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Composition-dependent superconductivity in $La_{2-x}Sr_xCuO_{4-\delta}$

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We report the dependence of the superconducting critical temperature on x for a series of $La_{2-x}Sr_xCuO_{4-\delta}$ samples prepared under identical conditions. A strong peak in the fraction of the sample which is superconducting occurs near $x=0.15$, the composition which also gives the highest transition temperatures as measured by resistivity and the dc Meissner effect. Relatively high onset temperatures are observed, and we infer the presence of another, possibly metastable, material with a critical temperature substantially higher than that of bulk K_2NiF_4 structure-type $La_{2-x}Sr_xCuO_{4-\delta}$.

While materials such as $La_2CuO_{4-\delta}$ and the solid solutions $La_{2-x}Sr_xCuO_{4-\delta}$ and $La_{2-x}Ba_xCuO_{4-\delta}$ have been known for many years,[1,2] it is only recently that their high-T_c superconductivity has been identified. Bednorz and Müller first reported a possible superconducting transition in the Ba-La-Cu-O chemical system in a mixture of phases.[3] The superconductivity was subsequently verified by Takagi, Uchida, Kitazawa, and Tanaka,[4] and the superconducting phase was identified as having the stoichiometry $La_{2-x}Ba_xCuO_{4-\delta}$ in the tetragonal K_2NiF_4 structure type. The midpoint of the resistive transition in this material was 30 K, while the dc magnetic susceptibility implied a bulk transition at 28 K. We recently reported[5] results on $La_{1.8}Sr_{0.2}CuO_4$ with a resistive onset at 38.5 K zero resistance at 35.5 K, and a bulk diamagnetic transition at 36 K. Mattheiss[6] has suggested a theoretical framework for understanding the occurrence of high-T_c superconductivity in these materials. In this paper we report the dependence of the superconductive properties of the $La_{2-x}Sr_xCuO_{4-\delta}$ solid solution on Sr concentration, and identify an optimal composition. For this composition, namely, $x=0.15$, the resistive midpoint is at 37.5 K, with a transition width (10–90%) of 1.5 K. The dc diamagnetic susceptibility indicates a bulk transition at 37.5 K, with 40% of the signal expected for an ideal bulk superconductor. We also report nonsystematic occurrence of enhanced conductivity at temperatures as high as 70 K, possibly signaling the presence of small regions with extremely high critical temperatures.

$La_{2-x}Sr_xCuO_{4-\delta}$ compounds were prepared from high-purity $La(OH)_3$, $SrCO_3$, and CuO powders using standard powder ceramic procedures. These include, among other steps, reaction at 1000 °C in air for several days with intermediate grindings, pressing into pellets, sintering at 1100 °C in air, and a final oxygen anneal at 700 °C. This procedure yields relatively dense pellets (~80% of the theoretical density) which were used for resistivity as well as magnetization measurements. The properties of compounds prepared in this fashion are stable and reproducible. The process has been optimized for the $x=0.15$ composition but does not represent optimization of all possible process variations for all compositions. As described previously,[5] we have found that the final anneal in O_2 is crucial in establishing the best bulk superconducting properties, presumably because this yields the smallest oxygen deficiency and most uniform oxygen content. Annealing in an oxygen pressure greater than 1 atm has not yet been examined but may lead to improved properties. To facilitate comparison all samples were given identical heat treatments.

Resistive transitions were measured in a four-wire van der Pauw configuration. Geometrical considerations limit the absolute accuracy of this technique, but since the samples were of relatively constant shape and thickness an experimental correction factor was applied and is expected to yield an overall accuracy of ~10%. Contacts were made using silver epoxy or soldered indium contacts; indium is preferable as it yields low-noise connections with a low contact resistance. Both ac and dc resistance measurements were employed and gave identical results within the accuracy of the measurement.

dc magnetic measurements were made in a SQUID magnetometer in an applied field of ~30 Oe. In general, the samples were cooled to 4.2 K in zero field, a constant field was then applied, and the resulting magnetization was monitored as a function of temperature. A 30 Oe field was used in order to enhance the sensitivity over previous measurements,[5] although for all samples it has the effect of decreasing the maximum degree of flux expulsion.

Figure 1 depicts the temperature dependence of the resistivity over the range 0–100 K for three typical samples with compositions as labeled, while Fig. 2 plots five temperatures characteristic of the resistive transition as a function of Sr content. In all cases the transition width is fairly broad; even the best transition, for $x=0.15$, is 1.4 K wide. This is somewhat larger than the narrowest transitions (~0.25 K wide) seen in single-crystal samples of a similar oxide superconductor, $BaPb_{0.75}Bi_{0.25}O_3$. Because the Ginzburg-Landau coherence length in this material is very small[7] [$\xi_{GL}(0) \sim 20$ Å] compared to the grain size, the effect of fluctuations on the conductivity must be calculated in the three-dimensional limit[8] (we consider only the Aslamazov-Larkin term because the material is not in the clean limit):

$$\sigma'_{3D} = \frac{e^2}{32\hbar\xi_{GL}(0)}\left[\frac{T}{(T-T_c)}\right]^{1/2} .$$

This conductivity enhancement is roughly as large as the

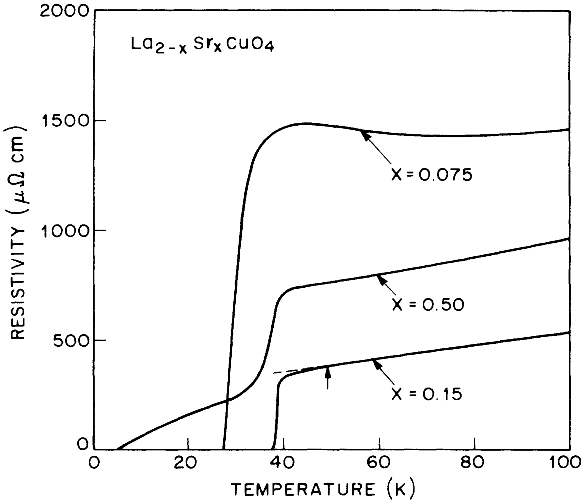

FIG. 1. Temperature dependence of the resistivity for three typical $La_{2-x}Sr_xCuO_{4-\delta}$ compositions. The arrow indicates the onset of the resistive transition for the $x=0.15$ sample at 49 K.

normal-state conductivity only within ~7 mK of T_c, so it contributes negligibly to the transition width and we conclude that the width is due to sample inhomogeneity. Indeed, this is readily apparent in the low-field behavior of the resistive transition,[7] in which the development of a small foot is seen at very low fields (~100 Oe). We attribute this foot to the breakdown of coupling between high-T_c grains through lower T_c (T_c ~ 15–25 K) weak links.

The upper whiskers in Fig. 2 indicate the temperatures at which the onset of the superconducting transition could be detected as indicated, for example, by the arrow in Fig. 1 directed to the $x=0.15$ sample. This temperature T_c^{onset} does not vary systematically with x for the preparation conditions described, and while it points enticingly to the highest T_c which might be achieved under proper conditions, it is not representative of the sample as a whole. In this spirit we note that we have observed values for T_c^{onset} as high as 52 K in $La_{1.925}Sr_{0.075}CuO_4$ and 70 K and even 110 K in $La_{1.85}Sr_{0.15}CuO_4$ prepared under somewhat different conditions. The former is a reproducible result, observed in many samples, and is accompanied by a diamagnetic signal corresponding to ~0.1% of that expected for a bulk superconductor. The latter results were observed both in $\rho(T)$ and $M(T)$ measurements, but are irreproducible and absent in other samples prepared similarly.

Resistive transitions can be misleading in materials which may be inhomogeneous, and cannot be used to infer the presence of bulk superconductivity. This is seen in Fig. 3, which plots as a function of temperature the dc magnetization of some typical samples, normalized to the value expected for a bulk superconductor [i.e., 30 G × $(-1/4\pi)$] of the same volume. The low-temperature asymptote for each sample is plotted in Fig. 4 as a function of x. While the onset of superconductivity is only marginally affected by x, the fraction which is superconducting at 4.2 K, and even more so, the fraction which is superconducting at high temperatures, peaks dramatically near x ~ 0.15. The maximum signal seen in the magnetometer is 40% of the ideal value—this is a reasonable value for a sintered pellet which is 80% dense. The authors believe that in these materials, the partial substitution of Sr for La is charge compensated by two mechanisms: (a) the partial oxidation of the Cu^{2+} to a higher effective average valence, and (b) the occurrence of vacant oxygen sites, most likely in the (La/Sr)-O layers. For material prepared in air at 1000 °C, for instance, at a composition $x=0.25$, charge

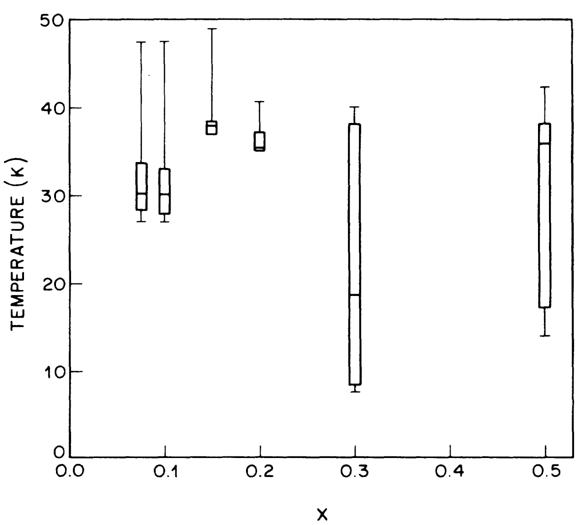

FIG. 2. The resistive transition plotted as a function of composition in $La_{2-x}Sr_xCuO_{4-\delta}$. This notation is similar in spirit to a statistical boxplot: The upper and lower whiskers indicate the onset of the resistive transition and the zero resistance state, respectively, the upper and lower box limits denote the 90% and 10% points, and the central bar indicates the resistive midpoint.

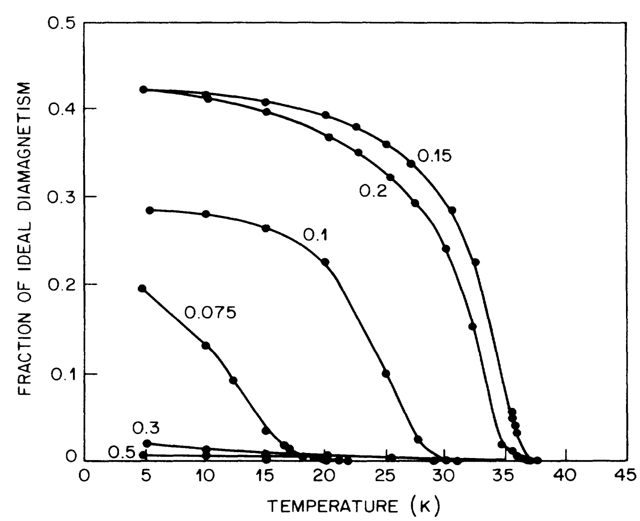

FIG. 3. Temperature dependence of the magnetization for various $La_{2-x}Sr_xCuO_{4-\delta}$ samples, plotted as a function of temperature. The data were taken in a field of 30 Oe and are normalized to the value which would obtain if the sample were an ideal bulk superconductor.

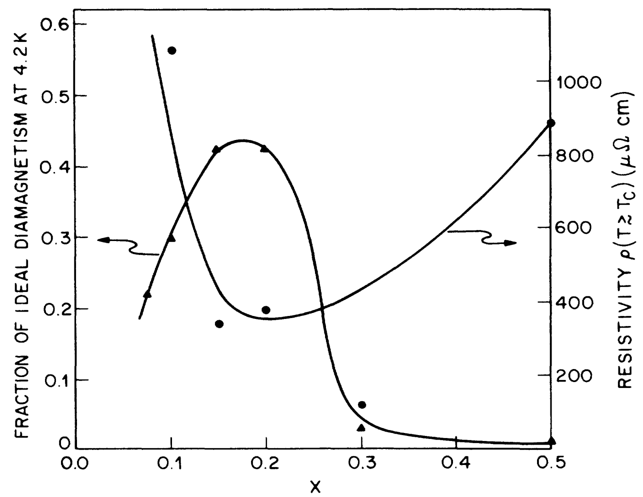

FIG. 4. Left-hand scale: A lower limit for the fraction of the sample which became superconducting at 4.2 K, as inferred from magnetization measurements and plotted vs composition. Right-hand scale: The normal-state resistivity, measured just above T_c, as a function of composition. The resistivity of a sample with $x=0.05$ reaches 0.015 ohm cm at 4.2 K.

compensation is accomplished by creation of 0.065 oxygen vacancies per formula unit, and an oxidation of Cu to an average effective valence of 2.12.[1] The low-temperature oxygen anneals employed here presumably result in a decrease (and homogenization) in the concentration of oxygen vacancies and an increase in the effective copper valence. At high Sr content ($x > \sim 0.3$), the effective valence state of copper reaches some upper limit for our synthetic conditions and charge compensation by oxygen vacancies becomes increasingly more important. The strong variation of the fraction of the superconducting material with x indicates that even for compositions away from the optimal there are regions with the correct Cu^{3+}-to-oxygen deficiency ratio for high-T_c superconductivity. Evidently, the role of Sr in this material is not so much to make high-T_c superconductivity possible (since this occurs even for low Sr content) as to stabilize a homogeneous high-T_c phase. All of the samples described in this paper are structurally single-phase K_2NiF_4-type, so we suggest that what is actually being stabilized and made homogeneous is the O deficiency, δ, in $La_{2-x}Sr_xCuO_{4-\delta}$.

Another indication of the quality of the samples prepared with $x=0.15$ is seen in the behavior of the normal-state resistivity, which is plotted in Fig. 4. The resistivity at $T > T_c$ reaches a low minimum value for the $x=0.15$ and 0.2 samples, which is apparently not dominated by extraneous contributions from intergrain regions. We have found La_2CuO_4 to be semiconducting at low temperatures, and this is reflected in the rapid increase of the resistivity seen in Fig. 4 for low Sr content. It is not presently clear why the sample with $x=0.3$ has such an anomalously low resistivity. For $x=0.15$ the residual resistivity ratio [defined as $\rho(300\text{ K})/\rho(T > T_c)$] is 3.1; the values for $x=0.1$ and 0.5 are 2.1 and 1.8, respectively. The low value for the resistivity of the $x=0.15$ sample, in what is expected to be a low-carrier-density material, means that the grains must be relatively free of impurity scattering. If we estimate the carrier density to be roughly 1 electron per formula unit, $n \sim 5\times 10^{21}\text{ cm}^{-3}$, we find that the mean free path $l_{mfp} \sim 20$ Å is comparable to the BCS coherence length $\xi_0 \sim 23$ Å. For these estimates we use a value for γ evaluated[7] from the thermodynamic critical field, the upper-critical-field slope, and heat-capacity measurements, namely, $\gamma = 6 \pm 1.5\text{ mJ mol}^{-1}\text{ K}^{-2}$. These materials are thus just on the boundary between the clean and dirty limits for type-II superconductors, and more complete data will be necessary to refine our understanding of their properties.

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