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Oxidation state of copper in optimally oxygen-doped 1:2:3 Ca-La-Ba-Cu-O superconductors

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This paper describes an investigation of the family ''CLBLCO'' of 1-2-3 superconductors CLBLCO $[(Ca_xLa_{1-x})(Ba_{c-x}La_{2-c+x})(Cu_{1-z}M_z)_3O_y]$, with values $x=0.1$, 0.2, 0.3, and 0.4, $c=2.00$, 1.75, and 1.55. The impurity M substituting for Cu was one of Zn, Ni, Co, and Ga, and the value of z was taken from zero to 0.1. Although the maximal value of the transition temperature T_c occurs at different values of the oxygen content y, the average oxidation state of copper for maximal T_c is found to be approximately constant. The data for Ni-doped CLBLCO suggest that the oxidation state of Ni in this system appears to be 3.
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I. INTRODUCTION

The family $(Ca_xLa_{1-x})(Ba_{c-x}La_{2-c+x})(Cu_{1-z}M_z)_3O_y$ (CLBLCO or, in some of the previous literature, CaLaBaCuO) of high-T_c superconductors is especially interesting for the following two reasons.

(a) In the 1-2-3 superconductors, the transition temperature T_c depends on the oxygen content y. T_c increases with increasing y, up to an optimal value, for which T_c is maximal. For the usual 1-2-3 materials, this optimum y is somewhat below 7. With further increase of y (the ''overdoped'' region), T_c begins to fall. However, it is not usually possible to reduce T_c by more than a few K—e.g., for overdoped YBCO the greatest possible depression of T_c is only some 2 to 3 K, and corresponds to a value of y which is still slightly below 7. The CLBLCO family is one of the exceptions, in that it is possible to attain values of y up to about 7.3, and to reduce T_c, by over 50 K, to as little as 5 K. This is obviously well into the overdoped region.

(b) The crystal structure of CLBLCO remains tetragonal *for all values of the parameters x, c, z, and y*. This avoids the complications in interpreting experimental data, arising from the ordered CuO chains.

In the following discussion, it will be convenient to discuss the ''oxidation state'' of each atom in the compound[1] rather than the somewhat ill-defined concept of the ''valence.'' The superconductivity of the cuprates is believed to arise from the CuO_2 planes in their structure. It therefore follows that a study of the effect of replacing some of the copper in these planes by impurity atoms should yield useful information about the nature of their superconductivity. In YBCO, it is known[2] that many Zn or Ni impurity ions sit on these planes. If this is also true for CLBLCO, it will be particularly interesting to compare the behavior of Zn and Ni here. According to the spin-fluctuation theory of Monthoux and Pines,[3] we should expect that Ni, being a magnetic ion, will have less influence on the spin fluctuations than the nonmagnetic Zn, and therefore that Ni will depress T_c much less than Zn (as is observed[4] to be the case in YBCO). In the 1-2-4 system, Williams *et al.*[5] found no difference between the effects of Zn and Ni. In an earlier paper of our group,[6] we also failed to see this expected difference between Ni and Zn. In the present paper, we investigate the effect of Ni doping in more detail. *A priori*, one might think that Ni will tend to have the same oxidation state as the Cu in the CuO_2 planes, i.e., 2. However, our results tend to suggest that this expectation is not correct.

We report a study of the dependence of T_c on the various parameters. Our tentative conclusion is that in the absence of an impurity M, T_c is always optimized at a nearly constant value of the average oxidation state of the copper. This conclusion remains valid in the presence of Ga or Co impurities, which have unambiguous oxidation state 3. If this conclusion is also valid for Ni, it follows that in this system the average oxidation state of the Ni is 3 (although in general, Ni can have oxidation state 2, 3, or 4). We are aware that the oxidation state is not necessarily descriptive of the actual distribution of charge; nevertheless it is often a useful guide. We are therefore led to suggest that either (a) the impurity ions do not sit on the CuO_2 planes, (b) that although the impurity ions do sit on the planes, the charge distribution near the impurity ion differs significantly from the suggested oxidation state, or (c) that the spin-fluctuation mechanism of Ref. 3 may be inadequate, although it would be premature to conclude that this mechanism fails. Additional experiments will be required to clarify this point.

II. EXPERIMENTAL TECHNIQUE

We prepared specimens of pure CLBLCO as well as Ni- and Zn-doped specimens with various values of the parameters x, c, z, and y, as described in previous publications.[6,7] For the present paper, we also prepared specimens with Ga and Co impurities, by reacting the appropriate oxide and/or carbonate powders. The starting materials were La_2O_3, 99.98% pure, and free of hydroxide, following preheating at 1000 to 1050 °C for a few days; CuO, >99% pure; Ga_2O_3, 99.99% pure; Co_3O_4,nH_2O, >99% pure, containing 71%

Co, $BaCO_3$, 99% pure, preheated at 900 °C for one day (during which the volume decreases); and $CaCO_3$, >99% pure, preheated at 450 °C until constant weight was achieved (in order to remove traces of H_2O). The preheated substances were cooled in a desiccator.

Stoichiometric proportions of these compounds were ground for 15 min in a zirconia planetary ball mill. They were fired three times, at 950 °C for 16 to 20 h in a box furnace in air. After each firing, they were transferred from the hot furnace to a desiccator and were reground with an agate pestle and mortar.

The fired powders were pelletized into bars measuring $2.5\times2.5\times13$ mm, and weighing 0.3 to 0.4 g, under a pressure of 6 kbar. The pellets were sintered in dry oxygen at 960 °C for 60 h, and slowly cooled to room temperature, at a rate of 10 °C/h.

Underdoped samples were prepared by reducing the as-prepared pellets in oxygen, at 300 to 500 °C, for 16 to 25 h, and quenching them at liquid-nitrogen temperature. Optimally doped and overdoped samples were prepared by annealing in oxygen at high pressure (100 to 1200 bar), at 300 to 460 °C for 20 to 60 h, and quenched by switching the furnace off. They cooled to room temperature in about 30 min. (Further details will be published in a subsequent paper.)

It is worth remarking that the possibility of overdoping in this material is special. In the usual 1-2-3 compounds without any substituted metallic ions, overdoping can at best depress T_c very slightly.[8] This is the case for YBCO, which is unstable under high oxygen pressures, and for YbBCO and HoBCO, which, although they remain stable, do not absorb additional oxygen. SmBCO and NdBCO, which also remain stable under high oxygen pressures, cannot be overdoped at all. We even tried to overdope a material similar to CLBLCO, but with Nd instead of La. This material exists, but we were not able to overdope it, up to an oxygen pressure of 1200 bar.

The oxygen content y of our samples was measured by iodometric titration.[9] We stress that the calculation of the value of y, as found by titration, does not require any knowledge of the oxidation state of Cu or of Ni *in the compound*. All that matters is the oxidation state of these elements after the reaction of the cuprate with the iodine anion; it is known that, after the reaction, Cu has oxidation state 1, while Ni and Co both have oxidation state 2.

III. EXPERIMENTAL DATA

In Fig. 1, T_c is plotted against the oxygen content y, for pure CLBLCO, with varying values of the Ca concentration x. For all x, T_c as a function of y first rises, achieves a maximum at a value y_0 (''optimal doping''), and then falls. The data for the underdoped region contain previously published results.[6,10]

In all our samples, it was possible to get data extending from well-underdoped to well-overdoped regions by varying only the oxygen content y. Thus we are able to determine y_0 directly, without any need for extrapolation. The only uncertainty in determining y_0 stems from the fact that the graph of T_c vs y is flat around the maximum. We used the fact that the curve looks symmetric about the maximum to determine y_0.

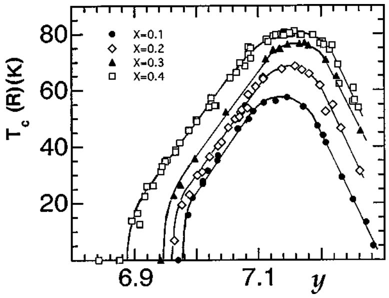

FIG. 1. T_c vs y for $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x}Cu_3O_y)$, for $x=0.1, 0.2, 0.3, 0.4$.

Figure 2 shows T_c vs y, for various concentrations z of Ni, as well as for one sample each with Co and Ga as the impurity. In all these data, the Ca concentration x was 0.4.

The most interesting feature in Fig. 1 is that the *position* of the maximum T_c occurs at approximately the same oxygen concentration $y_0\simeq7.15$, although the maximum value of T_c depends on x. On the other hand, Fig. 2 shows that Ni not only reduces T_c, but that the position of the optimum y_0 increases from 7.15 to 7.23, as z increases from 0 to 0.1.

We note in passing that introducing Zn as an impurity in YBCO,[11] in the 1-2-4 cuprates,[12] and in CLBLCO,[6] does not change the number of charge carriers, for a given value of y. In the case of CLBLCO, this result also applies for the case of Ni impurity.[6]

IV. INTERPRETATION

We note that in the pure CLBLCO system, all elements except copper have unique oxidation states: ($q_{Ba}=2$, $q_{Ca}=2$, $q_{La}=3$, $q_O=-2$). We define Q, the sum of the oxidation states of all the cations excluding the copper and any copper-site substitutional cations, as

$$Q\equiv2x+3(1-x)+2(c-x)+3(2-c+x)\equiv9-c, \quad (1)$$

independent of x. Hence, for electrical neutrality, the average oxidation state P_0 of Cu must be $(2y-Q)/3$. In the more general system $(Ca_xLa_{1-x})(Ba_{c-x}La_{2-c+x})(Cu_{1-z}M_z)_3O_y$, where some of the copper is replaced by an impurity with oxidation state q_M, the average oxidation state P_0 of the copper (averaged over *all* the Cu atoms, both in the CuO_2 planes and in the ''chain'' layers) is

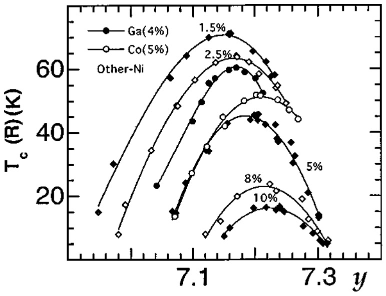

FIG. 2. T_c vs y for $(Ca_xLa_{1-x})[Ba_{1.75-x}La_{0.25+x}(Cu_{1-z}M_z)_3O_y]$. The data shown here are for $M=Ni$ with $z=0.015$, 0.025, 0.05, 0.08, 0.10, for $M=Co$ with $z=0.05$, and for $M=Ga$ with $z=0.04$.

TABLE I. Average oxidation state of Cu ions at optimal doping.

Group	M	z	Q	x	y_0	P_0	Grp. av. P_0
1		0	7.25	0.1	7.135	2.340	2.35±0.01
				0.2	7.149	2.349	
				0.3	7.160	2.357	
				0.4	7.146	2.347	
2		0	7.45	0.4	7.250	2.353	2.34±0.01
			7.25		7.146	2.347	
			7.00		7.000	2.333	
3	Zn	0.015	7.25	0.4	7.154	2.358	2.36±0.00
		0.025			7.152	2.360	
		0.040			7.147	2.362	
4	Ga	0.040	7.25	0.4	7.168	2.335	2.35±0.01
	Co	0.025			7.180	2.354	
	Co	0.050			7.210	2.358	
5	Ni	0.015	7.25	0.4	7.144	2.336	2.34±0.01
		0.025			7.164	2.343	
		0.050			7.185	2.340	
		0.080			7.216	2.341	
		0.100			7.225	2.333	
6	Ni	0.025	7.25	0.1	7.174	2.350	2.35±0.00
				0.2	7.174	2.350	
				0.3	7.174	2.350	
				0.4	7.164	2.343	
			Average of all groups				2.35±0.01

$$P_0 = \frac{2y - Q - 3zq_{\mathrm{M}}}{3(1-z)}. \tag{2}$$

Our data are presented in Table I. The two right-hand columns display, respectively, P_0 for each sample, and the average P_0 for each group of samples. We see that P_0 is nearly constant, $=2.35\pm0.01$, for groups 1 through 4. We have assumed that Co has oxidation state 3, in agreement with the general consensus of workers in high T_c.

The oxidation state of Ni can be 2, 3, or 4. If the above empirical rule (that P_0 is constant,$=2.35$) holds also in the presence of Ni impurity, then we must have for the average oxidation state of the nickel, $\langle q_{\mathrm{Ni}}\rangle = 3$, which seems to us the most natural assumption. This is the value which has been taken for groups 5 and 6 in Table I.

We thus conclude that when an impurity cation with well-defined oxidation state is introduced, the average oxidation state of the copper for maximal T_c is unchanged: $P_0 = 2.35$. We can thus predict what value of the oxygen concentration y_0 will yield the highest T_c. Moreover, when the oxidation state of an impurity cation is *a priori* uncertain, we can use the position of the T_c maximum to assign an oxidation state for the impurity. Thus the values of P_0 for the Ni-containing samples in Table I have been calculated assuming that $\langle q_{\mathrm{Ni}}\rangle = 3$. If we were to assume that $\langle q_{\mathrm{Ni}}\rangle = 2$ (similar to the generally accepted oxidation state of the Cu in the $\mathrm{CuO_2}$ planes), we would find that P_0 will vary strongly with z, ranging from 2.36 for $z = 0.015$ to 2.44 for $z = 0.1$. Similarly, if we were to assume the oxidation state of the Ni to be 4, we would find P_0 decreasing from 2.33 to 2.22 over the same range of z. It will be interesting to examine whether the physical charge distribution (as measured, e.g., by XAFS), matches our tentatively assumed value for the Ni oxidation state.

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[1] For example, C. F. Bell and K. A. K Lott, *Modern Approach to Inorganic Chemistry*, 2nd ed. (Butterworths, London, 1966), p. 40; H. Remy, *Treatise on Inorganic Chemistry* (Elsevier, Amsterdam, 1956), pp. 9–11. From its definition, following well-specified rules, the oxidation state of any atom is necessarily an integer. It need not be equal to the actual charge residing on an ion, as found, e.g., from x-ray absorption spectra, though they are often quite close.

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