Effects of Field-Induced Hole-Density Modulation on Normal-State and Superconducting Transport in $YBa_2Cu_3O_{7-x}$

X. X. Xi, C. Doughty, A. Walkenhorst, C. Kwon, Q. Li, and T. Venkatesan[(a)]

Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742

(Received 21 November 1991)

The hole-density dependence of the normal-state resistivity and transition temperature T_c of $YBa_2Cu_3O_{7-x}$ was studied using the electric field effect in ultrathin films of 1 to 8 unit cells thickness. The change in resistivity was found to be equal to the field-induced variation in the areal carrier density, leading to a relation that the conductivity is proportional to the hole density. A similar linear dependence was also found in T_c. However, a saturation occurred in both cases but at different hole densities. The result reveals different effects of hole filling in influencing normal-state and superconducting transport of $YBa_2Cu_3O_{7-x}$.

PACS numbers: 74.30.−e, 74.70.Vy, 74.75.+t

The charge-carrier density dependence of normal-state and superconducting properties of high-T_c superconductors carries fundamental information about the electronic structures of these materials. Much work has been done by doping either holes or electrons into initially antiferromagnetic insulators, converting them into either p-type or n-type metallic superconducting compounds [1]. For $YBa_2Cu_3O_{7-x}$ (YBCO), mobile holes in the conducting CuO_2 planes are created by adding oxygen to the insulating $YBa_2Cu_3O_6$, through a charge-transfer process between the planes and the intercalating layers containing Cu-O chains [2]. This process is accompanied by an orthorhombic-to-tetragonal phase transition associated with defect ordering in the chains. The hole density can also be changed by substitution of other elements into Y or Cu sites, which often introduces magnetic moments or disorder [3]. Questions also remain concerning the role of holes at the plane and chain sites in influencing transport properties in the normal and superconducting states [4,5]. It is desirable to vary the hole concentration in YBCO in a controllable way without involving chemical substitution or structural phase transition.

In this Letter, we report on the responses of normal-state resistivity and transition temperature T_c of YBCO as the hole concentration was directly modulated by applying a voltage to a parallel-plate capacitor in which one plate was an ultrathin YBCO film. The first electric field effect was demonstrated in low-T_c superconductors by Glover and Sherrill [6]. In a later experiment in In/InO_x, Hebard and Fiory observed modulations of conductivity and T_c in qualitative agreement with the free-electron model and BCS theory [7]. Recently, there has been an increasing interest in the study of electric field effects in high-T_c superconductors [8,9]. In our work, a quantitative study on the hole-density dependence of resistivity and T_c was conducted in YBCO films of a few unit cell thicknesses in an effort to elucidate the effects of hole filling in YBCO.

The samples for this work consisted of c-axis-oriented YBCO films with thicknesses ranging from 1.2 to 10 nm (1 to 8 unit cells thick). A 400-nm (001) $SrTiO_3$ dielectric layer and a gold gate electrode were deposited on top of the YBCO layer. Details of sample configuration and preparation have been published previously [10]. Cross-sectional TEM study indicates a good epitaxy between the (001) $SrTiO_3$ substrate, the YBCO, and the $SrTiO_3$ layers. A dc voltage V_G was applied to the gate and the charge induced on the films was measured with an electrometer and divided by the gate area ($\sim 0.3\times 1$ mm^2) to give the field-induced charge per unit area ΔQ. The field-induced change in areal carrier density was given by $\Delta N = \Delta Q/q$, where q is the charge on the carriers and $q=+e$ for YBCO. There was an asymmetry in the breakdown voltage E_{BD} of the $SrTiO_3$ layer and therefore only the results of $\Delta N<0$ (i.e., hole filling) are discussed in this Letter. With a dielectric constant ε ranging from 300 to 900, εE_{BD} was $\sim 5\times 10^8$ V/cm for this polarity [11].

The thickness of the YBCO films is critical for the field-effect experiments. First, the maximum field-induced charge attainable is limited by εE_{BD} of the insulation layer. For this to be a substantial percentage change in the carrier density, the YBCO film should only be a few unit cells thick. Second, due to screening, the field-induced charges are confined to a thin layer near the superconductor-dielectric interface. In a three-dimensional free-electron system, the Thomas-Fermi charge screening length, λ, is given by [12] $\lambda = (\hbar^2\pi\varepsilon/4m_ck_Fe^2)^{1/2}$. For YBCO, $n=5\times 10^{21}$/cm^3, $\varepsilon_{YBCO}=26$ (see Ref. [13]), and thus $\lambda \approx 0.45$ nm. Since YBCO has a two-dimensional layered structure, we presume that the charge screening will occur in the first unit cell at the surface.

The field-effect experiment was thus carried out in a series of YBCO samples with different thicknesses. In Fig. 1, the R vs T curves for (a) 8-, (b) 4-, (c) 2-, and (d) 1-unit-cell-thick YBCO films measured with and without a gate voltage are plotted and ΔN is indicated for each sample. The thickness quoted in the figure represents an average and the fluctuation in thickness should not affect the trend of the carrier-density dependence. As shown in the figure, when the hole concentration in the YBCO

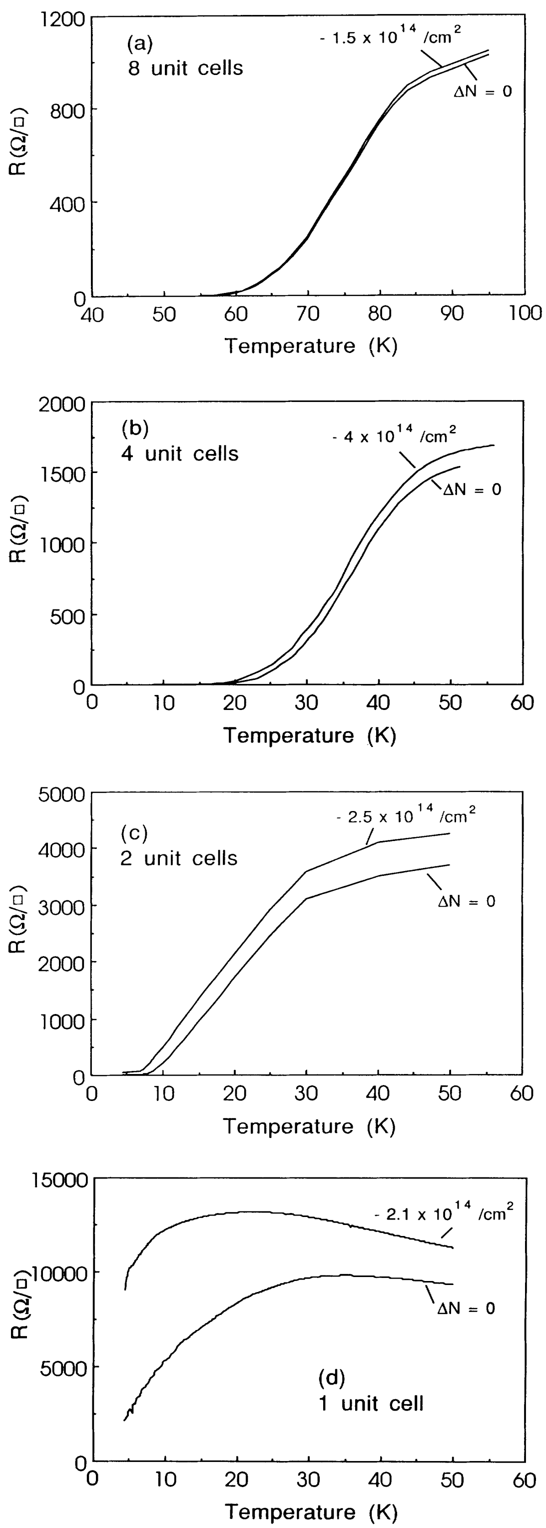

FIG. 1. Sheet resistance R vs temperature curves for YBCO films of (a) 8-, (b) 4-, (c) 2-, and (d) 1-unit-cell average thicknesses with zero and a finite carrier-density modulation. By capacitively charging the sample, the hole concentration in YBCO was decreased, causing an increase in the normal-state resistivity and a suppression in T_c.

films was reduced, the resistivity was increased and the transition temperature suppressed. In Ref. [10], Xi *et al.* also reported a decrease in resistivity and an enhancement of T_c for increasing hole concentration. The observation of the effect in both directions rules out explanations by the leakage current, which was lower than several nA, much smaller than the measurement current of 1 μA, or by the stress, which was estimated to be of the order of 10^{-7} (see Ref. [14]). The polarity of the field-induced change indicates that a higher hole carrier density favors normal-state conductivity and superconductivity in YBCO. The field effect became progressively larger as the film thickness was decreased and the relative changes in the normal-state resistance $\Delta R/R$ obtained for 8-, 4-, 2-, and 1-unit-cell-thick films were 2%, 8%, 15%, and 24%, respectively. The suppression of the zero resistance temperature, $-\Delta T_c/T_c$, showed a similar trend. In the 1-unit-cell film, a negative temperature coefficient of resistivity became even more pronounced when the field was applied, a remarkable effect of the hole filling on the transport characteristics of YBCO.

By controlling the gate voltage, we were able to study quantitatively the normal-state transport as a function of the carrier density. In Fig. 2, $\Delta R/R$ is plotted versus the change in the areal carrier density $\Delta N/N$ ($N = nd$, where d is the film thickness) for the four samples in Fig. 1. The nominal film thickness and $n = 5\times10^{21}/\mathrm{cm}^3$ are used to calculate N, which can be determined from the experimental data, as will be discussed later. $\Delta R/R$ was constant above the onset of the superconducting transition and the measurement temperatures are indicated in the figure. Also plotted is a straight line $\Delta R/R = -\Delta N/N$. As shown in the figure, the percentage of change in the normal-state resistivity is equal to the fractional variation

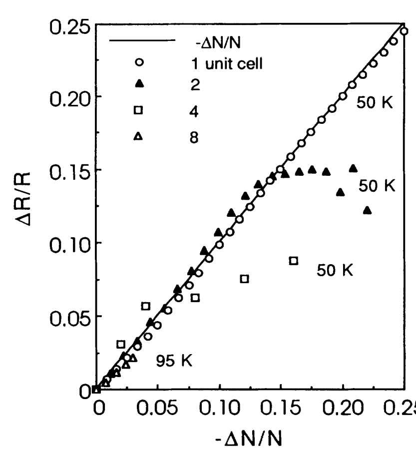

FIG. 2. The modulation of normal-state resistivity $\Delta R/R$ vs the relative change in the areal carrier density $\Delta N/N$ for the samples in Fig. 1. The straight line represents $\Delta R/R = -\Delta N/N$ predicted by the free-carrier model. The film thicknesses are of 8 (△), 4 (□), 2 (▲), and 1 (○) unit cells. The measurement temperature is indicated for each sample.

of the areal hole density over a wide range. The data from all samples fitted the straight line strikingly well except for a saturation in the 4- and 2-unit-cell films at high $\Delta N/N$ values. The $\Delta N/N$ value for the saturation seems to scale with the film thickness and, in the 1- and 8-unit-cell films, the saturation was not observed probably because $\Delta N/N$ was not large enough before gate breakdown occurred.

The electric field modulation of the resistivity can be analyzed using a parallel-conductor model [7]. In this model, a film is treated as two conductors: one, within the charge screening length from the interface, affected by the electric field, and the other unperturbed. Assuming a free-carrier expression, $\sigma = ne\mu$, in which the scattering rate $\tau^{-1} = e/m_e^* \mu$ is n independent, a relation $\Delta R/R = -\Delta N/N$ is obtained regardless of the film thickness and the charge screening length. The result of Fig. 2 is an experimental proof of this dependence which leads to a relation that σ is proportional to n for YBCO. Having this established, the carrier density in the YBCO films can be determined by the expression $n = -(d\delta R/R\delta N)^{-1}$, and the agreement between the data and $\Delta R/R = -\Delta N/N$ indicates that it is close to the assumed value of $n = 5\times10^{21}/\mathrm{cm}^3$, comparable to the result of Fiory *et al.* obtained in thick films [9]. The fluctuation of n among different samples, which depends on the oxygen content, and the uncertainties in the film thickness are reflected by the deviations from the straight line. The saturation of $\Delta R/R$ at high $\Delta N/N$ values shows that the linear relation between σ and n is no longer valid under certain conditions. This could be caused by a change in the scattering mechanism [i.e., $\tau^{-1}(n)$], but, more likely, it may be an indication that some holes do not contribute to the conductivity of YBCO and filling these holes does not change the measured mobile hole density.

Unlike the normal-state resistivity, the hole-density dependence of T_c is less clear because the depth within which T_c is affected depends also on the coherence length $\xi(T)$ which diverges at T_c. If we assume that only in the top unit cell is T_c directly affected by the electric field, the T_c modulation we observed could be caused by the reduction of the thickness of the unaffected layer (T_c drops rapidly when the YBCO film is thinner than ~ 4 unit cells [15]) or the inhomogeneity of the film thickness. In our experiment, a zero resistance temperature was not achieved in the 1-unit-cell film. In Fig. 3 we plot $\Delta T_c/T_c$ as a function of $\Delta N/N$ for the 2- and 4-unit-cell films. T_c is defined here as the zero resistance temperature and is determined from a logarithmic plot of R vs T when the noise level of the measurement is reached. ΔT_c is ~ 2 K for both samples. As shown in the figure, $\Delta T_c/T_c$ depends linearly on $\Delta N/N$ and, surprisingly, the data fall again on a straight line, $\Delta T_c/T_c = \Delta N/N$. As in the case of resistivity, this could imply that the T_c of the YBCO films is proportional to the hole carrier density n. Note that no saturation occurs in the 2-unit-cell film,

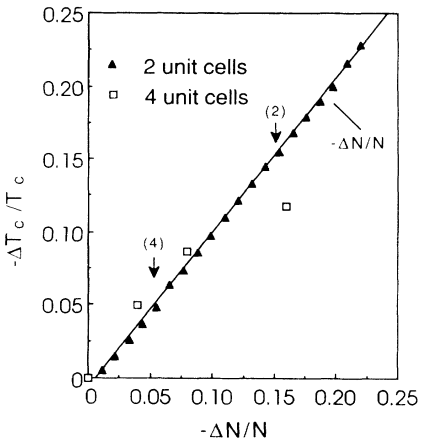

FIG. 3. The modulation of transition temperature $\Delta T_c/T_c$ vs $\Delta N/N$ for the 2- and 4-unit-cell-thick YBCO films. The straight line represents $\Delta T_c/T_c = \Delta N/N$. The arrows indicate the carrier densities where $\Delta R/R$ saturates.

contrary to the case of the normal-state resistivity. A saturation is seen in the 4-unit-cell film but at a different $\Delta N/N$ value from that for resistivity. The arrows in the figure indicate for both films the $\Delta N/N$ values for a saturation to occur in $\Delta R/R$. The result shows that at a certain hole concentration, the field-induced charges do not contribute to the normal-state conductivity but they still affect the transition temperature.

It is widely accepted that the mobile holes in the CuO_2 planes in YBCO participate in the normal-state conduction as well as superconductivity. The role of the holes on the Cu-O chains is not so clear. Using an iodometric titration technique, Tokura *et al.* concluded that the holes on the chains are localized and merely provide an insulating reservoir of charge [4]. Recent results on twin-free crystals, on the other hand, showed an anisotropy of dc and infrared conductivity along the a and b directions, which Schlesinger *et al.* attributed to the conduction of holes on the Cu-O chains [5]. Both proposed that there is 0.5 plane site hole per unit cell of YBCO. However, both the present work and the result of Fiory *et al.* on thick YBCO films showed a carrier density close to 1 hole per unit cell. Fiory *et al.* further showed that the number of normal carriers above T_c is equal to the number of superconducting carriers below T_c [9]. These results tend to indicate that the holes are mostly on the planes. Nonetheless, the saturation we observed suggests the existence of localized holes, which are likely located on the Cu-O chains. The other possibility is that the chain site holes are mobile, but since there are many twins and defects in our film samples, the conductivity along this one-dimensional path will be destroyed and we are unable to measure them. The chain may enhance the conductivity in the plane through some type of interaction rather than participating independently in the conduction. In any case, a change in the hole density and hence in the characteristics of the Cu-O chain can still affect T_c by changing the coupling between CuO_2 planes.

It is worth comparing our result with the oxygen doping of $YBa_2Cu_3O_6$ in which holes are generated and entirely accommodated in the Cu-O chains until a short-range ordering occurs in the chains and holes are then transferred to the CuO_2 planes [2]. The charge transfer between the plane and chain could also be important for the electric field effect. A possible explanation for our result is that the field-induced charges first enter the plane and fill the mobile holes there. When the first unit cell is depleted by $\sim(20\text{–}25)\%$, charges further induced by the field start to be transferred to the Cu-O chain sites. Then, as discussed above, there would be no further change in the conductivity, resulting in the saturation in $\Delta R/R$.

Despite the complications in interpreting the T_c data, the linear hole-density dependence agrees with the neutron-diffraction result by Cava *et al.* in which T_c is closely related to the charge in the plane Cu sites [2]. It is also consistent with the muon-spin-relaxation result by Uemura *et al.* in which a linear relation between T_c and n_s/m^* is derived [16]. The present work is the first experiment in which the hole-density modulation is directly measured. Since the linear relation between T_c and n was found by Uemura *et al.* in all cuprate superconductors, they proposed that it reflects intrinsic physical properties of the CuO_2 planes. In our ultrathin films, the zero resistance temperature may also represent a Kosterlitz-Thouless temperature T_{KT} which is proportional to $n_s(T_{KT})$ [17]. What needs to be explained is the saturation which is observed in the 4-unit-cell film. Presumably, if we could induce more charges than we have achieved in the present work, we could obtain a clearer picture on the effect of hole filling on resistivity and T_c. However, this depends on the improvement of dielectric properties of $SrTiO_3$ in terms of εE_{BD}, the limiting parameter for the maximum charges one can induce by the electric field.

In conclusion, we have found a linear dependence of the normal-state resistivity and T_c of YBCO on the hole density by the electric field effect. We also observed a saturation of the modulation which occurred at larger values of $\Delta N/N$ for T_c than that for resistivity. The carrier density obtained was close to 1 hole per unit cell and the result suggests that the filling of different holes may have different effects on the normal-state and superconducting transport properties of YBCO.

The authors would like to thank A. T. Fiory, A. F. Hebard, J. M. Tarascon, C. J. Lobb, S. Hagen, R. L. Greene, F. Wellstood, D. Drew, and S. Anlage for helpful discussions and comments on the manuscript.

[a]Also with the Department of Electrical Engineering.

[1] See, for example, papers in *Earlier and Recent Aspects of Superconductivity*, edited by J. G. Bednorz and K. A. Muller (Springer-Verlag, Berlin, 1990).

[2] R. J. Cava *et al.*, Physica (Amsterdam) **165C**, 419 (1990); J. D. Jorgensen *et al.*, Phys. Rev. B **41**, 1863 (1990).

[3] J. Clayhold *et al.*, Phys. Rev. B **39**, 777 (1989); Y. Dalichaouch *et al.*, Solid State Commun. **65**, 1001 (1988).

[4] Y. Tokura *et al.*, Phys. Rev. B **38**, 7156 (1988).

[5] T. A. Friedmann *et al.*, Phys. Rev. B **42**, 6217 (1990); Z. Schlesinger *et al.*, Phys. Rev. Lett. **65**, 801 (1990); L. D. Rotter *et al.*, Phys. Rev. Lett. **67**, 2741 (1991).

[6] R. E. Glover and M. D. Sherrill, Phys. Rev. Lett. **5**, 248 (1960).

[7] 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.

[8] J. Mannhart *et al.*, Z. Phys. B **83**, 307 (1991); J. Mannhart *et al.*, Phys. Rev. Lett. **67**, 2099 (1991).

[9] A. T. Fiory *et al.*, Phys. Rev. Lett. **65**, 3411 (1990).

[10] X. X. Xi *et al.*, Appl. Phys. Lett. **59**, 3470 (1991).

[11] A. Walkenhorst *et al.*, Appl. Phys. Lett. (to be published).

[12] N. W. Ashcroft and N. D. Mermin, in *Solid State Physics* (Saunders College, Philadelphia, 1976), p. 337.

[13] Z. Trybula *et al.*, Physica (Amsterdam) **156C**, 485 (1988).

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

[15] J.-M. Triscone *et al.*, Phys. Rev. Lett. **64**, 804 (1990); Q. Li *et al.*, Phys. Rev. Lett. **64**, 3086 (1990).

[16] Y. J. Uemura *et al.*, Phys. Rev. Lett. **62**, 2317 (1989).

[17] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).