Absence of superconductivity in 225 compositions of 19 partially-metal-substituted $LaCuO_3$ systems

A. W. Webb, E. F. Skelton, S. B. Qadri, V. Browning, and E. R. Carpenter, Jr.
Condensed Matter and Radiation Sciences Division, Naval Research Laboratory, Washington, D.C. 20375
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The compound $LaCuO_3$, and the substituted series $La_{1-x}M_xCuO_3$, where M=Mg, Ca, Sr, Ba, Pb, Sc, Y, Pr, Nd, Sb, Bi, Ti, Zr, or Ce and $LaCu_{1-x}M'_xO_3$, where M'=Cr, Fe, Ni, Zn, or Ag, have been prepared by high-pressure, high-temperature synthesis. The electrical resistivity was checked qualitatively, and the magnetic susceptibility measured to minimum temperatures of 2–50 K. No evidence of the Meissner effect was found in any of the compositions studied, indicative of the absence of superconductivity in at least 99% of the sample volume.

The explosion of work in high-temperature superconductivity (HTSC) based on copper oxides started with substituted La_2CuO_4.[1] The basic perovskite building block of this material is found in $LaCuO_3$, which can only be formed at high pressures.[2] General unavailability of this latter material has prevented any extensive investigation previously. The current study was undertaken with the hope that important questions might be answered about the contribution of the perovskite unit to the superconductivity of the related HTSC materials.

$LaCuO_3$ was formed from constituent oxides La_2O_3 and CuO and with an excess of $KClO_3$ to maintain an oxidizing environment favorable to Cu^{3+}; details of this are given elsewhere.[3–5]

Since many of the high-T_c materials first reported had substitutional impurities such as Ba or Sr, and subsequent materials either had favorable structures stabilized or the T_c elevated by elements such as Pb, Tl, or Ca, the substitutional series $La_{1-x}M_xCuO_3$ were also formulated with M=Mg, Ca, Sr, Ba, Pb, Sc, Y, Pr, Nd, Sb, Bi, Ce, Ti, or Zr, fixing x at 20 at. % intervals. Replacement of the Cu was also investigated, viz., $LaCu_{1-x}M'_xO_3$ with M'=Cr, Fe, Ni, Ag, or Zn. X-ray diffraction results, used to check for presence of the desired $LaCuO_3$ structure in each sample, and the results of other studies are reported in greater detail elsewhere.[5] Some CuO and $La(OH)_3$ were found to be present in all the samples, and many also contained KCl. Since these components did not affect the magnetic susceptibility, no attempt was made to remove them. This left the bulk of each sample, about 0.02 cm^3, for superconductivity tests. Although gross resistivity was also checked, magnetic-susceptibility measurements were favored for screening purposes, since a continuous path of superconductor would not be necessary.

ELECTRICAL CONDUCTIVITY

$LaCuO_3$ has been reported to have metallic conductivity.[2] $LaCuO_{3-y}$ was recently reported to be metallic in both tetragonal $(0 \le y \le 0.2)$ and monoclinic $(0.2 \le y \le 0.4)$ structures, but an insulator in the orthorhombic $(0.43 \le y \le 0.5)$ form.[6] $LaCa_{0.5}CuO_3$ has also been reported as metallic.[7] Single-phase $La_{1-x}Sr_xCuO_3$ was reported to be an insulator for $x=0$ (no details given), and metallic for $x=0.3$,[8] $x=0.17$,[9] and $0.20 \le x \le 0.25$.[10] $LaSr_{0.5}CuO_{3-y}$, not of the La_2CuO_4 structure, was reported as strongly semiconducting, and becoming metallic after annealing under oxygen.[11] $LaCrO_3$ has intrinsic p-type conductivity;[12] it remained semiconducting with substitution of up to 50% Cu for Cr, but a metal-insulator transition was expected at around 77% Cu.[13] A compound reported to be $LaTi_{0.5}Cu_{0.5}O_3$ was semiconducting with a conductivity at 500 K of 2.5×10^4 ohm cm.[14] $LaNiO_3$ has been stated to be a narrow-band metallic conductor which became semiconducting below 130 K;[15] another work reported it to be metallic.[16]

The multiphase product slugs resulting from our high-pressure, high-temperature (HPHT) synthesis were generally found to be insulators using a two-probe rapid survey system. The $La_{1-x}Pb_xCuO_3$ samples with $x>0.75$, however, were relatively good conductors. The present study supported the results given by Khan that $LaCuO_3$ was an insulator.[8] Demazeau *et al.*[2] implied full oxygen stoichiometry from TGA, while other studies did not report oxygen content. It may be that, as with La_2CuO_4,[17,18] slight variations in oxygen content are possible, that such do occur depending on the synthesis technique, and that the resultant variation in either hole or electron conduction markedly affects the observed conductivity.

MAGNETIC SUSCEPTIBILITY

The susceptibility of $LaCuO_3$ has been variously reported: it decreases weakly linear with temperature;[2,19] it is possibly antiferromagnetic, but without observation of a Néel point;[20] or, along with $LaNiO_3$, it is a Pauli paramagnet.[19] No Néel temperature has been observed down to 80 K for this latter compound.[21] $La_{0.8}Ba_{0.2}CuO_{2.68}$ was probably a Pauli paramagnet with a susceptibility nearly independent of temperature.[22]

The magnetic susceptibility is obtained from the magnetic moment, measured in emu, by dividing the latter by the field and the volume of the sample. The samples used in this study all had similar volumes, while the fields varied according to the technique used.

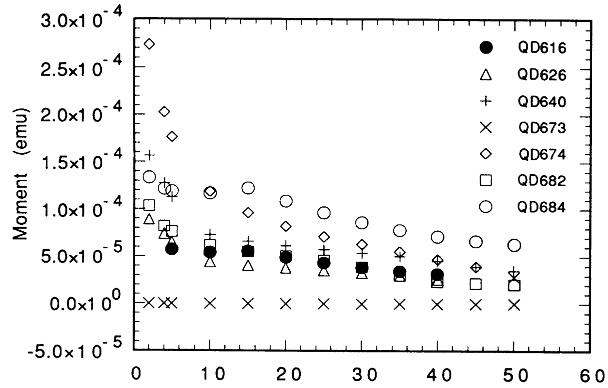

FIG. 1. Magnetic moment of samples observed with Quantum Design magnetometer. Samples include No. 616-$La_{0.4}Pr_{0.6}CuO_3$, $PrCuO_3$, $La_{0.2}Bi_{0.8}CuO_3$; No. 626-$MgCuO_3$, $La_{0.2}Mg_{0.8}CuO_3$, $La_{0.8}Bi_{0.2}CuO_3$; No. 640-$La_{0.4}Bi_{0.6}CuO_3$, $La_{0.6}Sb_{0.4}CuO_3$, $SbCuO_3$; No. 673-$La_{0.6}Pr_{0.4}CuO_3$, $LaCuO_{2.8}$, $La_{0.6}Mg_{0.4}CuO_3$; No. 674-$La_{0.4}Sb_{0.6}CuO_3$, $La_{0.8}Mg_{0.2}CuO_3$, $LaCuO_{2.7}$; No. 682-$LaCuO_{3.0}$, $La_{0.8}Pr_{0.2}CuO_3$, $LaCuO_{2.9}$; No. 684-$La_{0.8}Sb_{0.2}CuO_3$, $PrCuO_3$, $La_{0.2}Pr_{0.8}CuO_3$.

The early magnetic checks were made with an ac susceptibility apparatus operated at 400 Hz with a net ac field of about 100 mG. All these samples were tested to temperatures as low as 15 K, and many to around 10 K. Data were acquired via an interfaced computer during cool down. Initially only one sample was tested per coil, but even with four coils available, this proved time consuming, so that two samples were loaded in each coil to speed the survey. This apparatus should have detected superconductivity if one part in a thousand were to have transformed.

A second batch of samples was surveyed with a BTI SQUID magnetometer in a field of 200±30 G. These samples were screened to a minimum temperature of 5–6 K, with measurements taken at 5-K intervals, and generally starting from 50 K. Many of the samples showed evidence of paramagnetic behavior, but no evidence of a Meissner effect was found in any sample. These measurements were estimated to be sensitive to about 1% of the sample volume. During a period of extreme demand for the equipment, perhaps two dozen samples were summarily checked by immersion of batches at 5 K to check for the presence of superconductivity; none of these samples gave results suggesting more detailed examination.

The last of the samples surveyed were studied using a Quantum Design magnetometer which determined the moment in a field of 20 G at temperature intervals of 5 K from about 50 K down to 2 K. Samples were screened in batches of three using a quartz tube holder.

A summary of the results from this last device is given

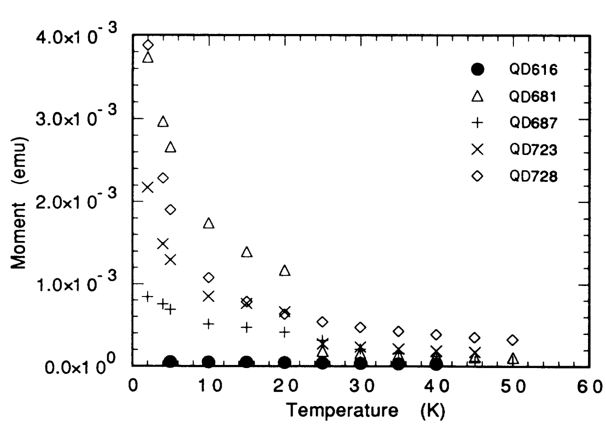

FIG. 2. Magnetic moment of samples observed with Quantum Design magnetometer which had more pronounced paramagnetic response. Samples include No. 616-$La_{0.4}Pr_{0.6}CuO_3$, $PrCuO_3$, $La_{0.2}Bi_{0.8}CuO_3$ (compare with Fig. 1); No 681-$La_{0.8}Nd_{0.2}CuO_3$ (run 1), $La_{0.8}Nd_{0.2}CuO_3$ (run 2), $NdCuO_3$; No. 687-$La_{0.2}Sb_{0.8}CuO_3$, $La_{0.4}Pr_{0.6}CuO_3$, $La_{0.6}Bi_{0.4}CuO_3$; No 723-$La_{0.6}Nd_{0.4}CuO_3$, $La_{0.4}Nd_{0.6}CuO_3$, $La_{0.2}Nd_{0.8}CuO_3$; No. 728-Nd_2CuO_4, $La_{0.4}Sr_{0.2}CuO_3$, $LaCu_{0.2}Zn_{0.8}O_3$.

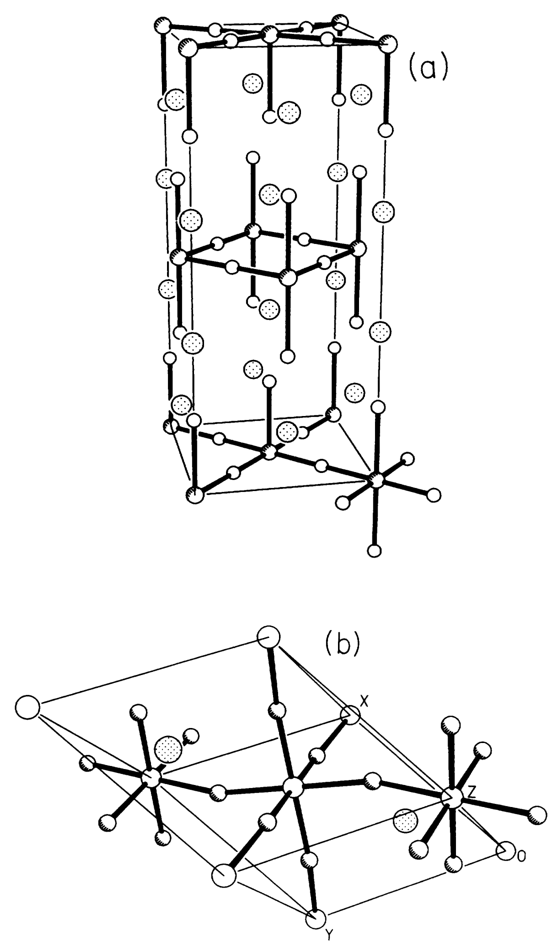

FIG. 3. Comparison of Cu-O environment in La_2CuO_4 (a) and $LaCuO_3$ (b), with the Cu—O bonds marked to show the two-dimensional nature of the Cu-O octahedra in the former, and the nonlinearity of these octahedral linkages which form three-dimensional networks in the latter. For clarity only those portions of the Cu-O octahedra in the unit cell (except for one full octahedron) are given for La_2CuO_4, and only those forming one chain (of a three-dimensional network) through the $LaCuO_3$ cell are given, with all related Cu-O linkages. Note the nonlinearity of the Cu-O-Cu linkages in the $LaCuO_3$ cell. The outlines are also given for the orthorhombic (a) and rhombohedral (b) unit cells to indicate the orientation of these networks.

in Figs. 1 and 2. The first figure summarizes seven scans for a total of 21 samples. The second figure summarizes results for four additional scans (12 samples), with that from scan No. 616 again included for sake of comparison. These all showed more marked paramagnetism, and included all the scans which had at least one sample containing Nd. Scan 687 had one sample with Pr content; other scans with one or more Pr-containing samples showed little difference from the general trend established by the other samples, however. This is curious since the effective magnetic moments of Pr and Nd are essentially equal at 300 K.[23] This discrepancy possibly derives from the fact that Pr may exist in either tri- and quadrivalent states. The mixed valency reactant, Pr_6O_{11}, was used, and the highly oxidizing environment may also have encouraged the higher valence in the product. The resultant Pr^{4+} would be a smaller ion which might comfortably fit on a Cu site. It would also be expected to have a smaller magnetic moment.

SUPERCONDUCTIVITY

Two unrelated studies on $La_{1-x}Sr_xCuO_3$ made in 1987 studied the superconductivity. The first reported it to have a T_c of about 50 K for $x=0.2$,[7] while the second found no superconductivity in their studies down to 77 K,[9] nor in later studies which extended to 10 K.[24] The second study noted the presence of the La_2CuO_4 structure under some treatment conditions, whereas the first study did not specify the preparation conditions.

None of the conditions or compositions prepared to date in this study have yielded superconductivity above the minimum test temperatures, which varied from 5 to 50 K. This negative result does not fully rule out the possibility, and there are many other combinations of composition, temperature, treatment procedure, time, pressure, flux, etc., which could be tried. Recall that the La_2CuO_4 system was thought for some time to require doping to become superconducting.[18] Subsequent work found that an involved heat treatment with slow cooling in pure oxygen yielded a superconducting product.[25] A common theme of the study of these copper oxide ceramics has been the critical nature of the processing procedures chosen. Although the additional restraints of working at HPHT restricts some processing options, a number of combinations are still possible. Within the limits chosen for this study, however, the tentative conclusion must be that the $LaCuO_3$ structure evidently does not contain all the criteria requisite for high-temperature superconductivity.

The environment of the Cu-O linkage does, it should be noted, differ markedly between La_2CuO_4 and $LaCuO_3$, as may be seen in Fig. 3. Note that the Cu, octahedrally surrounded by O in both cases, forms a two-dimensional structure with no linkages along the *c* axis in the first case. This is due to the insertion of NaCl-structured layers of La-O. In $LaCuO_3$, however, there is a three-dimensional network of Cu-O linkages. Although the La atoms are nearly cubic in symmetry (they are at equal distances, but the La—La—La angles are 89.2° and 90.2°), the marked deviation of the Cu—O octahedra can be readily seen in the figure. The O—Cu—O angles are not 180°; such a condition was also noted in the monoclinic $LaCuO_{3-y}$ $(0.2 \le y \le 0.4)$.[6] These units show an alternating tilt along a given chain direction. This nonlinearity of the —O—Cu—O— chains may itself disrupt potential superconductivity. Conversely, the increased dimensionality (three versus the two in La_2CuO_4) may be the impediment, as proposed recently by the calculations of Randeria *et al.*[26] The current work may, therefore, provide an important theoretical clue to the origin of superconductivity in copper oxide ceramic materials.

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