Wide-range oxygen doping of $Bi_2Sr_2CaCu_2O_{8+\delta}$

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The high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ has been doped with oxygen at pressures ranging from a few μbar to 4 kbar. The doping is reversible by heat treatment in air at ambient pressure. Electrical-resistivity and infrared-optical-transmission measurements indicate that the carrier density increases monotonically with the oxygen annealing pressure. The superconductor transition goes through a maximum near 90 K and can be reduced by at least 30 K on both sides of the doping curve. In the oxygen-rich material the resistivity in the a-b plane exhibits a superlinear T^{1+x} behavior while the c-axis resistivity shows a positive slope in the temperature dependence.

The effect of chemical substitution on the electrical and structural properties of high-temperature superconductors has been studied extensively. These studies were motivated by the desire to vary the density of charge carriers. Exploring the correlation between the electron plasma frequency, the superconducting transition temperature, the impurity scattering of electrons and other properties influenced by doping helps to elucidate the mechanism of charge transport in the normal and superconducting states of these materials.

As long as the crystal structure does not change, the variation of composition can be best discussed in terms of excess holes in the CuO planes. For $Tl_2Ba_2CuO_{6+\delta}$ (Ref. 1) and for $La_{2-x}Sr_xCuO_4$ (Refs. 2 and 3) it is well established that there is an "optimum" composition, for which the critical temperature is the highest and the temperature dependence of the resistivity is close to linear. For underdoped materials, the resistivity vs temperature curves indicate electron localization at low temperatures; for overdoped ones the resistivities resemble those of conventional metals, $\rho=\rho_0+AT^n$, although there is no agreement on the exponent n.[1,2]

Here we report the electrical resistivity and the infrared transmission of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) single crystals. By performing heat treatments in reduced oxygen pressures and in oxygen pressures up to 4.4 kbar, we are able to vary the composition of the material from the underdoped to the overdoped range. The normal-state resistivity of the overdoped samples is reduced, and the optical measurement indicates that an enhanced carrier density is responsible for the lower resistance. We show, for the first time, that critical temperature around 60 K can be reached by oxygen addition or depletion, using the same starting compound. By varying the oxygen content, the superconducting transition temperature can be tuned through the maximum of 90 K.

The crystals were grown by a method described elsewhere.[4] The Bi:Sr:Ca:Cu composition was determined to be 2.14:1.93:0.92:2.02; the oxygen content was not measured. With this cation stoichiometry, one obtains $x=0$ hole per Cu, similar to the "ideal" 2:2:1:2 composition (assuming eight oxygen atoms per formula unit and Bi^{2+}, Sr^{3+}, Ca^{2+}, Cu^{2+} ions). It is well known, however, that the oxygen content of this material varies with heat treatment.[5] Our "as-grown" crystals had a critical temperature of 65–70 K, and a resistivity vs temperature curve typical of an oxygen-deficient sample.[4] Heat treatment in air at 600 °C increases the transition temperature to 90 K. Other authors[6,7] obtain the highest T_c by annealing in reducing atmosphere. We attribute this to the slightly different cation composition of their crystals which results from differences in the growth conditions. The complete phase diagram, describing the equilibrium oxygen concentration as a function of temperature and pressure, is presumably rather complicated. However, it is safe to assume that at a given temperature the oxygen content of the sample increases for higher oxygen pressures and decreases for low pressures, while the rest of the composition remains otherwise unchanged.

The heat treatment at high oxygen pressures was performed in a cell made of SWAGELOK components.[8] We cleaved the crystals to platelets of 100 μm$\times$2 mm$\times$2 mm, and subjected them to oxygen pressure of 4 kbar at 500 °C for 12–24 h. The surface of the samples developed a thin, transparent, insulating layer. The critical temperature of some of the samples was measured in a mutual inductance bridge. Samples annealed for shorter than a day typically had broader transitions. Other crystals were prepared for resistivity and optical measurements. For these studies the surface layer was removed by further cleavage. Electrical contacts for the four-probe resistivity measurement were made by evaporation of gold. On another set of crystals from the same batch we performed anneals at various reduced oxygen pressures at 600 °C.[9] Subsequently, all samples were heat treated in air flow at 600 °C for several hours, and the measurements were repeated. This allowed for a very accurate determination of the relative changes in the resistivity and in the infrared transmission, since the geometric factors were unchanged. We found that annealing in air flow at 600 °C completely reversed the changes induced by other heat treatments.

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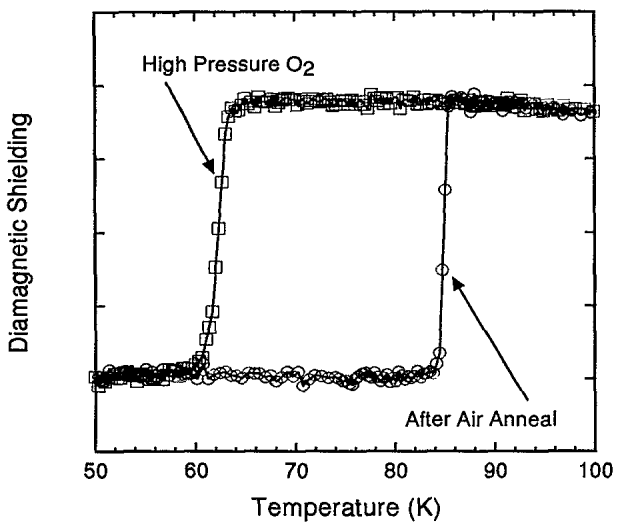

FIG. 1. Superconducting transition, measured by a mutual inductance bridge for a thin single crystal of $Bi_2Sr_2CaCu_2O_{8+\delta}$. The transition temperature is reduced by the high-pressure oxygen treatment, but annealing in air restores the original higher T_c.

Figure 1 shows the effects of a high-pressure oxygen anneal on the superconducting transition, as measured in a mutual inductance bridge. In Fig. 2 the a-b plane resistivity is shown for various annealing conditions. The low-pressure treatments led to underdoped samples. The upturn in the resistance at low temperatures signifies electron localization as has been seen in other doping studies.[2,3,10] High-pressure oxygen annealing resulted in an overdoped material. The lowest transition temperature reached in this manner was 59 K. The results shown in Fig. 2 unambiguously illustrate that overdoped and underdoped materials can be obtained by performing heat treatments on the same BSCCO starting compound. In BSCCO samples of slightly different cation composition, Lombardo and Kapitulnik[11] obtained $T_c=70$ K by annealing in 15 bars oxygen at 400 °C, and in an early study Morris *et al.*[7] suppressed T_c by about 20 K (150 bars oxygen atmosphere at 600 °C).

The overdoped sample has enhanced carrier density relative to the others. This is seen in the optical transmission measurements in Fig. 3. The measurements were performed at the infrared beamline U4IR of the National Synchrotron Light Source at Brookhaven National Laboratory. For a thin layer of metal, with electrons described by the Drude model, the optical transmission is approximately $t \approx (4c^2/d^2)(\omega^2+\Gamma^2)/\omega_p^4$, where c is the velocity of light, d is the thickness of the sample, ω_p is the plasma frequency, and Γ is the relaxation rate. Therefore, in a first approximation, the plasma frequency appears in the coefficient of the ω^2 term. Thus, the measurements clearly indicate an enhanced carrier density for the oxygen-doped sample. A more detailed fit to the data, including a Drude component and a midinfrared oscillator,[12] yields (at 300 K) $\omega_p=13\,000$ cm^{-1} (1.6 eV) for the overdoped material. This is to be compared to $\omega_p=9500$ cm^{-1} (1.2 eV) for the air treated sample.[12,13] Such a change in ω_p suggests a factor of 1.9 increase in the carrier concentration, n. The carrier concentration was measured to be 3.5×10^{21} cm^{-3} at 300 K for an air annealed sample,[4] resulting in $n=6.5\times10^{21}$ cm^{-3} for the oxygen-doped crystal. This concentration is consistent with the resistivity at 300 K of the 2-kbar crystal in Fig. 2.

The results presented here, together *with the resistivity* and Hall effect data on $Tl_2Ba_2CuO_{6+\delta}$ (Ref. 1) and $La_{2-x}Sr_xCuO_4$ (Refs. 2 and 3) clearly show that enhancing the carrier density over the optimum value suppresses the superconducting transition temperature. The thermo-

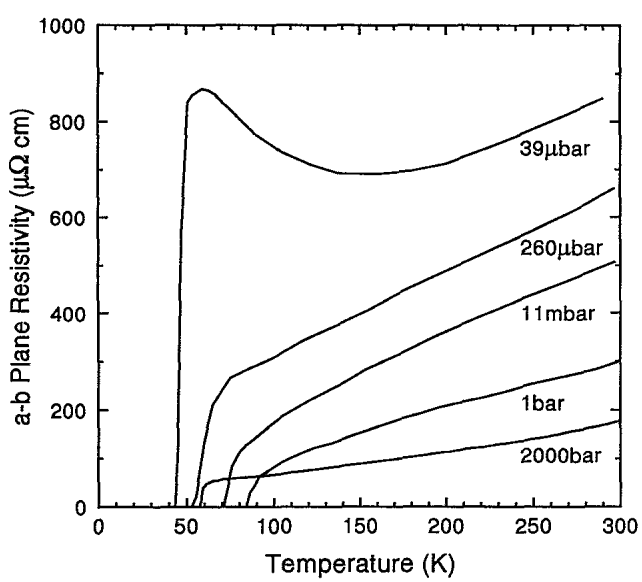

FIG. 2. Resistivity in the a-b plane, as measured after heat treatment in various oxygen pressures (indicated in the figure) is shown as a function of temperature.

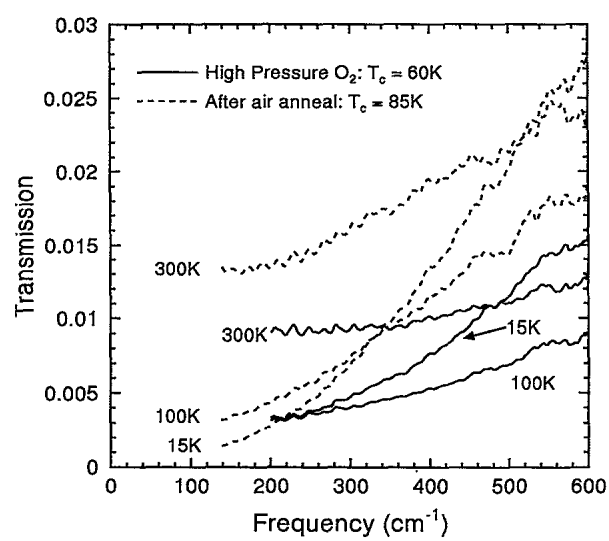

FIG. 3. Optical transmission of a thin single crystal of $Bi_2Sr_2CaCu_2O_{8+\delta}$ at 300, 100, and 15 K temperature. The first set of data was collected after a high-pressure oxygen treatment and the measurement was repeated after an anneal in air.

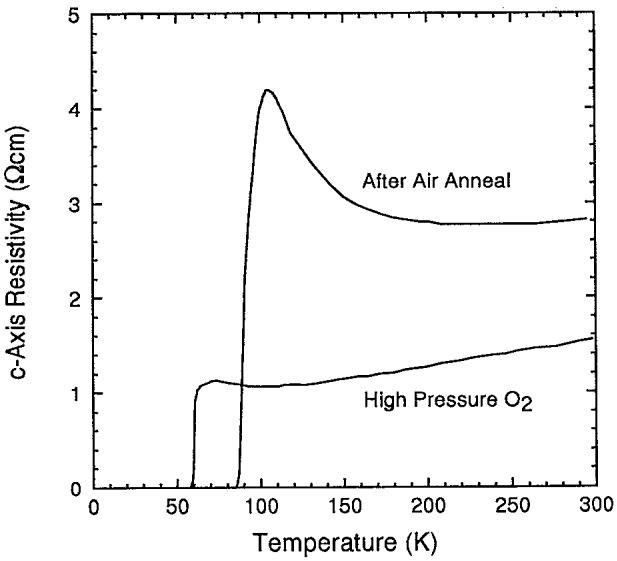

FIG. 4. The c-axis resistivity of the oxygen treated and air annealed $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystal is shown as a function of temperature.

dynamic instability leading to the $YBa_2Cu_4O_8$ phase prevented the observation of a similar, large suppression in $YBa_2Cu_3O_7$. When significant overdoping is achieved, the temperature dependence of the resistivity exhibits a positive curvature, but the similarity to conventional metals is only qualitative. The best fits of $\rho=\rho_0+AT^n$ to the $\rho(T)$ curves for the overdoped nonsuperconducting samples yield $n=2$ (Ref. 1) or 1.5.[2] Using a similar fit we obtain $n=1.6$ for our data. However, the transition temperatures of our overdoped samples are still in the 60-K range, and therefore a comparison to the exponents derived from the data in Refs. 1 and 2 is not straightforward.

In Fig. 4, the c-axis resistivity of a BSCCO single crystal is shown after a heat treatment in high-pressure oxygen and after a subsequent anneal in air. The measurements were made with four electrical contacts in a Montgomery configuration.[14] Although the absolute values of the resistivities contain geometrical factors with an uncertainty of about 20% (mostly due to inaccuracy in determining the thickness of the sample), the relative magnitude is accurate within 1%, since the contact configuration was not changed. The overdoped sample shows "metallic" character in the temperature dependence, similar to that observed by Xiang *et al.*[15] on iodine intercalated BSCCO crystals. However, the extremely short mean free path in the c direction ($l\approx 0.03$ Å or about 10^{-3} lattice spacings as estimated from the absolute value of the resistivity) (Ref. 16) suggests that the c-axis conduction is diffusive rather than metallic. Using a diffusive model, the temperature dependence of the interplane tunneling rate is influenced by the temperature-dependent relaxation time in the a-b plane. Such an interpretation was first suggested to explain the behavior of other anisotropic metals, like TTF-TCNQ,[17] and more recently, Forro *et al.*[16] applied the same idea to the out-of-plane conductivity of $YBa_2Cu_3O_7$.

In conclusion, we have shown that heat treatment in oxygen at various pressures can drive the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ into an underdoped and overdoped state. The enhanced charge carrier density of a high-pressure oxygen annealed crystal was directly probed by optical spectroscopy. For the overdoped material, the transition temperature is reduced, the resistivity in the a-b plane has a positive curvature, and the c-axis resistivity increases with temperature. In these features there is a general agreement between this material, $Tl_2ba_2CuO_{6+\delta}$ and $La_{2-x}Sr_xCuO_4$.

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