	11.74	10.88
Cu(2)-O(2)	17.00	14.85	14.73	13.74	12.58
Cu(2)-O(3)	17.01	14.85	14.73	13.74	12.58
Ba-O(1)	5.63	6.38	6.42	6.83	7.38
Ba-O(2)	5.57	6.33	6.36	6.78	7.33
Ba-O(3)	5.56	6.32	6.36	6.78	7.33
Ba-O(4)	5.58	6.31	6.36	6.76	7.31
Y-O(2)	6.18	5.82	5.81	5.64	5.44
Y-O(3)	6.20	5.84	5.81	5.64	5.44
Ca-O(2)	9.27	8.77	8.77	8.54	8.26
Ca-O(3)	9.33	8.82	8.77	8.54	8.26

[a]Reference 2.

experiment.[6,8,13] Our results also show reasonable agreement with those of Cava *et al.*[27] using the BVS calculation in $YBa_2Cu_3O_7$. The covalency difference between bonds in the CuO chain [Cu(1)-O(4)] and the CuO_2 plane [Cu(2)-O(2,3)] decreases with decreasing oxygen content in fully oxygenated region, which corresponds to a decrease in T_c, whereas in a partially oxygenated or an oxygen-deficient region, the decreased covalency difference corresponds to an increase in T_c.

Finally, in the third group [Tables II (set C), IV, and V], in which oxygen content is relatively constant and the structure is orthorhombic for a fully oxygenated sample and tetragonal for a fully reduced sample, it is seen that our results for the valences of Cu(1) and Cu(2) agree well with those from BVS calculations,[7,27] particularly for $YBa_2Cu_3O_7$ (i.e., $x=0.0$). The results also indicate that the valences of Cu(1) remain relatively constant (Table II, set C) or slightly increase because of the slight increase of oxygen content (Table IV and V), whereas those of Cu(2) increase. This indicates that Ca substitution brings the hole density only to the CuO_2 plane, in good agreement with experiment.[8] On the other hand, we notice that because of the oxygen compensation, the hole density in the CuO_2 plane increases slowly (Table IV) with an increase of the Ca doping level, reflecting the competitive mechanism for the hole density residing in CuO_2 planes and in reasonable agreement with experimental results.[6,8,13] These phenomena were observed in the other two groups as well. The bond covalencies in the CuO_2 plane increase with an increase of Ca doping for both fully oxy-

TABLE II. Valences of Cu(1) and Cu(2) and bond covalencies (in %) of chemical bonds in $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$. The structural data were taken from Ref. 3.

	Set A			Set B			Set C		
x	0.00	0.10	0.20	0.00	0.10	0.20	0.00	0.10	0.20
y	0.97	0.92	0.83	0.62	0.55	0.49	0.05	0.04	0.04
Valence									
Cu(1)	2.354	2.279	2.144	1.837	1.737	1.653	1.063	1.050	1.050
Cu(1)[a]	2.378								
Cu(2)	2.293	2.330	2.358	2.201	2.231	2.264	2.019	2.065	2.115
Cu(2)[a]	2.209								
Bond covalency									
Cu(1)-O(1)	20.78	20.13	19.13	17.74	17.44	17.27	19.36	19.46	19.43
Cu(1)-O(4)	20.92	20.27	19.29	17.91	17.63	17.47	19.68	19.78	19.76
Cu(2)-O(1)	13.05	13.58	13.88	11.66	12.04	12.49	9.38	9.88	10.45
Cu(2)-O(2)	16.44	16.65	16.62	14.55	14.58	14.66	11.45	11.71	12.05
Cu(2)-O(3)	16.45	16.66	16.63	14.55	14.58	14.66	11.45	11.71	12.05
Ba-O(1)	5.50	5.58	5.73	6.17	6.31	6.44	7.63	7.65	7.65
Ba-O(2)	5.43	5.51	5.67	6.10	6.25	6.38	7.58	7.60	7.60
Ba-O(3)	5.43	5.52	5.67	6.11	6.25	6.39	7.58	7.60	7.60
Ba-O(4)	5.45	5.53	5.68	6.11	6.25	6.37	7.56	7.58	7.57
Y-O(2)	6.27	6.22	6.12	5.94	5.86	5.80	5.37	5.35	5.34
Y-O(3)	6.28	6.23	6.12	5.95	5.87	5.80	5.37	5.35	5.34
Ca-O(2)		9.33	9.18		8.84	8.76		8.13	8.12
Ca-O(3)		9.35	9.21		8.86	8.75		8.13	8.12

[a]Reference 27.

TABLE III. Valences of Cu(1) and Cu(2) and bond covalencies (in %) of chemical bonds in $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$. The structural data were taken from Ref. 6. The data with an asterisk were calculated from the original data [O(4) and O(5) were separated].

x	0.00	0.05	0.10	0.15
y	0.76	0.755	0.717	0.594
Valence				
Cu(1)	2.041	2.034	1.978	1.800
Cu(2)	2.240	2.263	2.278	2.269
Bond covalency				
Cu(1)-O(1)	18.56	18.52	18.23	17.60
Cu(1)-O(4)	18.74	18.69	18.41	17.83
Cu(1)-O(4)*	18.74	18.69	18.41	17.83
Cu(1)-O(5)*	18.70	18.65	18.38	17.80
Cu(2)-O(1)	12.25	12.58	12.81	12.69
Cu(2)-O(2)	15.29	15.48	15.50	15.10
Cu(2)-O(3)	15.29	15.49	15.51	15.10
Ba-O(1)	5.87	5.88	5.95	6.23
Ba-O(2)	5.81	5.82	5.89	6.17
Ba-O(3)	5.81	5.82	5.90	6.17
Ba-O(4)	5.82	5.82	5.90	6.17
Ba-O(4)*	5.82	5.82	5.90	6.17
Ba-O(5)*	5.81	5.82	5.89	6.17
Y-O(2)	6.07	6.06	6.02	5.93
Y-O(3)	6.07	6.06	6.02	5.93
Ca-O(2)		9.11	9.05	8.93
Ca-O(3)		9.13	9.07	8.94

TABLE IV. Valences of Cu(1) and Cu(2) and bond covalencies (in %) of chemical bonds in $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$. The structural data were taken from Ref. 4.

x	0.00	0.15	0.24	0.26	0.28
y	0.16	0.16	0.18	0.20	0.20
Valence					
Cu(1)	1.205	1.205	1.231	1.257	1.257
Cu(2)	2.058	2.133	2.185	2.201	2.211
Bond covalency					
Cu(1)-O(1)	18.26	18.09	18.01	17.86	17.85
Cu(1)-O(4)	18.57	18.37	18.29	18.13	18.12
Cu(2)-O(1)	9.87	10.54	11.35	11.58	11.70
Cu(2)-O(2)	12.08	12.49	13.02	13.21	13.28
Cu(2)-O(3)	12.08	12.49	13.02	13.21	13.28
Ba-O(1)	7.33	7.25	7.23	7.17	7.16
Ba-O(2)	7.27	7.21	7.18	7.12	7.12
Ba-O(3)	7.27	7.21	7.18	7.12	7.12
Ba-O(4)	7.26	7.17	7.16	7.10	7.09
Y-O(2)	5.50	5.44	5.48	5.50	5.49
Y-O(3)	5.50	5.44	5.48	5.50	5.49
Ca-O(2)		8.26	8.32	8.33	8.33
Ca-O(3)		8.26	8.32	8.33	8.33

genated and fully reduced regions, but those in the CuO chain either decrease (Tables IV and V) or remain relatively unchanged (Table II, set C). Therefore, it can be seen that for the fully oxygenated region, the larger covalency difference corresponds to higher T_c, in accordance with the conclusion obtained in the first and second groups, whereas for the fully reduced region in which the structure is tetragonal, it is just opposite, namely, the larger covalency difference corresponds to lower T_c, as in the partially oxygenated region in the second group.

Our results also suggest that the bond covalencies of Ba-O(1,2,3,4), Y-O(2,3), and Ca-O(2,3) are sensitive to the change of oxygen content, but not to the Ca doping level. With the decreasing oxygen content, the covalencies of Ba-O increase and those of Y(Ca)-O decrease. The ordering of covalencies in YCBCO obey the sequence Cu(1)-O(4) $>$ Cu(1)-O(1) $>$ Cu(2)-O(2,3) $>$ Cu(2)-O(1) $>$ Ca-O(2,3) $>$ Y-O(2,3) $\sim$ Ba-O(1,2,3,4). The order shows an interesting picture that CuO fragments (including the CuO_2 plane and the CuO chain) with higher covalencies are separated by BaO and Y(Ca)O fragments with higher ionicities.

In conclusion, the valences of Cu and bond covalencies for the constituent bonds in YCBCO are calculated using the complex chemical bond theory, which is the generalization of the PVL scheme. Three groups of structural data, that is, constant Ca doping level and decreasing oxygen content (the first group), increasing Ca doping level and decreasing oxygen content (the second group), and increasing Ca doping level and relatively constant oxygen content (the third group), are selected. It is found that in the first and second groups (fully and partially oxygenated regions), with decreasing oxygen content, the valences of Cu(1) decrease, whereas those of Cu(2) increase. In the third group (fully oxygenated and oxygen-poor regions), the valences of Cu(1) remain relatively unchanged (Table II, set C) or slightly increase because of a slight increase in the oxygen content (Tables IV and V), while those of Cu(2) increase. These conclusions are in good agreement with those of BVS calculations. Our results also suggest that the holes in the CuO chain are mainly influenced by oxygen content, whereas those in the CuO_2 plane are influenced by both Ca doping level and oxygen content, in satisfactory agreement with experimental findings that the holes introduced by calcium substitution reside only in CuO_2 planes and that there is a competitive mechanism between Ca doping and oxygen depletion for the hole density in CuO_2 planes. The larger covalency differences between bonds in the CuO chain and the CuO_2 plane correspond to higher T_c in the fully oxygenated region, whereas it is the opposite in partially oxygenated and fully reduced regions. The calculated ordering of bond covalencies in YCBCO follows the sequence Cu(1)-O(4) $>$ Cu(1)-O(1) $>$ Cu(2)-O(2,3) $>$ Cu(2)-O(1) $>$ Ca-O(2,3) $>$ Y-O(2,3) $\sim$ Ba-O(1,2,3,4).

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TABLE V. Valences of Cu(1) and Cu(2) and bond covalencies (in %) of chemical bonds in $Y_{1-x}Ca_xBa_2Cu_3O_{6+y}$. The structural data were taken from Ref. 7.

x	0.00	0.02	0.04	0.05	0.07	0.09	0.10	0.12	0.14	0.15	0.17	0.20
y	0.995	0.967	0.980	0.979	0.981	0.976	0.963	0.963	0.975	0.960	0.960	0.960
Valence												
Cu(1)	2.392	2.350	2.370	2.368	2.371	2.364	2.344	2.344	2.362	2.339	2.339	2.339
Cu(1)[a]	2.168	2.135	2.143	2.163	2.144	2.160	2.158	2.137	2.178	2.150	2.171	2.172
Cu(1)[b]	2.378											
Cu(2)	2.299	2.302	2.315	2.320	2.330	2.339	2.341	2.351	2.364	2.365	2.375	2.390
Cu(2)[a]	2.167	2.167	2.170	2.169	2.165	2.173	2.167	2.175	2.171	2.176	2.170	2.179
Cu(2)[b]	2.209											
Bond covalency												
Cu(1)-O(1)	21.09	20.71	20.88	20.87	20.88	20.81	20.63	20.64	20.79	20.59	20.58	20.57
Cu(1)-O(4)	21.23	20.85	21.01	21.00	21.02	20.95	20.78	20.78	20.92	20.72	20.72	20.71
Cu(2)-O(1)	13.09	13.11	13.31	13.39	13.55	13.68	13.70	13.85	14.05	14.07	14.25	14.47
Cu(2)-O(2)	16.55	16.49	16.66	16.71	16.81	16.88	16.86	16.97	17.14	17.10	17.21	17.36
Cu(2)-O(3)	16.56	16.50	16.67	16.72	16.83	16.90	16.88	16.98	17.15	17.12	17.22	17.37
Ba-O(1)	5.45	5.50	5.47	5.48	5.47	5.48	5.50	5.50	5.48	5.50	5.50	5.50
Ba-O(2)	5.38	5.42	5.40	5.40	5.40	5.41	5.43	5.43	5.41	5.43	5.43	5.43
Ba-O(3)	5.38	5.43	5.41	5.41	5.40	5.41	5.43	5.43	5.41	5.44	5.44	5.44
Ba-O(4)	5.41	5.45	5.43	5.43	5.42	5.43	5.45	5.45	5.43	5.45	5.45	5.45
Y-O(2)	6.29	6.26	6.27	6.27	6.27	6.26	6.25	6.25	6.26	6.24	6.24	6.24
Y-O(3)	6.30	6.27	6.28	6.28	6.28	6.27	6.25	6.26	6.26	6.25	6.25	6.24
Ca-O(2)		9.38	9.40	9.40	9.40	9.39	9.37	9.37	9.38	9.36	9.36	9.35
Ca-O(3)		9.41	9.43	9.42	9.42	9.41	9.39	9.39	9.40	9.38	9.38	9.37

[a]Reference 7.

[b]Reference 27.

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[1] S. K. Bandyopadhyay, Pintu Sen, P. Barat, P. Mukherjee, A. Bhattacharyay, P. Rajasekar, P. Chakraborty, F. Caccavale, S. LoRusso, A. K. Ghosh, and A. N. Basu, Phys. Lett. A **226**, 237 (1997).

[2] J. Hejtmánek, Z. Jirák, and K. Knízek, Phys. Rev. B **54**, 16 226 (1996).

[3] P. Berastegui, S.-G. Eriksson, L. G. Johansson, M. Kakihana, M. Osada, H. Mazaki, and S. Tochihara, J. Solid State Chem. **127**, 56 (1996).

[4] J. B. Parise and E. M. McCarron, J. Solid State Chem. **83**, 188 (1989).

[5] E. M. McCarron III, M. K. Crawford, and J. B. Parise, J. Solid State Chem. **78**, 192 (1989).

[6] V. P. S. Awana, S. K. Malik, and W. B. Yelon, Physica C **262**, 272 (1996).

[7] G. Böttger, I. Mangelschots, E. Kaldis, P. Fisher, Ch. Krüger, and F. Fauth, J. Phys.: Condens. Matter **8**, 8889 (1996).

[8] K. Widder, D. Berner, J. Münzel, H. P. Geserich, M. Kläser, G. Müller-Vogt, and Th. Wolf, Physica C **267**, 254 (1996).

[9] V. P. S. Awana, A. Tulapurkar, and S. K. Malik, Phys. Rev. B **50**, 594 (1994).

[10] V. P. S. Awana and A. V. Narlikar, Phys. Rev. B **49**, 6353 (1994).

[11] I. R. Fisher, P. S. I. P. N. de Silva, J. W. Loram, J. L. Tallon, A. Carrington, and J. R. Cooper, Physica C **235–240**, 1497 (1994).

[12] C. Legros-Glédel, J.-F. Marucco, E. Vincent, D. Favrot, B. Poumellec, B. Touzelin, M. Gupta, and H. Alloul, Physica C **175**, 279 (1991).

[13] G. Xiao and N. S. Rebello, Physica C **211**, 433 (1993).

[14] H. Casalta, H. Alloul, and J.-F. Marucco, Physica C **204**, 331 (1993).

[15] J. C. Phillips, Rev. Mod. Phys. **42**, 317 (1970).

[16] J. C. Phillips, Phys. Rev. Lett. **20**, 550 (1968).

[17] J. A. Van Vechten, Phys. Rev. **182**, 891 (1969).

[18] J. C. Phillips and J. A. Van Vechten, Phys. Rev. Lett. **22**, 705 (1969).

[19] B. F. Levine, J. Chem. Phys. **59**, 1463 (1973).

[20] B. F. Levine, Phys. Rev. B **7**, 2591 (1973).

[21] D. Xue and S. Y. Zhang, Appl. Phys. Lett. **70**, 943 (1997).

[22] D. Xue and S. Y. Zhang, J. Phys.: Condens. Matter **8**, 1949 (1996).

[23] Q. B. Meng, Z. J. Wu, and S. Y. Zhang, J. Phys.: Condens. Matter **10**, L85 (1998).

[24] F. Gao and S. Y. Zhang, Acta Chim. Sin. **52**, 320 (1994).

[25] S. Tanaka, Physica C **220**, 341 (1994).

[26] J. L. Tallon, Physica C **168**, 85 (1990).

[27] R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, Jr., and L. W. Rupp, Jr., Physica C **165**, 419 (1990).