Evidence for Superconductivity in La_2CuO_4

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We report evidence for superconductivity in undoped La_2CuO_4 obtained from resistivity, thermoelectric power, and susceptibility measurements. The onset temperature is near 40 K and we have determined its pressure and field dependence in resistivity. The superconducting behavior is of a trace and filamentary nature and is quite sensitive to stoichiometry. Its occurrence is extremely process dependent and can be controlled by oxygen pressure. We discuss several likely sources for the superconducting activity.

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Much attention has recently centered on the superconducting members of the Cu-O perovskite family. Historically, developments began with the discovery of superconductivity above 30 K by Bednorz and Müller[1] in $La_{2-x}Ba_xCuO_{4-y}$, and have culminated (for the moment) in the 90+ K series based on $YBa_2Cu_3O_x$,[2] and its yttrium-lanthanide substitutions.[3] The parent compound of the former material is the layered perovskite La_2CuO_4 which has been extensively studied for some years[4-9] and displays a number of interesting transport properties in and of itself. However, La_2CuO_4 has in the past not shown any evidence in its transport properties of superconducting behavior; in fact, all reported data to date[9-11] exhibit strong increases in resistivity with decreasing temperature, consistent with the establishment of an insulating ground state.

In this paper we present the first strong evidence for trace superconducting behavior in pure La_2CuO_4. We have observed on a number of occasions over the past few months that the thermoelectric power of undoped La_2CuO_4 goes to zero at low temperatures, even though the sample resistance continued to increase. Further indications of incipient superconductivity were found by Greene *et al.*[12] in the magnetic field dependence of the low-temperature susceptibility. We now have direct evidence in transport that indeed a small portion of the material is superconducting, without alkaline-earth doping. This discovery takes on unusual significance given the detection of strong electron-electron correlations and a spin-density wave or antiferromagnetic transition in La_2CuO_4 near 250 K.[11,12] The fact that trace superconductivity can be found in nominally pure La_2CuO_4 is also quite interesting in light of occasional reports[2] of resistive anomalies near 240 K in other systems.

Our sample-preparation technique was taken from our earlier studies[13] on $YBa_2Cu_3O_x$ which showed that both the amount and the ordering of oxygen was extremely important in optimizing superconducting behavior in this compound. There the best results were obtained by our heating at 900 °C in flowing oxygen and slow cooling to room temperature at a rate around 100 °C/h. Previous discussions[4-8] of the preparation of La_2CuO_4 make no comment on quench rate after heating, which was usually done at temperatures in excess of 1100 °C. Our preparation follows directly those conditions employed for $YBa_2Cu_3O_x$. A mixture of La_2O_3 and CuO (2:1 molecular ratio) was ground to a fine powder in a mortar with a pestle. This mixture was heated in an alumina crucible at 900 °C for 12 h under oxygen atmosphere. The resulting dark brown powder was reground and pellets were cold pressed at 7 kbar. A second anneal was done under the same conditions as described above. Samples were slow cooled from 900 °C to room temperature over a period of 8 h under oxygen flow. The resulting pellets were the appropriately sectioned for resistance, thermopower, and magnetometry measurements.

Powder x-ray diffraction on samples prepared as above indicated single-phase material with the orthorhombically distorted K_2NiF_4 structure described by Longo and Raccah.[5] Electron microprobe studies showed the nominal stoichiometry to be $La_{2.01}CuO_{4.6}$, with no other elements present within the sensitivity of the instrument. A subsequent trace-impurity scan by inductively coupled plasma/mass spectrometer revealed Ca, Sr, and Pb as the major trace components, present in concentrations of 60, 0.4, and 19 ppm, respectively. Although the microprobe indicated rather high oxygen levels, we note that the excess amount is within the error limits of the measurement.

Resistivity data were taken by the four-probe technique with use of silver-paste contacts painted around the sample and lock-in detection with current densities kept less than 10 $\mu A/cm^2$. The sample itself was centered directly onto a Lake Shore diode (calibrated to ± 0.5 K) with General Electric varnish, assuring that both the thermometer and the sample were in equilibrium at all temperatures. The thermopower measurements were performed with use of an apparatus similar to that described by Chaikin and Kwak.[14] Samples of rectangular dimension of the order of a few tenths of a millimeter with a length-to-width ratio of 5:1 or higher were cut from pressed pellets. These samples were attached to 10-mil gold wires with silver paste. The gold wires served as both electrical and thermal contacts. The differential temperature across the gold-sample series network was measured with an iron-gold-Chromel thermocouple. Magnetometry measurements were performed with use of an SHE Corporation. Series 900 variable-temperature SQUID susceptometer.

Figure 1 displays resistivity-versus-temperature data typical of several samples prepared under conditions as described above. Note the overall tendency toward insulating behavior as the temperature is lowered. However, near 40 K, the resistivity suddenly plummets, achieving instrumental noise levels near 3 K. We observe this behavior in a number of samples, some which attain "zero resistance" as high as 16 K. It is possible that the actual onset temperature is considerably higher given the strong insulating behavior of the normal part of the sample. We also observe the temperature at which the resistance peak occurs to increase to nearly 50 K, along with a broadening of the transition width, under an applied pressure of 10 kbar. The inset to Fig. 1 shows the magnetic field dependence of the sample resistance. As expected for superconducting behavior, the resistance drop moves to lower temperature with applied field. Note the curious kink near 40 K at low fields in this sample which may signal the actual onset of superconductivity. Figure 2 depicts the temperature dependence of the thermopower in two other samples drawn from the same batch. At higher temperatures, the thermopower remains large as expected for a low–carrier-concentration metal, but then below 40 K it vanishes, as expected for the superconducting state. There is no indication that the thermopower is changing sign. The thermopower begins to decrease around 100 K, perhaps indicating that superconducting activity is commencing far above 40 K. As stated previously, zero thermopower has been observed at some temperature in every sample of La_2CuO_4 that we have looked at, including those obtained from our colleagues in IBM Zurich and Yorktown. Finally, Fig. 3 contains the results of the mass susceptibility of La_2CuO_4 measured in a 1.0-T field. Note the sharp diamagnetic dip beginning around 40 K. Greene *et al.*[12] also observed such a dip, which could be suppressed with applied field and whose magnitude diminished with time.

The data contained in these three figures clearly suggest evidence for filamentary superconductivity in undoped La_2CuO_4. The net amount of diamagnetic shift at an applied field of 250 Oe indicates that at least 1 part in 6000 of the sample is superconducting. The actual amount of the material that is superconducting is certainly greater than this for several reasons. As shown by Maletta *et al.*,[15] the diamagnetic shielding is significantly reduced in fields above 1 Oe in the LaSrCuO system. Moreover, the penetration depth is likely to be

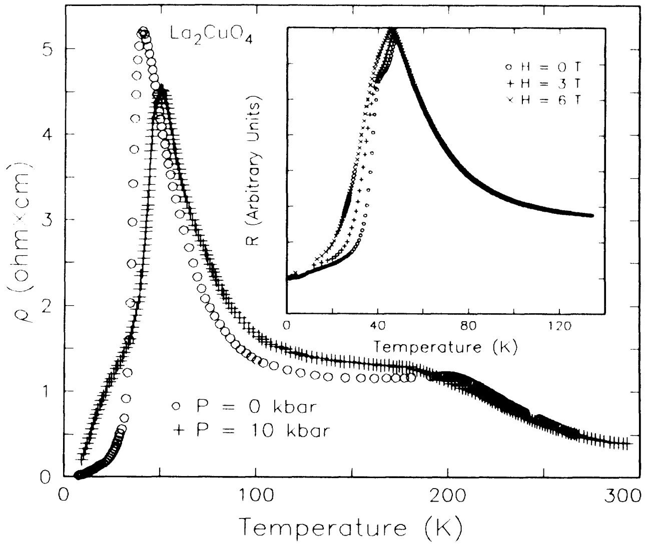

FIG. 1. Resistivity vs temperature in sintered La_2CuO_4 at ambient pressure and with 10 kbar applied. Inset: Magnetic field dependence of the sample resistance at ambient pressure for fields of 0, 3, and 6 T.

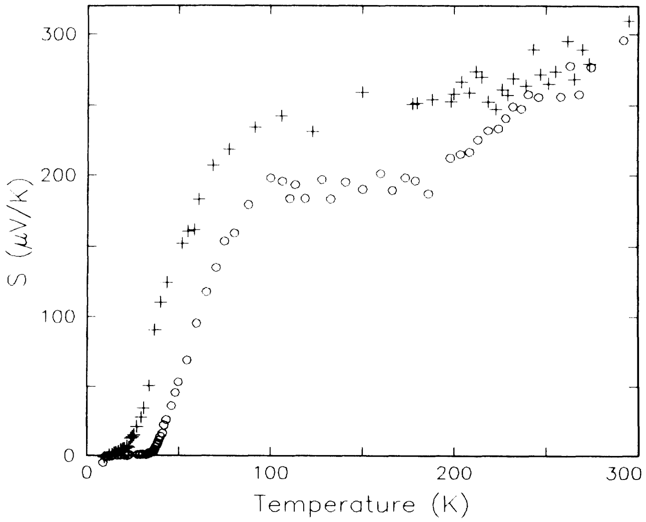

FIG. 2. Thermopower vs temperature in sintered La_2CuO_4. Data are shown for two separate samples from the same batch.

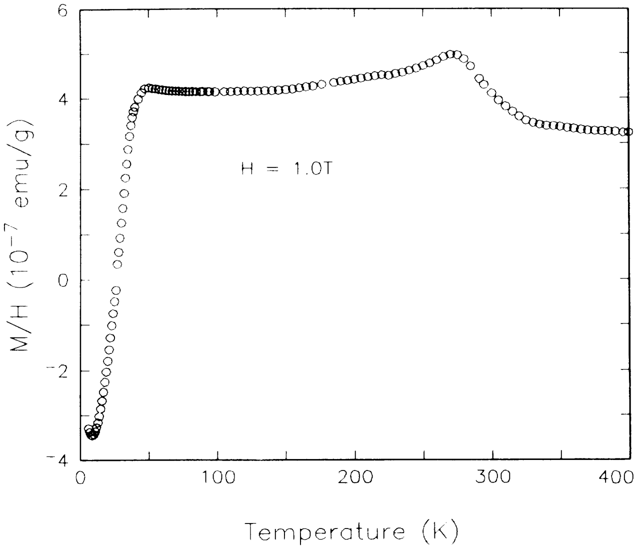

FIG. 3. Mass susceptibility vs temperature in sintered La_2CuO_4. The data were obtained by cooling in an applied field of 1.0 T.

comparable to the size of the superconducting regions in our samples. Both of these effects will cause us to underestimate the superconducting fraction. It is also probable that there will be superconducting glass behavior as recently discussed by Müller, Takashige, and Bednorz,[16] which would also lead us to underestimate the superconducting fraction. Given these uncertainties in the estimating of volume fractions in filamentary superconductors, it is not unreasonable that perhaps as much as 1% of our samples could be superconducting. For samples annealed in a reducing atmosphere, a suppression of the superconducting transition in resistivity was observed, with insulating behavior as T approached 0 K. The low-temperature resistive state also appeared approximately 10–12 days after sample preparation. These results suggest that oxygen processing is playing a dominant role in the transport phenomena.

The observation of zero thermopower at temperatures where the sample resistivity was rapidly increasing appears to be a paradoxical result. We propose the following simple model as a basis for understanding how this situation can occur. Consider a rectangular sample with an applied temperature differential along its long axis. Take this sample to be composed of two small superconducting rectangular sections extending from each end of the sample and narrow enough to overlap but not contact. Such an arrangement would have finite resistance but yield zero thermopower, indicating the presence of small noncontacting superconducting segments.[17] This argument, along with our experimental findings, suggests that thermopower may be the transport measurement most sensitive to minute superconducting components in an otherwise normal sample.

Our susceptibility data between 100 and 300 K, shown in Fig. 3, are similar to the results of others,[11,12] in that they contain structure probably related to an antiferromagnetic or spin-density-wave transition near 250 K. We note, however, that our resistivity and thermopower data also have variations in the same region, a previously unreported observation. It is likely that this variation is related to the same transition affecting the susceptibility.

At this time, we can only speculate on the source of filamentary superconductivity in La_2CuO_4. Several possibilities suggest themselves. The sensitivity to oxygen processing implies that the superconductivity may arise from regions of excess occupation, although this is unlikely since the layered perovskite structure, as opposed to $YBa_2Cu_3O_x$,[13] does not contain inherently empty sites. On the other hand, it is known that lanthanum-deficient La_2CuO_4 can be produced.[18] Both oxygen excess and/or lanthanum absence (the more likely situation) would shift the average copper valency upward, a condition believed necessary for superconductivity.[1] Another possibility is that different processing conditions may quench in minor portions of the tetragonal phase, which is generally accepted as the phase responsible for superconductivity in alkaline-earth-doped La_2CuO_4. In addition, Kasowski, Hsu, and Herman[19] have pointed out that the orthorhombic phase of La_2CuO_4 is not necessarily detrimental to superconductivity as they have shown this phase to be intrinsically metallic. These authors have also made the interesting suggestion that the low-temperature semiconducting behavior must arise from another phase transition, perhaps to a monoclinic form, since both the tetragonal and the orthorhombic phases are metallic. In this event, the superconductivity that we observe could arise from the retention of small amounts of orthorhombic La_2CuO_4. We must also mention that, given the evidence[12] for inherently strong electron-electron correlations in La_2CuO_4, it is certainly possible that interactions of the kind discussed by Anderson,[20] by Lee and Read,[21] and by Scalapino, Loh, and Hirsch[22] may be operative, especially in interfacial regions of the material. More work will be necessary to see if it is possible to stabilize larger superconducting volumes in La_2CuO_4. Hints that superconducting activity exists in excess of 40 K should make this a worthwhile effort.

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