Metallic and Superconducting Surfaces of $YBa_2Cu_3O_7$ Probed by Electrostatic Charge Modulation of Epitaxial Films

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Transport in $YBa_2Cu_3O_7$ was studied by modulating the resistance and superconductive kinetic inductance via capacitively charging (001) surfaces. The mobility varies inversely with temperature, the effective mass is $5(\pm 1)m_e$ at low temperature, and hole carrier densities are temperature independent and nearly the same in normal and superconducting states. Transition temperatures at ideal surfaces are equal to the bulk and show notably weak modulation with carrier density.

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The quest to understand the mechanisms of high-T_c superconductivity has recently been focused on transport parallel to the copper-oxygen planes, especially the linear temperature dependence and the two dimensionality of the normal-state resistance.[1] The microscopic, free-particle transport parameters, which in the dc limit are carrier concentration, effective mass, and scattering rate, have thus far been estimated via penetration depth[2] and optical reflectivity measurements.[3] In $YBa_2Cu_3O_7$ calculations of the carrier density from the Hall coefficient are of dubious value because of the anomalous temperature dependence and change in sign near the superconducting transition.[4] Also unresolved is the relationship between carrier density and T_c and, particularly, the effect of withdrawing a small amount of oxygen.[5]

This Letter addresses these problems using a new experimental approach, in which transport parameters in both the normal and superconducting states were determined by direct electrostatic modulation of the carrier density in a surface layer on $YBa_2Cu_3O_7$ films. The modulation in T_c with carrier density was found to be very weak and was studied without modifying stoichiometry. Surfaces can be prepared with low residual disorder, as demonstrated in this work by metallic surface transport in the normal state and a surface superconducting transition temperature equal to the bulk, results which suggest bulklike CuO_2 "planes" at the surface. The two-dimensional metallicity and the weak coupling between the layers in high-T_c cuprates are the basis for the model proposed to interpret the modulation effects.

The transport coefficients studied were, in the normal state, the sheet resistance R and, in the superconducting state, the sheet kinetic inductance L. Free-particle expressions for these quantities are given by $R=m^*/N_N e^2\tau$ and $L=m^*/N_S e^2$, where m^* is the effective mass and N_N is the areal density of normal carriers (volume density times film thickness d_F) and N_S that of superconducting carriers. The carrier mobility in the normal state is $\mu=e\tau/m^*$. At zero temperature, the kinetic inductance is directly related to the London penetration depth $\lambda_L(0)$ by $L(0)=4\pi\lambda_L^2(0)/c^2 d_F$. Among the points addressed in this work are factoring out the carrier density and showing that it is temperature independent, determining that all normal carriers participate in the superconducting condensate ($N_N=N_S$), and indicating whether the same effective mass m^* enters into the expressions for R and $L(0)$.

The $YBa_2Cu_3O_7$ films for this work were grown epitaxially on $LaAlO_3$ substrates by coevaporation of Cu, Y, and BaF_2 in O_2, annealing in moist O_2 at 850 °C, and slowly cooling in dry O_2.[6] The films were oriented with the c axis perpendicular and ranged in thickness from 300 to 1000 Å. A parallel-plate capacitor was fabricated with one electrode being a $YBa_2Cu_3O_7$ film, the dielectric spacer a 7-μm layer of Kapton, and the counter electrode a 100-Å-thick Au film deposited on Kapton. This gentle fabrication method serves to minimize reaction between the prepared surface and the dielectric. In the normal state, the sheet electrical resistance was measured using four contacts at the perimeter of the film. For the kinetic inductance, the capacitor was positioned between two coils, to induce screening currents (10^4 Hz) in the plane of the film, and L was computed from the ac mutual inductance.[7] A dc voltage was applied to the capacitor, a charge per unit area δQ induced on the film (the charge measured with an electrometer was divided by the area of the film), and changes in R or L, denoted by δR or δL, respectively, were recorded. Apart from a region near T_c, these changes are linear functions of δQ. Hence, considering the anisotropic structure of $YBa_2Cu_3O_7$, the data can be interpreted using a model whereby a thin surface layer is modulated by the applied charge density and the material underneath is unaffected. For example, R would be comprised of surface and bulk resistances in parallel, where only the surface

TABLE I. Parameters for (001)-plane transport in $YBa_2Cu_3O_7$ films, of thickness d_F, resistivities ρ, transition temperatures T_c, surface mobilities μ_s, and carrier concentrations n ($\pm 5\%$) at $T = 295$ K; effective masses m^* ($\pm 25\%$) and penetration depths λ ($\pm 10\%$) at $T \simeq 4$ K.

d_F (Å)	T_c (K)	ρ(295 K) ($\mu\Omega$ cm)	μ_s(295 K) ($cm^2 V^{-1} s^{-1}$)	n (10^{21} cm^{-3})	m^*/m_e	λ(4 K) (μm)
300	89.9	330	4.6	4.1	5.0	0.20
300	89.8	415	3.5	4.3		
500	90.1	270	4.3	5.4	4.0	0.18
500	91.4	194	4.6	7.0	4.7	0.18
500	90.2	270	4.6	5.1	4.6	0.17
1000	90.2	418	4.1	3.6	5.5	0.25

component is modulated electrostatically.[8]

Upon charging the capacitor, the carrier density in the surface layer is changed by a small amount given by $\delta Q/q$, where q is the charge on the carriers. For a typical charge density $\delta Q = 10^{-3}$ C/m^2 used in this work, the change in surface carrier density is $\delta N = \delta Q/q = 6.3 \times 10^{15}$ m^{-2}. The sign of the effect, denoted by a decrease (increase) in R and L when δQ is positive (negative), establishes that both the normal excitations and superconducting pairs carry the same, positive charge, i.e., $q = +e$. From the change in total resistance δR, the surface mobility computed according to the parallel-resistance model is given by the expression $\mu_s = -R^{-2} \times \delta R/\delta Q$. Analogously, using a parallel-inductor model, the change in kinetic inductance at low temperature yields the effective mass, given by the expression $m^* = -eL^2 \delta Q/\delta L$. Note that, for linear response, neither the charge penetration profile nor the thickness of the modulated layer enter explicitly. Table I lists numerical results for the transport parameters obtained for some of the films.

Surface mobilities in the normal state were measured for as-grown films, which have an insulating-oxide coating, and for films etched in a Br-methanol solution. Previous tunneling and photoemission studies showed that such etching yields reproducible surfaces.[9,10] Figure 1 presents a comparison of the temperature dependences of μ_s^{-1} and R for a 300-Å film. Note that μ_s^{-1} obeys a linear dependence on temperature, extrapolating near to the origin. The small $T \rightarrow 0$ intercept indicates negligible scattering from defects on the surface, since any disorder scattering would appear as a temperature-independent addition to μ_s^{-1}. Successive removal of thin layers of surface material by repeated etching leaves the surface mobility unchanged, to within experimental error. We conclude from these results that the surfaces have substantially the same behavior as the intrinsic bulk.

Since both R and L are inversely proportional to areal carrier density, the observed fractional changes $-\delta R/R$ and $-\delta L/L$, typically on the order of 10^{-5}, in effect measure fractional changes in carrier density $\delta N/N$. Using the relation $\delta N = \delta Q/e$, the volume carrier densities were determined experimentally as $n = -R\delta Q/ed_F\delta R$ in

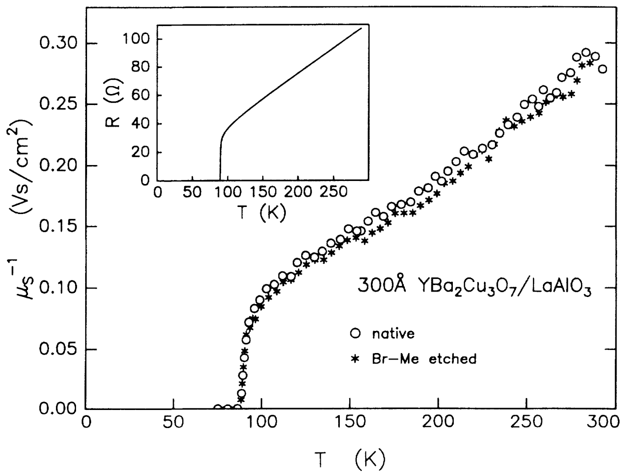

FIG. 1. Inverse of surface mobility μ_s vs temperature for a 300-Å film with native and etched surfaces, measured electrostatically. Inset: Sheet resistance.

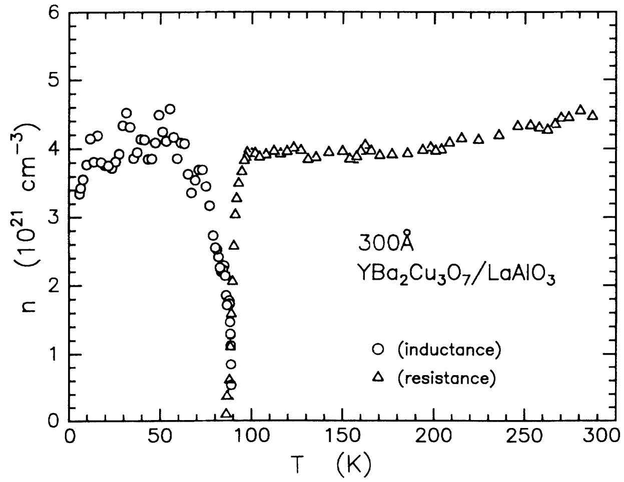

FIG. 2. Volume carrier densities computed from modulation of the superconducting kinetic inductance or normal resistance. The dip near T_c is discussed in the text.

the normal region and as $n=-L\delta Q/ed_F\delta L$ in the superconducting region. Figure 2 shows these two results for the carrier density as functions of temperature. Except for the transition region near T_c, the free-particle carrier densities obtained by the two methods are in good agreement, showing that to within experimental uncertainty (20%) the normal excitations in the system condense into superconducting pairs below T_c. Furthermore, this provides the first confirmation that the carrier density in the normal state is essentially temperature independent, as expected intuitively. The superfluid density vanishes as T_c is approached from below, and similarly for the normal density from above, but the behavior is not precisely the same as shown in Fig. 3, since the analysis ignored fluctuations near the phase transition and the modulation in T_c, which are discussed below. Results for n ranged from 3.5×10^{21} to 7×10^{21} cm^{-3} among the films studied, indicating the typical stoichiometric variations found in films.

Recent studies of the optical conductivity suggest n/m^* is temperature independent, to about 20% accuracy, as deduced by comparing the area under the far-infrared peak above T_c with the missing area below T_c.[3] Combining the optical and electrostatic results, if both n/m^* and n are constant, then obviously so is m^*. Changes in effective mass with temperature, due to dressing by phonon and electron interaction, are evidently below experimental resolution. If it were possible, at finite temperature, to decompose $\delta Q/e$ into its separate superfluid δN_S and normal δN_N components, then the temperature dependence of m^* could be determined. The present quasistatic analysis is uncorrected for the reduced superfluid fraction at finite temperature, and so the result for m^* appears to increase with temperature. Examples of this effect are shown in Fig. 3 for two films. The dashed curve displays the temperature dependence of a two-fluid model for a correction factor proportional to $(N_S+N_N)/N_S$.

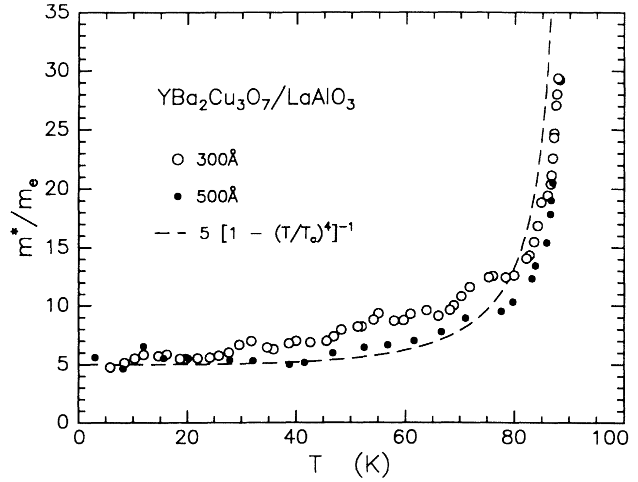

FIG. 3. Effective-mass parameters (m_e denotes electron mass) computed from modulation of kinetic inductance, corrected for the small modulation in T_c (see Fig. 4) but not for normal-fluid excitation. The dashed curve shows a two-fluid expression.

Since the mobility varies as T^{-1}, a constant m^* implies a scattering rate proportional to temperature. Taking the value $m^*=5m_e$ from the kinetic inductance at low temperature (Table I), the result for the inelastic-scattering rate is of the form $\tau^{-1}=2\pi\lambda\hbar^{-1}k_BT$, with $\lambda=0.35\pm0.08$ μm. The error encompasses results on six films. Analysis of optical reflectivity data indicates about the same value ($\lambda\sim0.2$ μm), which, in view of the uncertainties in treating the non-Drude frequency-dependent τ and m^*, is consistent with our result.

Near the superconducting transition, the current carried by superconducting fluctuations makes μ^{-1} seem to vanish near T_c (Fig. 1). However, a narrow peak is observed in δR just above T_c, located at the peak in the temperature derivative dR/dT, suggesting a charging effect on T_c.[8] Nonlinear contributions also appear near T_c, which may be due to the nonuniform charge penetration and the electrostatic stress (quadratic in δQ).[11] Figure 4 illustrates a similar peak the in-phase component of mutual inductance (δM) which is linear in δQ. The solid curve is the temperature derivative dM/dT, multiplied by a factor $\delta T_c'$, chosen to give overlap. The points closely correspond to the curve because the T_c of the surface layer and the film itself are the same. Sputtering the surface with low-energy ions (50 eV) attenuates the peak in δM and shifts it to lower temperature, but chemically removing the damage restores the original result. This simple test is important corroboration that ideal surfaces have the same T_c as the bulk. Consequently, the scaling factor $\delta T_c'=0.11$ mK for $\delta Q=1.3$ mC/m^2, obtained for a 300-Å film, is related to a shift in transition temperature (T_c increases and M de-

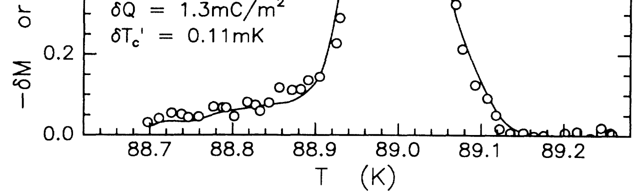

FIG. 4. Modulation of in-phase mutual inductance δM (normalized, component linear in δQ). The curve is the temperature derivative dM/dT scaled by the change in T_c.

creases for positive charging).

Two contributions to $\delta T_c'$ are expected theoretically, a shift in the mean-field T_{c0} in the surface region and a shift in the Kosterlitz-Thouless (KT) temperature (T_{KT}) with a change in total areal carrier density. For the 300-Å film, $T_{c0}=89.9$ K and $T_{\mathrm{KT}}=89.0$ K, as determined from $L(T)$.[7] Subtracting out the KT effect, by taking into account the steep slope of L near T_{KT}, yields a net temperature shift $\delta T_{c0}'=0.05$ mK for the component linear in δQ. The average thickness of the layer being modulated is assumed to be the perpendicular superconducting coherence distance $\xi_\perp$, which is less than the film thickness d_F. From our modulated-layer model, the actual change in the T_{c0} of this surface layer is given by $\delta T_{c0}=(d_F/\xi_\perp)\delta T_{c0}'$. The fractional change in volume carrier density in the surface layer, estimated to be 0.4%, is effectively the product of $d_F/\xi_\perp$ and the fractional change in total carriers [7.7×10^{-5}, as obtained from $-\delta L(0)/L(0)$]. The carrier-density dependence of T_{c0} is consequently found independently of $\xi_\perp$, with the result being $\delta T_{c0}/T_{c0}=+0.007\delta n/n$. Coefficients on the order of 10^{-2} were also obtained in several other films. A weak variation with n confirms the plateau at $T_c=90$ K in the doping dependence, i.e., that T_c is indeed insensitive to a small deficiency of oxygen.[5] If T_c were to depend primarily on electron density of states, then this small effect is understandable in terms of the constant density of states in two dimensions.

In conclusion, ideal free (001) surfaces of $\mathrm{YBa_2Cu_3O_7}$ were found by charge-modulation experiments to be metallic and superconducting, with microscopic free-particle transport parameters determined directly. The transport mobility varies as T^{-1}. Surface and bulk T_c are the same for undamaged surfaces and, significantly, show weak sensitivity to modulation in carrier density. Carrier densities were shown to be temperature independent and to be the same in the superconducting state as in the normal state, to within experimental error.

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[1] C. M. Varma *et al.*, Phys. Rev. Lett. **63**, 1996 (1989); P. W. Anderson, Phys. Rev. Lett. **64**, 1839 (1990).

[2] D. R. Harshman *et al.*, Phys. Rev. B **39**, 851 (1989).

[3] Z. Schlesinger *et al.*, Phys. Rev. Lett. **65**, 810 (1990); Z. Schlesinger *et al.*, Phys. Rev. B **41**, 11 237 (1990); G. A. Thomas *et al.*, Phys. Rev. Lett. **61**, 1313 (1988); K. Kamaras *et al.*, Phys. Rev. Lett. **64**, 84 (1990).

[4] T. Penney, M. W. Schafer, B. L. Olson, and T. S. Plaskett, Adv. Ceram. Mater. **2**, 577 (1987); S.-W. Cheong *et al.*, Phys. Rev. B **36**, 3913 (1987).

[5] R. J. Cava *et al.*, Physica (Amsterdam) **153–155C**, 560 (1988).

[6] P. M. Mankiewich *et al.*, Appl. Phys. Lett. **51**, 1753 (1987).

[7] A. T. Fiory, A. F. Hebard, P. M. Mankiewich, and R. E. Howard, Phys. Rev. Lett. **61**, 1419 (1988); Appl. Phys. Lett. **52**, 2165 (1988).

[8] A. F. Hebard, A. T. Fiory, and R. H. Eick, IEEE Trans. Mag. **23**, 1279 (1987); A. F. Hebard and A. T. Fiory, in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 9.

[9] A. M. Cucolo *et al.*, Physica (Amsterdam) **161C**, 351 (1989).

[10] R. P. Vasquez, B. D. Hunt, and M. C. Foote, Appl. Phys. Lett. **53**, 2692 (1988).

[11] D. J. Lischner and J. L. Juretschke, J. Appl. Phys. **51**, 474 (1980).