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Bulk superconductivity above 30 K in T^*-phase compounds

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High-pressure (3 kbar) oxygenation of $(La,Sm,Sr)_2CuO_4$ compounds having the T^* structure leads to bulk superconducting transitions above 30 K and the appearance of a diamagnetic response at temperatures as high as ~37 K. With increasing oxygenation pressure, the electrical resistivity and thermoelectric power progress from hoppinglike to more nearly metalliclike transport. The similarity in T_c and transport character with those of T-phase $La_{2-x}Sr_xCuO_4$, despite significant structural differences, further constrains possible mechanisms for superconductivity in the cuprates.

Three different but related rare-earth cuprate phases which form in a stoichiometric ratio of 2:1:4 (rare earth:copper:oxygen) are now known to be superconductors when either hole[1,2] or electron[3] doped away from half-band filling. Structurally, these tetragonal phases, frequently denoted as T, T', and T^*, all contain CuO_2 layers but differ from each other primarily, it appears, in the position of the out-of-plane oxygen atoms. This positioning leads also to substantial variation in the Cu-Cu spacing in the CuO_2 layers: The quasioctahedral oxygen coordination of copper in the La_2CuO_4 T-related phases is replaced by square-planar coordination in the T'-structure characteristic of R_2CuO_4 compounds, where R is one of the rare earths (Pr through Gd).[4] T^* phases appear to involve a mixture of these two coordinations, with approximately one half of the unit cell being T-like and the other half being T'-like.[5] It is the T^*-phase compounds that are of interest here.

There is an increasing number of indications that substantial variations of T_c in La_2CuO_4-based materials are correlated with various structural instabilities as a function of, for example, barium content.[6] An unusual feature of the T^* phase is its apparent lack of inversion symmetry;[5,7] in particular, the suggested structure lacks a mirror plane perpendicular to the fourfold axis. A definitive structural study of the T^* structure remains to be done, but these coarse features seem correct. In view of the above-mentioned structural correlation with T_c, the low-symmetry T^* phase offers an interesting new avenue into the physics of the superconductivity of the cuprates.

Until recently, only one compound $Nd_{1.32}Ce_{0.27}Sr_{0.41}CuO_4$ having the T^* structure was known to be superconducting with a transition temperature $T_c \sim 23$ K,[5] which depends only weakly on the oxygenation procedure.[8] In our investigations of the stability of the T^* structure, we have found a number of new compounds of the form $La(Pr)_{2-x-y}R_xM_yCuO_4$, where R is a rare-earth and M is one of the alkaline-earth elements that are predominantly, if not singly, T^* phase.[7] However, none of these T^*-phase compounds showed bulk superconductivity when prepared under ambient conditions.[9] Annealing these compounds at 550 °C under an oxygen pressure of 150 bars did produce, however, bulk superconducting transitions at temperatures $T_c \lesssim 20$ K in several of these, with a maximum T_c and diamagnetic response in the series $La_{2-x-y}Sm_xSr_yCuO_4$ for $x \gtrsim 0.9$ and $y \lesssim 0.2$. (Essentially, the same T_c was found in the range $0.7 \le x \le 1.1$ for $y = 0.2$ and $0.15 \le y \le 0.22$ for $x = 1.0$. T_c dropped rapidly toward zero once these limits were exceeded and the T^*/T and T^*/T' phase boundaries were approached.) The temperature-dependent resistance of these superconductors was unlike that of the T- and T'-phase superconductors and resembled the resistance expected of a dirty metal. This observation suggested that perhaps higher-pressure oxygen anneals might further modify the properties of these T^* superconductors.

Details of the sample preparation procedure and criteria for forming the T^* phase have been given earlier.[7] In this study, we have used samples prepared identically as before except that now some of these have been given a postsynthesis anneal at 575 °C in a 3-kbar oxygen atmosphere for 12 h at 575 °C, followed by a 100 °C/h cool. Samples were characterized by superconducting quantum interference device magnetometry, 4-probe dc resistance, x-ray diffractometry, and standard absolute thermoelectric power measurements.

Results of magnetic-susceptibility measurements on a $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_4$ sample annealed at 150 bar and 3-kbar oxygen pressure are shown in Fig. 1. X-ray diffraction shows this sample to be a clean T^* phase, with no detectable trace of either T or T' phases. We see that the bulk superconducting transition temperature has increased from $T_c \sim 21$ K for the 150-bars oxygenation to over 30 K for the 3-kbar oxygenation. It is interesting to note that the maximum diamagnetic response at 5 K is, however, identical, within our experimental uncertainty, for both samples. Though not readily apparent in this figure is the fact that diamagnetism is present already at between 37 and 38 K in the 3-kbar oxygenated material, as determined by both dc magnetization and rf impedance measurements.[10] What is very remarkable is that this T_c onset is very close to that of the T-phase compound

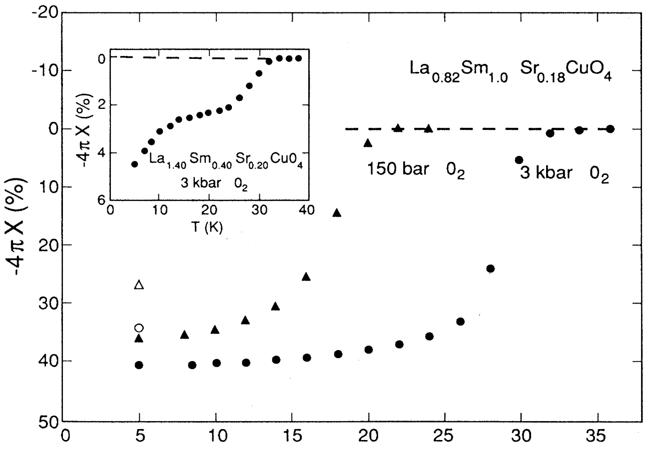

FIG. 1. Percent diamagnetism as a function of temperature for single T^*-phase $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_4$ annealed in oxygen at pressures of 150 bars and 3 kbar. Measurements, made in an applied magnetic field of 20 G, have been corrected for geometrical demagnetizing effects. Solid symbols represent zero-field-cooled results, whereas the open symbols are for field cooling from above T_c. Diamagnetism below 37 K is detected for 3-kbar oxygenation. The inset shows similar results on a predominantly T-phase sample $La_{1.40}Sm_{0.40}Sr_{0.2}CuO_4$. Note the vertical scale difference in the inset. Two transitions are apparent in the inset, the higher one due to a minority T^* phase and the lower due to the T phase.

$La_{1.80}Sr_{0.20}CuO_4$.[11] To show that this high-T_c onset in the T^* phase is not caused by excess oxygen loading as observed[12] in $La_2CuO_{4+\delta}$, we have performed a 3-kbar oxygen anneal at 575 °C on nominally $La_{1.40}Sm_{0.40}Sr_{0.20}CuO_4$ and $La_{0.97}Sm_{1.00}Sr_{0.03}CuO_4$ sintered samples that are predominantly T and T' phase, respectively.[7] Results for both samples were nearly identical and we show those for the former sample in the inset to Fig. 1. In this case there is a diamagnetic signal below 33 K. The size of the shielding effect is ~4% of bulk superconductivity, a factor of 10 down from the shielding signals of the T^*-phase sample shown. X-ray patterns of this T-phase sample indicate $12.5 \pm 1\%$ contamination with T^* phase, thus accounting for the small amount of superconductivity as arising from the minority T^* phase present.

An interesting progression in the temperature-dependent resistance of $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_4$ appears as a function of oxygen-annealing pressure, as shown in Fig. 2. For the "as-prepared" sample, i.e., annealed in 1-bar O_2, the resistance is semiconductorlike and there is no evidence for superconductivity. Annealing this sample in a 150-bars-O_2 atmosphere produces a temperature dependence like that of a dirty metal; whereas, a 3-kbar-O_2 anneal gives an essentially linear-in-T dependence from room temperature to T_c. (A small deviation from $R \propto T$ below about 120 K in the 3-kbar-O_2 sample suggests that the oxygenation procedure is nearly but not fully optimized.) Attempts to fit the 1-bar-O_2 data to an activated form were completely unsatisfactory; however, rather good fits to these data were found by assuming $\rho \propto \exp(T_0/T)^\alpha$, with $\alpha = \frac{1}{3}$ or $\frac{1}{4}$ below 57 or 26 K, respectively. These exponents are characteristic of hopping between localized states in either two ($\alpha = \frac{1}{3}$) or three dimensions ($\alpha = \frac{1}{4}$).[13] In view of the progression toward a linear temperature dependence with increased oxygen pressure, these results suggest that the transport mechanism proceeds from hopping (1-bar O_2) to a combination of hopping plus narrow-band transport (150 bars) and finally to narrow-band (3 kbar) conductivity with increased carrier concentration. It is interesting that, like our results at 3-kbar O_2 and those[14] on T-phase materials at 1-bar O_2, e.g., $La_{1.80}Sr_{0.20}CuO_4$, resistivity data reported[15] for a single crystal of the Ce-doped T'-phase superconductor $Nd_{1.84}Ce_{0.16}CuO_4$ also shows this linear-in-T dependence.

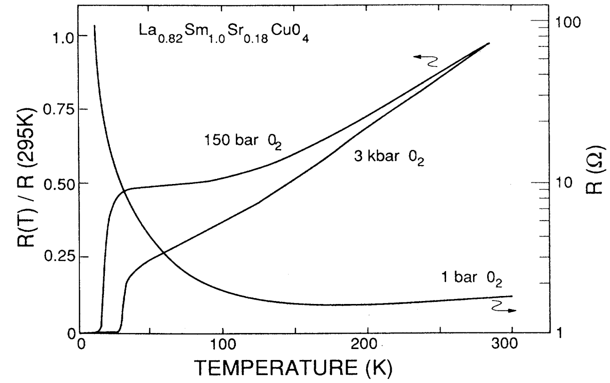

FIG. 2. Resistance vs temperature for a single T^*-phase sample of $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_4$ subjected to anneals in O_2 at 1 bar, 150 bar, and 3 kbar. In the latter two cases the resistance has been normalized to its value at 295 K (left vertical scale). Note the logarithmic right vertical scale appropriate to the 1-bar-O_2 oxygenation.

Figure 3 shows the corresponding development in the magnitude and temperature dependence of the thermoelectric power S of $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_4$ with oxygen-annealing pressure. S is positive regardless of the annealing treatment, indicating that transport occurs via the motion of holelike carriers. All three curves show qualita-

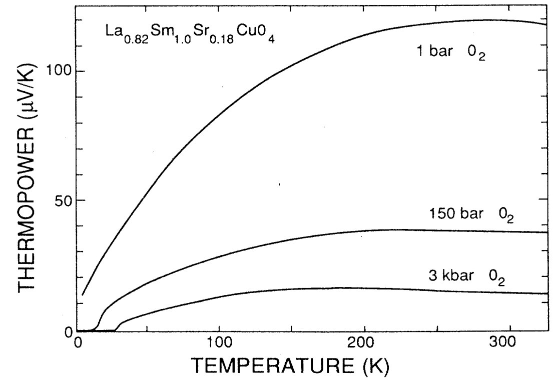

FIG. 3. Absolute thermoelectric power of $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_4$ as a function of temperature. The thermopower is positive and decreases in magnitude with increasing oxygenation pressure. See text for discussion.

tively similar temperature dependencies, with a temperature-independent thermoelectric power at high temperatures and a gradual reduction in S at low temperatures, which begins at roughly the same temperature where the resistivity starts to deviate from linearity. There is also a strong reduction in the magnitude of S with increasing O_2 pressure, implying that the resulting increase in the number of holes shifts the compound closer to a more metallic-like band. As with the resistivity data, S for the 1-bar annealed sample is consistent with hopping transport (S varies as $\sqrt{T}$ below ~ 150 K; a similar temperature dependence is evident over a more limited temperature range in the 150-bars and 3-kbar sample data). Further, a reduction in S with increased hole doping is consistent with the development of narrow-band transport. Hence, the trends evident in Fig. 3 track those shown in Fig. 2 and lead to the same conclusions for the progression in the transport mechanism as noted for the resistivity data.

We also observe that the magnitude and temperature dependence of S for the sample annealed at 3-kbar O_2 is similar to those found[16] for $La_{1.8}Sr_{0.20}CuO_4$ annealed at 1-bar O_2. That strontium is effective in stabilizing the T^* phase,[7,9] coupled with the high oxygen pressure necessary to fully develop the superconductivity and metalliclike transport properties, suggests that the oxygen stoichiometry is approaching four from lower values with increasing oxygen pressure.

The remarkable result, we reiterate, is that T_c is essentially unchanged in T^*-phase $La_{0.82}Sm_{1.0}Sr_{0.18}CuO_4$ relative to T-phase $La_{1.8}Sr_{0.2}CuO_4$, in spite of their structural differences and the observation[11] that lightly doping samarium into T-phase $La_{1.8-x}Sm_xSr_{0.2}CuO_4$ strongly depresses T_c. The origin of this latter effect, which produces an approximately 20-K decrease in T_c for $x = 0.2$, is unknown exactly but has been argued[11] to arise from a unit-cell contraction with increasing x that arises primarily, if not solely, from a decrease in the tetragonal c axis. We find similar, though less pronounced, volume changes in the T^* phase for $0.5 < x < 1.0$. However, at present there is insufficient data to warrant a definitive statement about any correlation between T_c and cell volume in T^*-phase compounds. It is natural to speculate that disorder in the rare-earth sites produced by introducing Sm in the T-phase material is responsible, at least partially, for the suppression of T_c. Our preliminary structural analysis[7] on T^*-phase $(La\text{-}Sm\text{-}Sr)_2CuO_4$ compounds indicates that the rare earths are only partially ordered such that samarium atoms prefer to assume positions in the T'-structure-like positions in the T^* unit cell. Therefore, an argument for disorder-induced suppression of T_c in the T^* phase seems unlikely as well, although it cannot be ruled out completely on the basis of information presently available. A more plausible explanation is that, in analogy to the T-phase $La_{2-x}Ba_xCuO_4$ system, proximity to a structural instability is important.[6] Clearly, studies on single crystals of T^*-phase superconductors would be valuable in this regard as well as in establishing precisely the crystal structure of T^* phases and in particular the location of oxygen atoms introduced by high-pressure oxygen anneals.

Finally, it appears that a diagnostic for full oxygenation is the appearance of a linearly temperature-dependent resistivity with strong metallic character. If useful speculation is to be made about the physics of the constancy of T_c, even with substantial changes in interatomic spacings and nearby environment, it seems important to compare the properties of materials which have the linear-in-T resistance characteristic.

In summary, we have prepared T^*-phase compounds with bulk superconducting transitions exceeding 30 K and the appearance of diamagnetism below ~ 37 K. The similarity in T_c and transport characteristics with those of the well-known T-phase compounds, in spite of significant structural differences, places further constraints on our thinking about the mechanism of superconductivity in cuprate materials.

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