Electrostatic tuning of the superconductor to insulator transition of YBa$_2$Cu$_3$O$_{7-x}$ using ionic liquids

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Abstract. Ultrathin YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) films were grown on SrTiO$_3$ (STO) substrates using a high-pressure oxygen sputtering system. The films were incorporated in a field effect transistor configuration to study the control of superconductivity by electrostatic charging. While devices using STO as both the substrate and gate dielectric have produced only small $T_c$ shifts, a clear transition between superconducting and insulating behaviour was realized using an electronic double layer transistor employing the ionic liquid DEME-TFSI as a gate dielectric. Employing a finite size scaling analysis, curves of resistance vs. temperature were found to collapse into two branches over the temperature range from 6 K to 22K suggesting the existence of a quantum critical point. However the scaling failed at temperatures below this range, indicating the possible presence of an additional phase between the superconducting and insulating regimes. Further depletion of holes appears to result in the accumulation of electrons resulting in a change of the majority carriers from holes to electrons and the emergence of what appears to be very weak re-entrant superconductivity. By changing the polarity of the gate voltage, an underdoped film was tuned into the overdoped regime by accumulating additional holes. An unexpected two-step mechanism for electrostatic doping was revealed. Hall effect measurements exhibited anomalous features, which suggest the occurrence of an electronic phase transition near optimal doping.

1. Introduction

High temperature superconductors (HTS Cs) with copper oxide planes are believed to be doped Mott insulators. Thus far many hole- [1, 2] and electron-doped [3, 4] HTSCs have been reported, with the doping process usually involving chemical substitution or oxygen stoichiometry modification. The modification of the electrical properties of such strongly correlated electron systems using an electric field as an external control parameter has been a long-standing goal in condensed matter physics [5, 6]. Field effect transistor concepts applied to HTSCs can provide a tool to control the superconducting condensate in a reversible manner, while keeping a fixed structure and avoiding altering the disorder associated with conventional approaches to doping. It can be a useful tool to study fundamental questions that still remain open regarding such systems.

Recently the development of electronic double layer transistors (EDLTs) that use ionic liquids (ILs) as gate dielectrics has been successfully employed to achieve levels of doping of the order of $10^{15}$/cm$^2$ [7–9]. Exploiting such large charge transfers, this approach has been used to tune the superconductor-insulator (SI) transition of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) [10] and of YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) [11] as well as explore aspects of the phase diagram of YBCO. In the following we focus on work...
relating to YBCO films where we exploit the possibility of large transfers of charge facilitated through the use of EDLTs employing ILs. We will describe experiments in which carriers are depleted and display the transition to the insulating regime and beyond, and those in which they are accumulated so as to tune an underdoped sample into the overdoped regime, going across the top of the superconducting dome in the phase diagram. Studies of $R(T)$ will be complimented by measurements of the Hall effect, which have been quite revealing in some instances.

Electronic Double Layer Transistors are configurations, which perform in a manner similar to conventional FETs. They contain a gate electrode, a semiconductor, an insulator or a metal into which charge can be accumulated or depleted, source and drain electrodes, and for purposes of characterization, electrodes for measuring longitudinal and transverse voltages relative to the current direction. In this instance the gate dielectric is an IL, although polymer electrolytes have also been employed. Ionic liquids are molten salts consisting of large ions such that their Coulomb interactions are sufficiently small to make them room temperature liquids. Upon applying a gate voltage, ions move to the surface of the semiconductor or insulator, forming an electric double layer (EDL) such that with the charge induced in the channel, acts as a capacitor of nano-scale thickness. This ultra-small effective thickness is what leads to the possibility of large charge transfer. A $T_c$ shift of about 50 K has been observed in YBCO thin films by earlier workers using ILs [12]. However, no transition from superconductor to insulator was found. The reason is that the films studied were substantially thicker than the Thomas- Fermi screening length, which roughly determines the depth of the induced charge. Thus the gating process would affect the order of only one UC. In the case of films of thicknesses of 10 UCs or greater, which were studied, the proximity effect would dominate, and no transition to an insulating regime would be possible.

2. Experimental
Films were grown on (001)-oriented SrTiO$_3$ (STO) substrates using a high-pressure oxygen sputtering system employing a nominally stoichiometric YBCO target. Previous work by others, using the same technique, has shown that high pressure oxygen sputtering can provide high quality epitaxial ultrathin YBCO films [13, 14]. Amorphous Al$_2$O$_3$ films were deposited as masks, and the substrates were etched in buffered (10:1) HF solution and annealed in an O$_2$/O$_3$ mixture for 6 h at 750°C. Atomic force microscopy (AFM) was used to make sure that the substrate surfaces were clean and were TiO$_2$ terminated. The oxygen pressure during deposition was 2.0 mbar and the substrate temperature was 900°C. After deposition, films were cooled in an 800 mbar O$_2$ atmosphere and annealed at 500°C for 30 min. Films were characterized ex situ by AFM and x-ray diffraction. Thickness was measured using x-ray reflectivity. A series of samples with thicknesses ranging from 5 to 10 UC was fabricated and measured using standard four-probe techniques. Films thinner than or equal to 6 UC were insulating whereas thicker ones were superconducting. This suggests that the first 5 to 6 UC are insulating and that a 7 UC film has a superconducting layer that is actually only 1 to 2 UC thick.

Ultrathin YBCO films are sensitive and react with most chemicals so we did not carry out any processing after film growth other than the deposition of Pt electrodes. The devices used were similar to the one shown in Fig. 1 of Ref. 8. Films were covered with the ionic liquid N, N-diethyl-N-(2-methoxyethyl)-N-methylammonium bis (trifluoromethyl sulphonyl)-imide (DEME-TFSI) [8] and were quickly cooled down to 240 K. The ionic liquid condenses into a rubberlike state at 240 K, a temperature at which most chemical reactions are suppressed. If the device is kept at room temperature for several hours with ionic liquid on it, we see an increase in resistance and a drop in $T_c$, possibly due to chemical reaction. However, after cooling down and being kept below 240 K, no changes are seen over many days. For measurements, the gate voltage was changed at 240 K where it was held for 1 h before cooling down. The gate voltage was kept constant during measurements. Gate voltages were always changed incrementally and the response of the films when hole doped was found to be reversible albeit with some hysteresis. We were not able to confirm this behavior in the electron-doped regime, which suggests that the changes effected in that regime may be chemical rather than physical.
3. The superconductor-insulator transition of YBCO

Curves of Resistance vs. temperature, $R(T)$, at various gate voltages of a 7 UC thick YBCO film are shown in Fig. 1. The sample starts as a superconductor with an onset temperature of about 77 K. Here the onset temperature is taken to be the temperature at which the sheet resistance falls to 90% of its normal value. We realized an insulator with a gate voltage ($V_G$) of only 1.52 V. We noticed that the onset temperature was a nonlinear function of $V_G$. There is a $V_G$ threshold of about 0.3 V below which almost no change can be seen. Then the onset temperature drops by about 30 K as $V$ increases from 0.5 to 1.1 V, which is about 5 K/0.1 V. However, as $V_G$ increases from 1.1 to 1.25 V, a change of 0.2 to 0.3 V can induce an onset temperature shift of about 5 K. This nonlinearity suggests that the gate voltage cannot be used as a tuning parameter for quantitative analysis.

As $V_G$ increases to 1.37 V, the $R(T)$ curves flatten out at the lowest temperature and then undergo a small upturn at $V_G \sim 1.40$ V, although their resistances initially decrease as temperature decreases. Finally, $R(T)$ evolves to an insulating state as $V_G$ increases further, as can be seen clearly in the inset of Fig. 1. Interestingly, we have found that the resistance in the insulating side up to $V_G \sim 1.48$ V is thermally activated with an Arrhenius type relation. Above this voltage the logarithm of sheet resistance is fit by a $T^{-1/3}$ dependence consistent with 2D Mott variable range hopping.

![Figure 1](color online). Logarithm of the sheet resistance vs. temperature with gate voltage varying from 0 to 1.52 V. From bottom to top: 0, 0.3, 0.5, 0.7, 0.8, 0.9, 1, 1.1, 1.12, 1.14, 1.17, 1.20, 1.25, 1.27, 1.30, 1.33, 1.35, 1.37, 1.40, 1.43, 1.44, 1.46, 1.48, 1.50, 1.52 (V). Inset: enlarged low temperature part near the transition between the superconducting and insulating regimes. (From Ref. 11.)

The low temperature upturn is similar to that observed in granular superconductors [15] and will dramatically affect any quantitative scaling analysis. We suggest that this is evidence of a mixed phase separating the superconducting and insulating regimes. Nevertheless, the thickness fluctuations in the
single unit cell active layer could also contribute to this upturn. We also cannot rule out the possibility that we have not completely depleted the superconductivity of the underlayers.

For further quantitative analysis of the data, we require the induced carrier concentration. As discussed above, gate voltage is not simply related to the carrier concentration and the Hall resistance cannot be used because of the complicated electronic properties of YBCO. We assume that Drude behavior is found at high temperatures and take $1/R_s (200 \text{ K})$ to be proportional to the carrier concentration measured as carriers per in-plane Cu atom. Comparing this with the carriers per in-plane Cu atom derived from the phase diagram of bulk YBCO [16], we find that they match with a constant coefficient 0.165 as shown in Ref. 11. This is especially true in the transition regime, which is the focus of quantitative analysis. It is not true for carriers/Cu in excess of 0.10, necessitating reliance on the empirical relationship between $T_c$ and carrier concentration to characterize the higher carrier concentration regime. This will be described in the next section.

Using measured $R(T)$ curves and calculated carrier concentrations, a phase diagram can be constructed and is plotted as Fig. 2. It is similar to the phase diagram of bulk high-$T_c$ cuprates derived from chemical doping. Here it is measured continuously and perhaps more accurately, especially in the transition and insulating regimes. The data plotted here are in the linear regime of the I-V curves. There are nonlinear I-V curves deep in the insulating regime, which are denoted by white in the figure.

When a Quantum Critical Point (QCP) is approached, resistance isotherms as a function of the carrier concentration should cross at the critical resistance $R_c$ and all resistance data should collapse onto a single scaling function. This was done in Ref. 10 in the case of LSCO, neglecting the lowest

![Figure 2](image-url)

**Figure 2.** (color online). Plot of the $R(T)$ and calculated carrier concentration. This figure can be interpreted as a phase diagram. Different colors represent different sheet resistances. The dash line is the onset temperature. The white area in the bottom left-hand corner is a regime with nonlinear I-V curves. (From Ref. 11)

...temperature isotherms. In the present work, the critical resistance per square was about 6.0 kΩ, which is very close to the quantum resistance given by $R_Q = h/4e^2 = 6.45 \text{ kΩ}$ considering that imprecise shadow masks were used to define the four-terminal configuration. It should be noted that in the work
of Ref. 10 on LSCO the critical resistance was found to be the quantum resistance for electron pairs. The critical carrier concentration was $x_c = 0.048$ carriers/Cu, which is close to that derived from the bulk phase diagram (0.05). But this is not surprising given that the bulk phase diagram was used to calibrate the carrier concentration.

As shown in Ref 11, all the sheet resistance data from 6 to 22 K collapsed onto a single function $R_s = R(cf(|x-x_c|/T)^{\nu_z})$ with $\nu_z = 2.2$. Assuming $z = 1$ [17], the value $\nu = 2.2$ is close to that of the universality class of a metal-insulator transition in an anisotropic 2D system (7/3) [18] or that of the quantum percolation model (2.43) [19]. The value of $\nu z = 2.2$ for YBCO is different from $\nu z = 1.5$ found for LSCO [10]. This could be a consequence of the difference in the disorder or the structure of the two systems. Since the transition was initially traversed by the depletion of carriers, one can rule out the possibility that layers underneath the top layer have been rendered conducting upon the application of voltage. However, the scaling of the YBCO data breaks down below 6 K, which is a consequence of the non-monotonic behavior of $R(T)$ at low temperature at gate voltages in the transition region. These results suggest that the transition from superconductor to insulator is indirect and may involve an intermediate phase and possibly multiple quantum critical points.

4. Accessing the overdoped regime

The possibility of accumulating charge carriers by the field effect, involving solid dielectric, to tune an underdoped cuprate into the overdoped regime has hitherto remained elusive. For the 123 family of cuprate compounds, it has been shown that the CuO$_2$ planes are only indirectly affected by the electric field since the injected holes are mainly induced in the CuO$_x$ chains [20]. Moreover, the systematic preparation of YBCO bulk samples by tuning the oxygen stoichiometry in the overdoped region is difficult to achieve and the highest level of over-doping is limited by the oxygen stoichiometric concentration, 0.194 holes/Cu for YBa$_2$Cu$_3$O$_7$ [21].

We have exploited the high local electric fields ($10^9$ V/m) induced by an ionic liquid at the surface of the sample to tune the concentration of holes in the superconducting condensate across the top of the superconducting dome. The experiment reveals that the electrostatic doping of YBCO involves a different doping mechanism, as well as an anomalous normal resistance behavior in the overdoped regime. Surprisingly, we also find that the Hall number measured at 180 K displays a maximum around the optimal doping level that suggests the occurrence of an electronic phase transition separating the underdoped and overdoped regimes.

We monitored the gating process of a 7 unit-cell YBCO film by measuring the sheet resistance as a function of temperature (see Fig. 3). The fresh sample, without any applied gate voltage, has a transition temperature $T_c \sim 42$ K. We determined $T_c$ as the temperature corresponding to the crossing of the extrapolation of the fastest falling part of the $R(T)$ curve to zero resistance. After the application of a negative gate voltage, $T_c$ increases and the normal state sheet resistance (the metallic region of the curve) drops. For higher negative gate voltages, $V_g = -2.24$ to -2.38 V, the rate of change of $T_c$ and the normal resistance slows down and saturates. $T_c$ reaches a maximum value of 67 K and the normal resistance reaches a minimum of 750$\Omega$ at 180 K. We also observed small fluctuations in both $T_c$ and the normal resistance in this regime. As shown in Fig. 3(b), upon a further increase of the negative gate voltage, $T_c$ decreases. In addition, the normal resistance increases with increasing negative gate voltage. For the highest negative gate voltages ($-2.46V < V_g < -2.56$ V) we note that the superconducting transition is not abrupt and a second transition is turned on at the lowest temperature part of the $R(T)$ curve. Next we reversed the polarity of the gating [see Fig. 3(c)], and we observed that after a threshold voltage of about +0.3 V, $T_c$ starts to increase and the normal resistance starts to drop. With further increase in the positive gate voltage, as shown in Fig. 3(d), $T_c$ drops and the normal resistance increases, and the sample returns to its initial state.

In order to obtain an independent variable to describe the process of accumulation or depletion of holes we inferred an effective hole doping ‘‘p’’ by using the universal empirical parabolic relation $T_c/T_{c,\text{max}} = 1-82.6(p - 0.16)^2$ [22], which has been proved to be true for bulk high $T_c$ superconductors.
including 123 compounds [23]. Using this calculated number of holes, the values of $T_c$ and of the normal resistance at 180 K have been plotted as Figs. 2(b) and 2(c) in Ref. 24. Without going into detail we present the conclusions.

The electrostatic doping of YBCO appears to be a two-step process. First carriers are induced only on the CuO$_x$ chains, and second, once a threshold concentration is reached, carriers can be induced on the CuO$_2$ planes. In the second step, the carriers could be indirectly doped on the CuO$_2$ planes through intra-cell charge transfer [20]. This two-step electrostatic doping process appears to be different from that of chemical doping, in which any changes of the hole doping under the superconducting dome will affect the normal resistance and the superconducting properties, simultaneously.

The normal resistance at 180 K exhibits a minimum at the optimal doping point. As stated before this is a surprising behavior since in the overdoped region of the general bulk phase diagram of cuprates, the normal state is a Fermi liquid and a lowering of the normal resistance would be expected as the doping level increases. We have no clear or definitive explanation for the observation of an increasing resistance with increasing doping in the overdoped regime.

To obtain further insight into this behavior we measured the Hall resistance at 180 K at different gate voltages. Figure 4 shows the normalized Hall number ($n_H$) as a function of $V_G$ (a) and effective hole doping (b). The Hall number is calculated using $n_H = I/R_H e$, $R_H$ being the Hall coefficient.
determined from the slope of the linear fit of the Hall resistance vs. magnetic field. Interestingly, we find that the Hall number shows a peak at a doping level of $p \sim 0.15$ holes/Cu ($V_G = -2.24$ V) which does not coincide with the maximum and minimum of $T_c$ and the normal resistance, respectively, ($p = 0.16$ holes/Cu or $V_G = -2.38$ V). Moreover, in between these levels of doping we observe fluctuations in both $T_c$ and the normal resistance.

Experimentally, an anomalous dependence of the normal state Hall coefficient on the doping level has been reported in chemically doped YBCO [25], Bi$_2$Sr$_{1.5}$La$_{0.5}$CuO$_{6+\delta}$ (BSLCO) [26] and LSCO [27]. For YBCO the Hall conductivity at 125 K showed an anomalous behavior around the 60-K phase and in BSLCO and LSCO, the Hall number peaks around the optimal doping level at low temperature when superconductivity is suppressed by an ultra high magnetic field. These anomalous behaviors are commonly interpreted as evidence of an unusual electronic state or a sudden change in the Fermi surface, although chemical doping might also change the magnetic coupling and thus the Hall scattering rate. For electrostatic doping, we do not believe that an electric field would change the magnetic coupling. The $n_H$ peak then suggests that an electronic phase transition is occurring, which is supported by the emergence of fluctuations in $T_c$ and the normal state resistance at this same level of doping.

![Figure 4. Normalized Hall number ($n_H$) vs. gate voltage (a) and effective hole doping (b). (From Ref. 24.)](image)

The peak of the Hall number is found to be at $p \sim 0.15$, to the left of the optimal doping point ($p = 0.16$). For a doping level of $p \sim 0.15$ the value expected for $T^*$, the pseudogap crossover temperature,
roughly matches 180 K [28]. Quantum oscillation experiments [18, 29–31] showed that while there is a large hole-like Fermi surface in the overdoped regime, there are only small pockets in the underdoped regime. Angle Resolved Photoemission Spectroscopy also showed that the transition from the overdoped to the underdoped regime is accompanied by an electronic reconstruction of the Fermi surface [32–36]. Thus an electronic phase transition, which would reconstruct the Fermi surface is expected around the optimal doping regime and could be confirmed by our measurements.

5. The electron doped regime

The electron-doped side of 123 compounds such as YBCO cannot be reached by oxygen manipulation because of the limits of chemical stoichiometry. To our knowledge, the only material reported thus far is lanthanum-doped YBCO, with lanthanum substituted on both the yttrium and barium sites, $Y_{1-z}La_z(Ba_{1-x}La_x)Cu_3O_y$ (YLBCO)[37]. These 123 compounds exhibit ambipolar transport on both the hole- and electron-doped regimes, but superconducting behaviour on the electron-doped side is not found. Extreme hole reduction and subsequent electron accumulation was demonstrated in YBCO films by an electrochemical technique by Nojima et al. [38]. After depleting the holes and driving the film insulating, additional electrons resulted in metallic $n$-type YBCO but with no sign of superconductivity. This work was done using ion-gels consisting of polyethylene oxide and an alkali metal perchlorate.
We have found that after depleting the holes and driving a YBCO film insulating using the ionic liquid DEME-TFSI, further addition of electrons results in metallic behavior and indications of superconductivity. Hall effect measurements suggested that the majority carriers are electrons, implying that electron-doped YBCO may be a superconductor. However the superconductivity weakens with decreasing temperatures and the ground state is apparently an insulator. Because the samples did not exhibit reversible behaviour we cannot rule out the possibility that the observations are not due to electrochemical rather than electrostatic effects.

A nominally 7 unit-cell (UC) thick YBCO film has only 1-2 UCs that are active and without a gate voltage is an underdoped hole superconductor. Its superconductivity can be completely eliminated with a 1.52 V positive gate voltage due to the depletion of holes. In Fig. 5 we plot the differential resistance vs. temperature, at different gate voltages and it is apparent that superconductivity begins to be recovered when $V_G = 1.70$ V. The onset of the transition can be as high as 60 K at the highest gate voltage ($V_G = 2.0$ V). In preparing this plot we used the differential resistance measured in the limit of the lowest current in the regions where the $I-V$ curves were nonlinear. When the $I-V$ curves are linear, the differential resistance determined this way is the same as the sheet resistance measured at constant current. The regime in which local minima in the resistance vs. temperature curves developed will be shown to be dominantly electron doped through the interpretation of Hall effect data.

High temperature $R(T)$ curves exhibit metallic behavior for $V_G > 1.75$ V but do not have a simple $T^x$ power law dependence. We know that in the hole-doped cuprates such as YBCO and LSCO, the high temperature $R(T)$ curves are linear [39] and in electron-doped cuprates such as Nd$_2$Ce$_x$CuO$_4$ (NCCO), the resistance shows a $T^2$ dependence[40]. Our data exhibit a totally different behavior and thus the mechanism of superconductivity might be different in an electrostatically charged system with carriers that are electrons. Another surprising feature is that the $\delta V/\delta I$ increases sharply as the temperature is lowered, resulting in local minima in the $R(T)$ curves.

Since we are applying a positive gate voltage, which causes depletion of holes or accumulation of electrons in the system, the superconducting state at this high gate voltage would be expected to be electron doped. In Fig. 6 we plot the high temperature ($T = 200$ K) Hall resistance vs. magnetic field for different gate voltages. The slope of this curve can be used to determine the Hall coefficient ($R_H$). Although we cannot use the Hall coefficient to calculate the carrier concentration but we can still use it ($1/eR_H$) to estimate the relative changes of the carriers [41] and to determine their sign [42]. The upper panel shows positive Hall coefficients at low gate voltages which are consistent with the fact that the sample starts as a hole-doped superconductor. As the gate voltage increases the Hall coefficient increases thus $1/eR_H$ drops which confirms the depletion of holes. The curve for $V_G = 1.70$ V is very noisy and we cannot determine any slope with gate voltages between $V_G = 1.70$V and 1.90 V.

The next measurable slope is found at $V_G = 1.95$ V and the Hall slope has changed sign, which strongly suggests that the carriers are electrons and that any superconductivity is electron-doped. The other feature is that the Hall coefficients in the lower panel are much larger than the ones in the upper panel. This suggests the carrier concentration on the electron-doped side is much smaller than the one on the hole doped side. It is long believed that the electron-doped superconductors have both electrons and holes as charge carriers [43]. The presence of holes on the electron-doped side can cause the measured net carrier concentration to be much smaller than the actual value of the electron concentration. The reason the regime of the crossover between holes and electrons is noisy is not understood.

The film reported here, before any gating, exhibited an onset temperature for superconductivity of 77 K. The differential resistance in the region of the local minimum dropped at about 50 K by several orders of magnitude from its normal state value and effectively into the noise of the measurement. Except for the reentrence to the insulating state with decreasing temperature, this regime of the phase diagram is very similar to what is found for the superconducting regime on the hole-doped side.
It is important to attempt to explain the reentrant behavior of the resistance as a function of temperature in the electron-doped regime. Along these lines we present a number of possible scenarios. First, local minima in $R(T)$ curves are features usually seen in disordered or granular superconductors as an indication of a local superconducting state[44-46]. Such transitions are often referred to as being “quasi-reentrant” superconducting transitions since the resistance usually fails to fall to zero with decreasing temperature before beginning to increase with decreasing temperature. The film in the electron-doped regime may behave as an intrinsic granular system with superconducting islands connected by superconducting weak links and/or tunneling junctions. The resistance would then drop at the onset temperature due to the formation of superconducting islands. Before the establishment of superconducting coupling through weak links, the resistance would be controlled by quasiparticle tunneling. After the islands form and the temperature is decreased further, the quasiparticle tunneling paths are partially suppressed as the gap opens up and the resistance increases, resulting in a local minimum in the $R(T)$ curve. In configurations in which the superconducting coupling dominates as the temperature is lowered, the superconducting islands will become coherently coupled and a global superconducting state will be achieved. However, a system in which the superconducting channels do not percolate will be an insulator even at $T = 0$.

If the local minima are a consequence of the disorder in the film, the latter must be a very disordered system since the film is insulating at the lowest temperature. In the study by Nojima et al. of electrochemically induced electron-doped YBCO [38], the sample was quite thick (50 nm), and the metallic state also disappeared at low temperatures. It was suggested by these authors that localization effects are more serious on the electron-doped side. The film in the present work has only a 1 to 2 UC thick active layer. Thus it can be viewed as a 2-dimensional (2D) system. Such a 2D system might
suffer more significant localization effects than a thicker film with interlayer coupling. Moreover, the charging process might also introduce disorder, as the layer of induced carriers would sample a random potential due to the ions of the electronic double layer. The presence of disorder may not be the explanation of the reentrant behavior as thin films prepared by high pressure oxygen sputtering are in general expected to be of high quality.

A second possibility is that electrostatically induced electron-doped reentrant superconductivity is mediated by spin fluctuations, but at low temperatures long-range antiferromagnetic (AF) order takes over. When this occurs, the spin fluctuations would then freeze out, suppressing the excitations that mediate the superconductivity. In the phase diagram of typical electron-doped superconductors, the insulating state protrudes into the superconducting regime at low temperature, which is different from what is found in hole-doped systems. This is found in the commonly studied electron-doped cuprate, NCCO, in which the AF state is very robust and persists to a very high doping level [4]. This type of reentrance would be distinct from that found in magnetic superconductors such as ErRh$_4$B$_4$ in that in this case the fluctuations associated with the magnetic order are intimately connected to the superconductivity, whereas they are not in the case of the latter [47].

It is possible that there are electrochemical reactions occurring in the ionic liquid based electrostatic charging process, which drives YBCO into the electron-doped regime. The fact that we could not demonstrate the electron charging process was reversible leaves this as a strong possibility. In the work of Nojima et al., an electrochemical process was proposed [38], in which the reduction of oxygen atoms, first in the CuO$_x$ chains and then in the CuO$_2$ planes, was the main mechanism for hole depletion and electron accumulation. In the present work the gate voltage was changed at 240 K and the device was always kept below this temperature during measurements. At these temperatures conventional electrochemical reactions are largely suppressed. On the other hand, the huge local electric fields in the electronic double layer ($>10^9$ V/m) might also change the valence state of the Cu in the CuO$_2$ planes from Cu$^{2+}$ to Cu$^{3+}$, resulting in electron doped metallic behavior and superconductivity. Although the superconductivity occurs on the CuO$_2$ planes, the interaction between the CuO$_x$ chains and CuO$_2$ planes could be similar to what happens in the YLBLCO system[37]. The possible electrochemical origin of these observations would not detract from the conclusion that electron-doped YBCO has been realized which shows tendencies towards superconductivity.

Finally, one can rule out an artifact that might occur in a four-terminal measurement of resistance that yields zero resistance. This is the possibility that the voltage probes are not sampling a region of the sample where there is a nonzero current density. This might occur if the electrical transport were to occur through the IL rather than through the film. However all of the measurements were obtained at temperatures at which the ionic liquid DEME-TFSI is strongly insulating. As a consequence this is an unlikely occurrence.

6. Summary

A transition from superconducting to insulating behavior has been induced in several ultrathin YBCO films prepared by high pressure oxygen sputtering and modified through electrostatic charging using an EDLT device configuration. A striking feature of the data is the similarity between the phase diagram and the bulk phase diagram. This is surprising given that the active layer in the film is only one to two UCs and that there are high electric fields in the double layer. The transition between superconducting and insulating behavior is not direct and resembles the transition found in granular ultrathin films. It is not known that this is a general result. We have also accumulated holes, changing from the underdoped to the overdoped regime. The results reveal a two-step doping mechanism that may be different from conventional chemical doping. The normal state resistance increased with hole concentration in the overdoped regime, which is different from what is found in bulk systems. There was also a peak in the high temperature (180K) Hall number at $p \sim 0.15$. This suggests that there is an electronic phase transition on the Fermi surface near the optimal doping point. Finally, we have electrostatically depleted the holes in a YBCO film and recovered indications of superconductivity when the majority of the carriers are electrons as determined from the sign of the Hall resistance. The
superconductivity does not persist to the lowest temperatures studied. Thus the ground state in this regime would appear to be insulating. However we were not able to test reversibility in this regime, in contrast with the hole doped regime. Thus it is an open question as to whether the apparent electron doped regime of YBCO realized in these experiments is a consequence of a physical process involving electrostatic charging or is due to chemical reactions at the interface between the ionic liquid and the YBCO film, which is an alternative scenario.

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