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Evidence for peroxide formation in superconducting $YBa_{2-x}La_xCu_3O_{7\pm\delta}$

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The system $YBa_{2-x}La_xCu_3O_{7\pm\delta}$ $(0 \leq x < 0.5)$, annealed to a maximum oxygen concentration under 1 atm of O_2, exhibits three distinct compositional ranges. (1) For $0 \leq x < 0.05$, the maximum oxygen concentration is $O_{6.94+0.5x}$; the intercalated oxygen atoms are monomeric and T_c increases to 99 K at $x = 0.05$. (2) For $0.10 \leq x < 0.5$, the maximum oxygen concentration is $O_{6.85+0.5x}$; beyond $x \approx 0.07$ the additional oxygen atoms appear to be intercalated as peroxide ions and T_c decreases linearly with x through a smooth orthorhombic-tetragonal phase transition at $x = 0.30$. (3) For $0.05 \leq x < 0.10$, a transition between the two regimes occurs.

I. INTRODUCTION

The oxide system $YBa_2Cu_3O_{7-\delta}$, $0.04 \leq \delta \leq 1$, consists of (001) layers in the sequence

$$Y\text{-}Cu(2)O_2\text{-}BaO\text{-}Cu(1)O_{1-\delta}\text{-}BaO\text{-}Cu(2)O_2\text{-}Y\ .$$

All the oxygen are bridged between two Cu atoms, but those in the BaO layers are displaced along the c axis away from a Cu(2) towards a Cu(1) atom.[1,2] Intercalation-disintercalation of oxygen occurs readily within the Cu(1) planes above 350 °C (Refs. 3 and 4), which allows adjustment of the oxygen content over the range $0.04 \leq \delta \leq 1$.

The superconducting transition temperature T_c exhibits a remarkable dependence on not only the oxygen content, but also the oxygen distribution within the Cu(1) layers.[5,6] Moreover, preliminary spectroscopic data have prompted speculation about the role of O $2p$ holes in the enhancement of T_c. In order to test whether an O $2p$ hole is a meaningful concept in the high-T_c copper oxides, we have chosen to study a system designed to trap out O $2p$ holes—if their existence is meaningful—into antibonding states of oxygen-atom clusters, the simplest such cluster being the dimeric peroxide ion O_2^{2-}.

The following observations are relevant to this study:

(1) An internal electric field parallel to the c axis confines the redox reaction associated with the intercalation-disintercalation of oxygen primarily to the Cu(1) atoms and their near-neighbor oxygen, so we refer to $[Cu(1)O_{3-\delta}]^{3-}$ layers.

(2) Two levels of ordering of the intercalated oxygen occur:[7] (a) ordering onto b axis sites of the Cu(1) plane transforms the structure from tetragonal to orthorhombic, and (b) ordering either within b axis chains or of completed chains introduces immiscibility domes within the orthorhombic phase field that separate fully ordered phases at $\delta = 0.125$, 0.25, 0.50, 0.75, and 0.875. Moreover, ordering suppresses direct contact between the intercalated oxygen atoms in the compositional range $0.04 \leq \delta \leq 1$.

(3) Samples prepared by low-temperature techniques contain disordered, low-mobility oxygen in the Cu(1) planes; these products, which had oxygen contents in excess of $O_{6.7}$, were tetragonal and not superconducting.[5,6] Since disorder creates direct contact between intercalated oxygen, these observations have led to the suggestion[7] that direct contact induces oxygen dimerization, i.e., formation of O_2^{2-} peroxide ions, in the Cu(1) layers at higher oxygen concentrations $(\delta < 0.5)$. The system $YBa_{2-x}La_xCu_3O_{7\pm\delta}$ was designed to introduce oxygen in excess of O_7 in order to ensure direct contact between bridging oxygen within the Cu(1) plane.

II. EXPERIMENT

Single-phase compositions $YBa_{2-x}La_xCu_3O_{7\pm\delta}$ $(0 \leq x < 0.5)$ were prepared by firing the required quantities of Y_2O_3, $BaCO_3$, La_2O_3, and CuO at 920 °C for 24 h; the Y_2O_3 and La_2O_3 starting materials were dried at 950 °C for 3 h prior to weighing. The product formed was cooled to 450 °C in the furnace over 3 to 4 h and then air quenched. In order to obtain maximum oxygen content, the samples were subsequently annealed in an oxygen atmosphere at 450 °C for 15 h and then 300–320 °C for 12 h followed by slow cooling in the furnace. All the end products were characterized by x-ray powder diffraction with a Philips diffractometer fitted with a diffracted beam monochrometer and Cu $K\alpha$ radiation.

The total oxygen content of the samples was determined by wet iodometric titration.[3] The disintercalation-intercalation of oxygen was studied in a Perkin-Elmer Series 7 Thermal Analysis System in both oxygen and nitrogen atmospheres.

The resistance of each sample was measured by a standard four-probe technique on a pressed pellet that had been reannealed in oxygen. The superconducting transition temperature T_c was taken to be the midpoint of the sharp drop in resistance.

III. RESULTS

Substitution of La for Ba in $YBa_{2-x}La_xCu_3O_{7\pm\delta}$ is possible up to $x = 0.5$; x-ray powder diffraction from samples with $x > 0.5$ showed weak reflections due to La_2CuO_4 and Y_2O_3. In all samples, we found $c \approx 3b$ (see Table I).

TABLE I. Oxygen content ($7\pm\delta$) and physical parameters of $YBa_{2-x}La_xCu_3O_{7\pm\delta}$.

x	$n_{y=0}$[a]	$7\pm\delta$	Lattice parameter (Å) a	b	c	b/a	Volume (Å^3)	T_c (K)
0.0	2.88	6.94	3.824(1)	3.890(1)	11.679(2)	1.017	173.73	97
0.025	2.87	6.95	3.820(1)	3.889(1)	11.670(3)	1.018	173.37	99
0.05	2.75	6.90	3.821(1)	3.889(1)	11.672(2)	1.018	173.44	99
0.075	2.73	6.90	3.827(1)	3.885(2)	11.659(4)	1.015	173.34	99
0.10	2.70	6.90	3.830(2)	3.883(4)	11.653(4)	1.014	173.30	95
0.20	2.70	6.95	3.839(2)	3.872(2)	11.618(4)	1.009	172.70	78
0.30	2.70	7.00	3.858(1)	3.859(1)	11.582(3)	1.000	172.43	67
0.40	2.70	7.05	3.858(1)	3.858(1)	11.580(2)	1.000	172.36	52
0.50	2.66	7.08	3.858(1)	3.858(1)	11.572(2)	1.000	172.20	38

[a] Formal oxidation state of Cu(1) where $y=0$.

The variation with x of lattice parameters and volume are shown in Fig. 1. Samples with $x\leq 0.3$ are orthorhombic; those with $x>0.3$ are tetragonal. In the tetragonal structure, there is no preferential ordering of oxygen on the orthorhombic b axis. An important anomaly occurs in all the parameters at $x\approx 0.05$; the transition at $x=0.3$ is smooth. The rate of change of volume with x, dV/dx, is more abrupt at $x\approx 0.05$ than at $x=0.3$.

The temperature variation of the resistance, Fig. 2, shows a sharp transition at $T_c=99$ K for $x=0.05$; it is significantly broader at $x=0.1$ and 0.2. There is no apparent change in the rate of decrease of T_c with increasing x on traversing the orthorhombic-tetragonal transition at $x=0.3$ (see Fig. 3); the normal resistance just above T_c is anomalously large in the tetragonal samples.

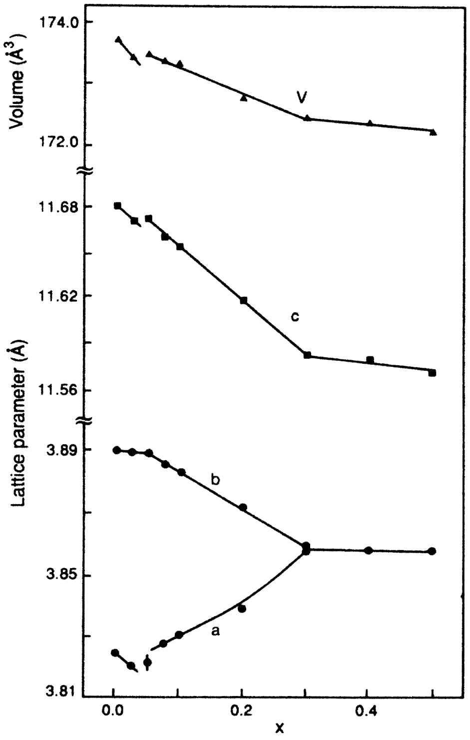

FIG. 1. Variation of lattice parameters and unit-cell volume with compositions x of oxygen-annealed $YBa_{2-x}La_xCu_3O_{7\pm\delta}$.

The total oxygen content per molecule increases in the interval $0\leq x<0.05$; it decreases abruptly in the range $0.05\leq x<0.1$ until it reaches a value of $6.85+0.5x$, which holds over the compositional range $0.1\leq x<0.5$. In this range, the total oxidation state of a $(CuO_{3\pm\delta})^{(3+x)-}$ layer remains constant.

The weight loss due to oxygen disintercalation on heating and the weight gain due to oxygen reintercalation on cooling in an oxygen atmosphere at a rate of 1 °C/min is reversible. However, at higher x, the equilibrium oxygen content is significantly higher at any temperature $T>400\,^\circ C$.

The thermogravimetric-analysis (TGA) curves for samples heated in nitrogen atmosphere at 2 °C/min show decomposition above about 780 °C. The limiting oxygen content below which the structure becomes unstable increases roughly as $6.08+x$ for $x\geq 0.1$.

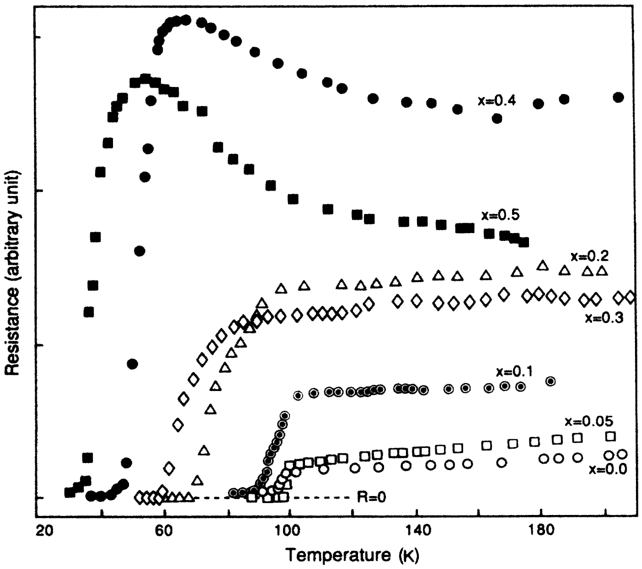

FIG. 2. Temperature variation of the resistance for different compositions x of oxygen-annealed $YBa_{2-x}La_xCu_3O_{7\pm\delta}$ polycrystalline pellets.

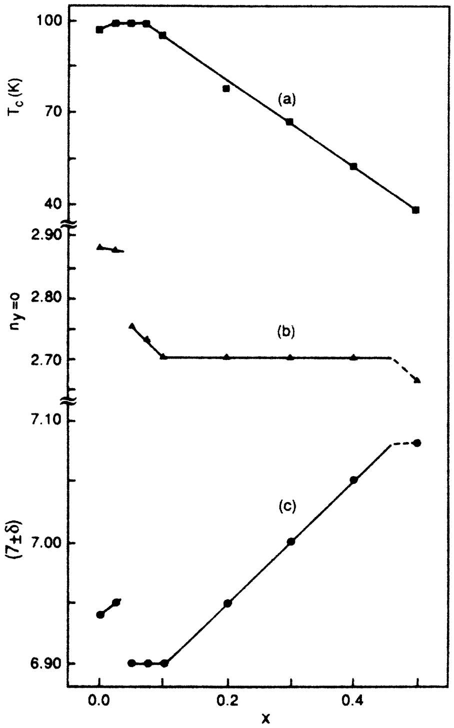

FIG. 3. Variation with composition x of (a) T_c, (b) formal oxidation state of Cu(1) were $y=0$, $n_{y=0}$, and (c) the total oxygen content $O_{7\pm\delta}$ for oxygen-annealed $YBa_{2-x}La_xCu_3O_{7\pm\delta}$.

IV. DISCUSSION

Substitution of La^{3+} ions for Ba^{2+} ions allows intercalation of more oxygen for the same oxidation state of the $Cu(1)O_{3\pm\delta}$ layer. The axial electric field remains to confine all oxidation-reduction reactions primarily to this layer. Therefore, if we allow for the possibility of peroxide-ion formation within the layer, preservation of local charge requires that we represent it formally as

$$[Cu^{n+}O_{3\pm\delta-y}{}^{2-}(O_2)_{0.5y}{}^{2-}]^{(3+x)-} , \tag{1}$$

$$n=3-y-x\pm2\delta . \tag{2}$$

We distinguish three distinct compositional domains:

(1) *$0\leq x<0.05$.* For small values of x, the lattice contracts as the smaller La^{3+} ion is substituted for Ba^{2+}. However, the orthorhombic b/a ratio increases, indicating that the extra oxygen are added to the b axis as monomeric oxygen, which means that $y=0$. If peroxide-ion formation occurs where intercalated oxygen makes direct contact, then there is an upper bound on the value of $\delta(x)$ for which the condition $y=0$ can hold. In the absence of twin planes, the upper bound for the total oxygen concentration would be O_7. Given a variable density of twin planes, a realistic upper bound for the oxygen concentration in a peroxide-free phase would be $O_{6.98\pm0.02}$. In addition, since the system $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ was shown[8] to have a T_c that decreased with increasing δ, we can also predict an increase and sharpening of T_c as the b-axis oxygen vacancies are successively filled with increasing oxygen content. Finally, if the maximum formal oxidation state for the Cu remains fixed over this compositional range, then the total oxygen concentration should increase with x as $0.5x$. The limited data for the small compositional range $0\leq x<0.05$ are compatible with this model.

(2) *$0.05\leq x<0.10$.* This compositional range is clearly transitional. The maximum formal oxidation state of the copper achieved by our oxygen anneal decreases with increasing x. A reduction in the orthorhombic b/a ratio indicates the presence of a-axis oxygen, and an increase in the volume despite substitution of a smaller La^{3+} ion for Ba^{2+} indicates a reduction in the formal valence state of copper. This reduction of the copper occurs sharply where x exceeds the critical upper bound for formal O^{2-}-ion intercalation, but stabilizes at a fixed oxidation state for the $(CuO_{3\pm\delta})^{(3+x)-}$ layer at $x=0.10$. It appears that the phases with $y=0$ and $y\neq0$ are distinct, and therefore the compositional range $0.05\leq x<0.10$ can be considered a two-phase region.

(3) *$0.10\leq x<0.50$.* Within this compositional range, the orthorhombic distortion decreases smoothly to an orthorhombic-tetragonal transition at $x=0.30$. Aside from a change in the rate of compositional variation of the volume (dV/dx) and the lattice parameters, no other parameter shows an anomaly across this transition. Over the entire compositional range, the maximum total oxygen concentration after an oxygen anneal varies as $O_{6.85+0.5x}$. For a positive sign in front of δ in expression (1), this relationship corresponds to $\delta=-0.15+0.5x$, and hence to

$$n=2.7-y . \tag{3}$$

Since $y=0$ for $x=0$ in our samples, we must anticipate a critical concentration x_0 for the generation of peroxide ions. Moreover, each additional oxygen in a peroxide ion carries only a single negative charge. Therefore, if the extra oxygen atoms introduced by $x\geq x_0$ are intercalated as peroxide ions, at least at lowest temperature, then

$$y=(x-x_0) , \tag{4}$$

and substitution of (4) into (3) gives

$$n=(2.7+x_0)-x . \tag{5}$$

In the high-T_c superconducting copper oxides, the appearance of superconductivity correlates well with a formal oxidation state on the copper that is greater than Cu^{2+}. Therefore, we can predict that T_c decreases with increasing x, disappearing at $n=2$. Extrapolation of T_c vs x to $T_c=0$, Fig. 3, gives $x\approx0.77$. From (5) with $n=2$ and $x=0.77$, we find

$$x_0=0.07 , \tag{6}$$

which is in the middle of the transition region $0.05\leq x<0.10$. Were the samples perfectly homogeneous, the upper bound of the $y=0$ phase would, according to this calculation, be $O_{6.98}$, which is as estimated.

The significance of this analysis is that it presents clear evidence for a T_c that varies linearly with the formal oxidation state on the Cu(1) atoms once the oxygen concentration is higher than a critical value. The superconducting transition temperature shows no change in its dependence on the formal copper oxidation state on traversing the orthorhombic-tetragonal transition.

In contrast, where only monomeric oxygen are present ($y=0$), T_c depends significantly on the b-axis anion-vacancy concentration as well as on the formal oxidation state of the copper.[8]

The introduction of peroxide ions creates acceptor states above the Fermi energy that trap out π^*-band holes and act like impurity scattering centers. As the concentration of "impurity" centers increases, so does the resistance of the normal state at low temperatures.

The TGA data indicate that the peroxide ions appear to retain their identity to at least 780 °C. Moreover, decomposition occurs at or before the oxygen concentration where the Cu(1) are all formally reduced to the Cu^+ state. In the $YBa_2Cu_3O_{7-\delta}$ system, decomposition occurs at $O_{6.00}$.[3] If the extra oxygen were introduced as formal O^{2-} ions, then decomposition should occur at $O_{6+0.5x}$. The fact that decomposition is observed to occur at roughly $O_{6.15+(x-x_0)}$ in the range $0.1 \leq x \leq 0.5$ indicates that, for $x > x_0$, the extra oxygen has been introduced as $O_2{}^{2-}$ ions.

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