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## Compensation effect of substitutions at Cu(1) and Y sites on superconductivity in the $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+z}$ system

Yong Zhao<sup>†</sup>, Yeye He<sup>‡</sup>, Han Zhang<sup>§</sup>, Xiangbin Zuge and Xiaoming Tang<sup>||</sup>

<sup>†</sup> Department of Physics, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China

<sup>‡</sup> Cryogenic Laboratory, Academia Sinica, PO Box 2711, Beijing 100080, People's Republic of China

<sup>§</sup> Department of Physics, Peking University, Beijing 100871, People's Republic of China

<sup>||</sup> Department of Physics, The Composition and Structure Analyses Centre, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China

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**Abstract.** A series of single-phase samples with the composition of  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{6.5+z}$  ( $0 < x < 0.25$ ;  $0 < y < 0.25$ ) have been synthesized and studied by x-ray powder diffraction analyses, and measurements of the resistivity, AC susceptibility, oxygen content and x-ray photoelectron spectroscopy (XPS). It is found that the reduction in the superconductivity induced by the substitution of Co for Cu(1) can be counterbalanced, to an extent, by the replacement of Ca for Y. This phenomenon has been explained with the opposite effect of Co doping for Cu(1) from Ca doping for Y, on the mobile hole concentration of the system. The substitution of Ca for Y induces a delocalization effect which releases the holes in the Cu–O chain and transfers them to the  $\text{CuO}_2$  sheets, leading to an increase in the mobile hole concentration while the substitution of Co for Cu(1) reduces the mobile hole concentration because of its localization effect on the holes. The XPS measurement for the core level of Cu 2p and O 1s reveals that the oxidation state of the copper changes with the dopant content, and a peak corresponding to the  $\text{Cu}^{3+}$  oxidation state is observed in some co-doped samples.

### 1. Introduction

Element substitutions have displayed great importance in the investigation on the physical properties and the mechanism of high- $T_c$  superconductivity [1–3]. Many significant results on this proposition have been obtained, especially in the  $[\text{Y}]:[\text{Ba}]:[\text{Cu}] = 1:2:3$  compound of the Y–Ba–Cu–O system. Concerning the substitution on the Y site, the isovalent dopant changes neither the electronic structure nor the superconductivity [4, 5] whereas the non-isovalent dopant gives rise to a series of significant changes in electronic properties, magnetism and superconductivity [5–10]. For example, the substitution of Pr for Y depresses the superconducting critical temperature  $T_c$  strongly because of the hole filling effect [7] or the localizing effect of the mobile holes [10]. In the case of Ca doping for Y, the  $T_c$  is also suppressed, but this is attributed to the overdoping of the holes since  $\text{Ca}^{2+}$  acts as a hole donor. When Pr and Ca co-substitute for Y, they counterbalance each other, resulting in an interesting variation in  $T_c$  with

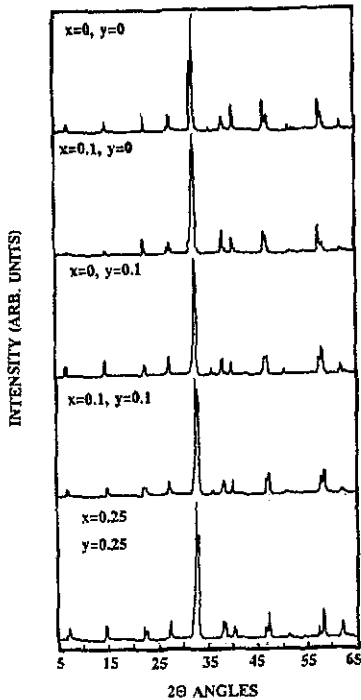


Figure 1. Some typical x-ray diffraction patterns of the  $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{6.5+z}$  system.

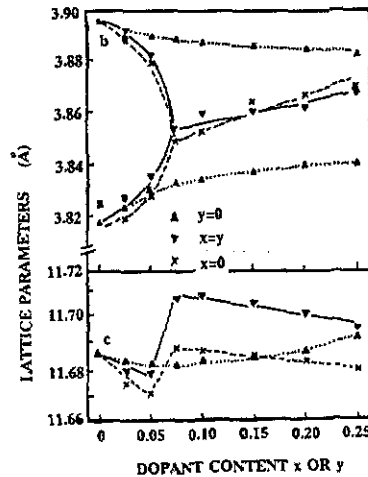


Figure 2. The relation between the lattice parameters and the dopant content of the  $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{6.5+z}$  system. The lines are drawn to guide the eye.

the dopant content, as described in [6]. As is known, the substitution of Co for Cu(1) induces a strong decrease in hole concentration [11] and an orthorhombic-to-tetragonal (O-T) structure transition [12]. Therefore, it is of significance to study the co-doping effect of Ca for Y and Co for Cu(1) since the Cu(1) layer influences not only the crystal structure but also the electronic properties dramatically.

## 2. Experimental details

A series of samples with the composition  $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{6.5+z}$  ( $0 < x < 0.25$ ;  $0 < y < 0.25$ ) were prepared by the solid state reaction method. The highly pure powders of  $Y_2O_3$ ,  $CaCO_3$ ,  $BaCO_3$  and  $CuO$  were sufficiently mixed, ground and heated at  $935^\circ C$  for 40 h in air. After this process had been repeated three times, the powders were pressed into pellets with a diameter of 15 mm and a thickness of 2.5 mm. The pellets were sintered at  $945^\circ C$  for 40 h in air and then cooled to  $500^\circ C$  and soaked at this temperature for 24 h; finally they were cooled to room temperature in the oven. The resistivity of the samples was measured with the standard DC four-probe technique; the resolution of the voltage measurement was  $1 \times 10^{-9}$  V. The AC susceptibility was determined by the mutual inductance method. The crystal structure of the samples was analysed with a Japanese Rigaku D/Max- $\gamma A^2$  rotating-target x-ray diffractometer; the lattice parameters were fitted with a computer program including the diffraction intensity

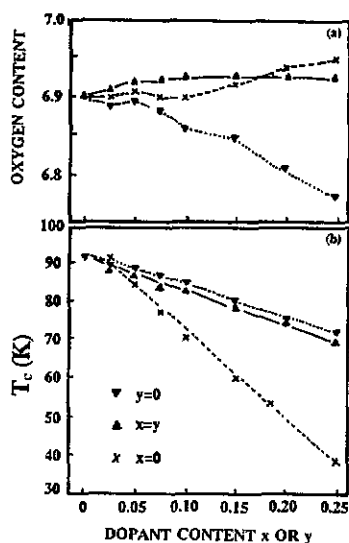


Figure 3. The relation between (a) the oxygen content and (b)  $T_c$  and the dopant content of the  $Y_{1-x}Ca_xBa_2Cu_{1-y}Co_yO_{6.5+z}$  system.

and angles. The oxygen content was determined by thermogravimetry analysis (TGA) with a Siemens DT-30 thermal analyser. The x-ray photoelectron spectroscopy (XPS) data of the core level for the elements were measured with a VG ESCALAB MK II electron spectrometer at room temperature; the basic pressure during the measurement is about  $10^{-9}$  mbar; the x-ray radiation of magnesium (Mg K, 1253.6 eV) was employed as the excitation source. The surfaces of the samples were scraped just before they were introduced into the preparation chamber.

### 3. Results and discussion

X-ray powder diffraction measurement shows that all the samples are, within the resolution power of the diffractometer (about 5%), the single-phase 1:2:3 compound. This means that the Ca substitutes for Y, and Co for Cu; otherwise second phases would be observable.

Some typical x-ray powder diffraction patterns of the samples are shown in figure 1. Figure 2 shows the variation in lattice parameters with the dopant content. It can be seen from figure 2 that, when equivalent amounts of Y and Cu are simultaneously replaced by Ca and Co, respectively, the transformation of the crystal structure is quite similar to that of the system in which only Cu(1) is substituted by Co, but quite different from the result of the substitution of Ca for Y. This means that the O-T transition in the 1:2:3 compound merely results from the disturbance of Cu-O chains.

The relation of the oxygen content to the dopant content is shown in figure 3(a). With successive increase in the dopant content, the oxygen content in the  $Y_{1-x}Ca_xBa_2Cu_3O_{6.5+z}$  system decreases, but that in the  $YBa_2Cu_{3-y}Co_yO_{6.5+z}$  system increases. In the co-doped system, the oxygen content is almost constant. According to the report of another group [13], the increase in the oxygen content induced by replacement of Co for Cu(1) is due to the octahedral coordination of the oxygen atoms required by the Co atom. However, the decrease in the oxygen content induced by  $Ca^{2+}$  substituting for  $Y^{3+}$  is attributed to the charge balance of the system. Therefore, the

approximate constancy of the oxygen content in  $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{6.5+z}$  system with  $x = y$  is simply the consequence of the counterbalancing effects of addition and reduction in the oxygen content induced by  $Co^{3+}$  and  $Ca^{2+}$  ions, respectively. The co-doped system can be regarded as a 'model system' in which the dopant content varies from sample to sample, but the oxygen content keeps constant. This 'model system' emphasizes the effects of the metallic dopants on the physical properties of the 1:2:3 system.

The variation in  $T_c$  (midpoint) with the dopant content is given in figure 3(b). When  $x = 0$ ,  $T_c$  changes dramatically with increasing  $y$  but, as  $y$  is given,  $T_c$  changes with  $x$  very smoothly. It is worth noting that, when equivalent amounts of Y and Cu(1) are replaced simultaneously by Ca and Co, respectively, i.e.  $x = y$ , the relation between  $T_c$  and dopant content is almost the same as that of the system in which only Y is substituted by Ca.

As mentioned earlier, the structure transformation in  $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{6.5+z}$  with  $x = y$  is quite similar to that of the  $YBa_2Cu_{3-y}Co_yO_{6.5+z}$  system; here it is seen that the variation in  $T_c$  with the dopant content in the co-doped system is quite similar to that of the  $Y_{1-x}Ca_xBa_2Cu_3O_{6.5+z}$  system. In other words, the co-doped system is similar to the Co-doped system in crystal structure but similar to the Ca-doped system in electronic structure. This strongly demonstrates that the orthorhombic distortion is not the predominant factor in the high- $T_c$  superconductivity in the 1:2:3 system.

In order to understand the results mentioned above, it is necessary to examine the behaviour of the hole concentration with the dopant content of the system. According to the viewpoint of Tokura *et al* [9], the holes in the 1:2:3 system can be divided into two types: the mobile and the non-mobile. The mobile holes are located in the  $CuO_2$  sheets, and the corresponding hole number per Cu atom is denoted as  $P_{sh}$ ; the others are non-mobile holes which are localized in the Cu-O chains, and the corresponding hole number per Cu atom is represented by  $P_c$ . These two parameters satisfy the following equations:

$$P_c = z/3 \quad (1)$$

$$3P = 2P_{sh} + 3P_c \quad (2)$$

where  $P$  is the total hole number per Cu atom of the system which is determined by the charge balance condition, i.e.

$$P = (x - y + 2z)/(3 - y) \quad (\text{for } x \neq y) \quad (3)$$

or

$$P = 2z/(3 - x) \quad (\text{for } x = y). \quad (4)$$

It can be seen from equations (3) and (4) that the total hole number per Cu atom of the system is determined by both the oxygen content and the dopant content. Figure 4 gives the variations in the hole concentration with the dopant content. In the case when  $x = 0$ ,  $P$  decreases with  $y$  smoothly, but  $P_c$  increases rapidly, leading to a decrease in  $P_{sh}$ , the hole concentration in the  $CuO_2$  sheets (see figure 4(a)). This is consistent with the results of the Hall effect experiment in which the Hall number decreases dramatically with increasing dopant content [11]. Our results reveal that the decrease in the mobile hole concentration originates from both the filling effect (demonstrated by the decrease in  $P$ ) and the localization effect of the holes (demonstrated by the increase in  $P_c$ ). The filling effect of the holes is simply due to the valence of the dopant Co which is higher

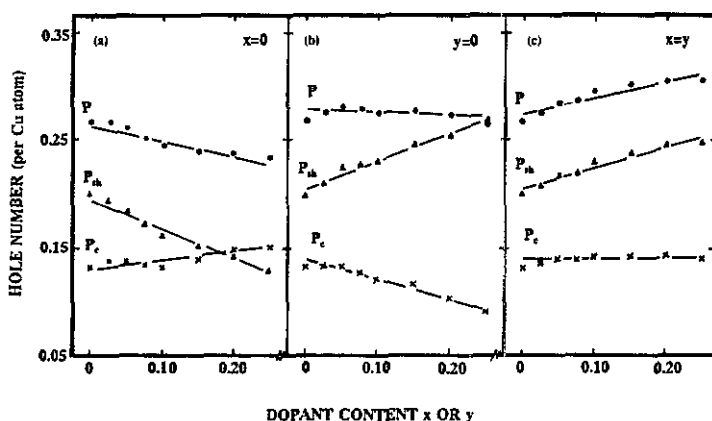


Figure 4. Variations in the hole number per Cu atom with the dopant content in  $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{6.5+z}$  system.

than that of the Cu. The filling effect is weakened to an extent, by the increase in the oxygen content, but this increase gives rise to another effect—localization of the holes. According to the results of the neutron powder diffraction [14], as the dopant content increases, the oxygen atom at the apical site (which is denoted as O(4)) is pulled away from the  $CuO_2$  sheets and the Cu(1)–O(4) bond length decreases strongly, leading to a surprisingly rapid increase in the charge transfer. From this result, it is believed that the consequence of the charge transfer is to form electron–hole pairs which are localized in the Cu–O chains. On the other hand, the substitution of Ca for Y results in decreases in both  $P$  and  $P_c$ . Consequently,  $P_{sh}$  increases with increasing dopant content since  $P_c$  decreases more rapidly than  $P$  does. Therefore,  $Ca^{2+}$  can be regarded as a hole donor since it increases the mobile hole concentration  $P_{sh}$  (see figure 4(b)). The increase in  $P_{sh}$  is never due to the addition of the total hole concentration but to the hole transfer from the Cu–O chains to the  $CuO_2$  sheets. In other words, the doping of Ca in the Y site can release holes localized in the Cu–O chains. This is the so-called delocalization effect. A more interesting phenomenon is the co-doping of Ca and Co in the Y site and Cu(1) site, respectively. From figure 4(c) it can be seen that, when equivalent amounts of Y and Cu(1) atoms are substituted simultaneously by Ca and Co, respectively, both  $P$  and  $P_{sh}$  increase, which is different from the situation in the system doped with only Ca or only Co. Moreover, the non-mobile hole concentration  $P_c$  is almost unchanged. There are at least two features which are worth noting. The first is that the holes in the Cu–O chains do not transfer to the  $CuO_2$  sheets since  $P_c$  is almost constant; this suggests that the effects of charge transfer induced by Ca and by Co are quite different and counterbalance each other. Secondly, the net addition of the holes in the  $CuO_2$  sheets as well as in the whole system originates totally from the metallic dopants. This is different from the system co-doped with Al and Ca [15] in which the delocalization effect plays an important role in the increase in the mobile hole concentration. Although the amounts of the donor  $Ca^{2+}$  and the acceptor  $Co^{3+}$  in the system are equivalent, a net increase in the holes remains in existence, which demonstrates that the doping effects at the different sites of the 1:2:3 system are not exactly equivalent.

Photoemission experiments [16] indicate that in the 1:2:3 system the holes reside in the orbital  $d^9L$  with predominantly O 2p character. The  $d^9L$  combination is equivalent

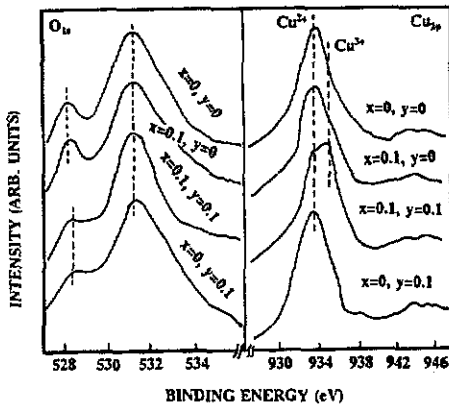


Figure 5. Some typical XPS spectra of the O 1s and Cu 2p core level of the  $Y_{1-x}Ca_xBa_2Cu_{1-y}Co_yO_{6.5+x}$  system.

to a formal valence of 3+ on the Cu site. Therefore, it is significant to investigate the electronic state of the copper and the oxygen so as to obtain a deeper understanding of the variation in the hole concentration with the dopants. It is found in our experiment that the oxidation state of the copper changes preferentially to the  $Cu^{2+}$  state with increase in the dopant content in the Co-doped system. However, in the case of Ca substituting for Y, there is no observable change in the oxidation state of the copper. When sufficient and equivalent amounts of Y and Cu(1) are replaced simultaneously by Ca and Co, respectively, the peak of the Cu 2p core level shifts towards a higher binding energy (figure 5). According to the analyses of Steiner *et al* [17] and Zhang *et al* [18], the peak with a binding energy of 933.4 eV corresponds to  $Cu^{2+}$  and the peak with a binding energy of 934.5 eV corresponds to  $Cu^{3+}$ . Our results show that an observable  $Cu^{3+}$  oxidation state appears in some samples of the co-doped system, and there is a positive correlation between the  $Cu^{3+}$  oxidation state and  $P$ , the total hole concentration of the system, but not any correlation between the  $Cu^{3+}$  and  $P_{sh}$  is found. Since the total hole concentration of the system is determined merely by the charge balance as described by equations (3) and (4), this correlation may suggest that the  $Cu^{3+}$  oxidation state is the consequence of the charge balance of the system; hence it is not crucial to the high- $T_c$  superconductivity. Also, it is found that there is a close relation between the  $dT_c/dx$  (or  $dT_c/dy$ , and denoted as  $T'_c$ ) and the  $|dP_{sh}/dx|$  (or  $|dP_{sh}/dy|$ , and denoted as  $P'_{sh}$ ) which is given in table 1. This indicates that  $T_c$  depends strongly on the itinerant hole concentration rather than on the total hole concentration of the system, which is consistent with the results obtained by other experiments [1]. In addition, it is also found that there is a correlation between the crystal structure distortion and the electronic states of oxygen. For the samples with an orthorhombic structure, the difference between the two states of O 1s is quite clear (see also figure 5) while, for the samples with tetragonal structure, the difference between the two states is greatly blurred. This may be attributed to the different distributions of the oxygen atom in different crystal structures and indicates that the change in the crystal structure is related to the distribution and state of the oxygen of the system.

From the results and analysis mentioned above, it can be seen that the hole concentration (especially the mobile hole concentration) is determined by several factors. Besides the filling effect, the hole localization and the delocalization effects which have a close relation to the charge transfer are also important factors affecting the mobile hole concentration and consequently affecting the superconductivity. The substitution

Table 1. Some physical parameters of the  $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_{6.5+z}$  system.

$x$	$y$	$6.5 + z$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$T_c$ (K)	$T_c^*$ (K (at.%) <sup>-1</sup> )	$P_{bh}^*$ (hole/at.%)	Valence of Cu
0	0.0	6.90	3.818	3.896	11.687	91.5			+2
0	0.025	6.90	3.819	3.882	11.667	90.3			+2
0	0.05	6.91	3.829	3.880	11.670	84.0			+2
0	0.075	6.90	3.849	3.849	11.689	77.2			+2
0	0.10	6.90	3.852	3.852	11.687	70.0	-2.08	$2.80 \times 10^{-3}$	+2
0	0.15	6.92	3.864	3.864	11.685	60.1			+2
0	0.20	6.94	3.866	3.866	11.684	53.2			+2
0	0.25	6.95	3.870	3.870	11.680	38.0			+2
0.05	0	6.90	3.829	3.890	11.682	88.0			+2
0.075	0	6.88	3.830	3.890	11.682	86.2			+2
0.10	0	6.86	3.832	3.888	11.683	84.1	-0.80	$1.40 \times 10^{-3}$	+2
0.15	0	6.85	3.834	3.887	11.685	79.8			+2
0.20	0	6.81	3.838	3.884	11.687	73.9			+2
0.25	0	6.77	3.840	3.882	11.694	70.6			+2
0.025	0.025	6.91	3.828	3.892	11.685	88.8			+2
0.05	0.05	6.92	3.835	3.882	11.679	86.0			+2
0.075	0.075	6.92	3.854	3.854	11.711	83.0			+2
0.10	0.10	6.93	3.860	3.860	11.710	82.1	-0.81	$1.65 \times 10^{-3}$	+2, +3
0.15	0.15	6.93	3.861	3.861	11.709	78.0			+2, +3
0.20	0.20	6.93	3.862	3.862	11.704	74.2			+2, +3
0.25	0.25	6.92	3.868	3.868	11.692	68.7			+2, +3

of Co for Cu(1) enhances the localization effect whereas the doping of Ca in the Y site enhances the delocalization effect. In the co-doped system these effects counterbalance each other. This may be the real cause of the compensation effect of the substitution in Y and Cu(1) sites on superconductivity. The  $Cu^{3+}$  oxidation state observed in this co-doped system does not result from the increase in the mobile hole concentration but from the addition of the total hole concentration; thus it is not crucial to the high- $T_c$  superconductivity. We believe that a deeper understanding of this topic is necessary and some new results will be presented in the near future.

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