Superconductor-to-Insulator Transition and Transport Properties of Underdoped $YBa_2Cu_3O_y$ Crystals

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The *carrier-concentration-driven* superconductor-to-insulator (SI) transition as well as transport properties in underdoped $YBa_2Cu_3O_y$ twinned crystals is studied. The SI transition takes place at $y \simeq 6.3$, carrier concentration $n_H^{\mathrm{SI}} \simeq 3 \times 10^{20}$ cm^{-3}, anisotropy $\rho_c/\rho_{ab} \simeq 10^3$, and the threshold resistivity $\rho_{ab}^{\mathrm{SI}} \sim 0.8$ mΩ cm which corresponds to a critical sheet resistance $\frac{h}{4e^2} \simeq 6.5$ kΩ per CuO_2 bilayer. The evolution of a carrier, $n_H \propto y - 6.2$, is clearly observed in the underdoped region. The resistivity and Hall coefficient abruptly acquire strong temperature dependence at $y \simeq 6.5$ indicating a radical change in the electronic state.

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A high-T_c superconductor (HTS) is obtained by doping a Mott-Hubbard insulator. Recently important progress has been made particularly in the underdoped region. The existence of a pseudogap has been confirmed [1–5] in many cuprates at temperatures far above T_c and it is recognized as a universal property of HTS. Moreover, a lot of attention has been directed towards the physics near the critical doping region which separates HTS from the antiferromagnetic (AF) insulator [6].

The superconductor-to-insulator (SI) transition of high-T_c cuprates has been reported on polycrystals [7], thin films [8,9], and single crystals [10,11]. All these experiments indicate the existence of a threshold resistance which separates superconductors from insulators [12]. Seidler *et al.* [10] reported the *magnetic-field-driven* SI transition of a $YBa_2Cu_3O_{6.38}$ underdoped crystal. They found that the critical sheet resistance of a CuO_2 bilayer is 13.6 k$\Omega \sim \frac{h}{2e^2}$. Fukuzumi *et al.* [11] reported the *disorder-driven* SI transition of underdoped crystals of $YBa_2(Cu_{1-z}Zn_z)_3O_{6.63}$ and $La_{2-x}Sr_xCu_{1-z}Zn_zO_4$ ($x = 0.10, 0.15$). They found that the SI transition occurs at $\rho_0 \simeq 400\ \mu\Omega$ cm which corresponds to a sheet resistance $\rho_0^{\mathrm{2D}} \simeq 6.8$ kΩ per individual CuO_2 plane. As far as our knowledge, there is no report on the *carrier-concentration-driven* SI transition in $YBa_2Cu_3O_y$ crystals. Here we report on that subject as well as the transport properties of underdoped $YBa_2Cu_3O_y$ crystals.

The crystals were grown in a yttria crucible by the Cu-Ba enriched self-flux method [13]. All the crystals used in the experiment were twinned. We controlled doping by annealing the samples in the equilibrium oxygen pressure $P_{O_2}(T, y)$ of $YBa_2Cu_3O_y$ [14]. The sample crystals were annealed for a few days in a temperature controlled quartz tube furnace from 650 °C to the temperature of the P_{O_2} control limit where the oxygen supply and heater power were automatically shut off. Then, the samples were cooled to room temperature over a few hours in pure argon. During the annealing, the microprocessor calculated that $P_{O_2}(T, y)$ was supplied by mass flow controllers as an argon-oxygen mixture. This method controls the oxygen pressure with an accuracy of a few percent and the control limit pressure was around 4 Pa. The annealing time was chosen long enough for oxygen to diffuse over the sample crystals [15]. As a marker of doping, $YBa_2Cu_3O_y$ polycrystals were also annealed with the sample crystals. We assumed the oxygen content of the polycrystals and the sample crystals were equal. The x-ray diffraction (XRD), iodemetry, and weight loss measurements were performed on the polycrystals. As a function of programmed oxygen content y, for both polycrystals and twinned crystals, the XRD showed that the change in the c-axis unit cell dimension agrees well with the neutron diffraction data [16]. The weight loss measurement showed that the accuracy of the nominal oxygen content y is ± 0.01.

The crystals were $2 \times 1 \times 0.03$ mm^3 in size. Good electrical contacts were made by using gold wire and gold paste (TR1301 Tanaka-Matthei) which was cured at 850 °C for 15 min before oxygen controlled annealing. The contact resistance was typically $\sim 1\ \Omega$. We used the conventional six-probe method for the in-plane resistivity and Hall measurements. We attached current leads to the side face of the platelet to ensure homogeneous current flow in the sample. For the out-of-plane resistivity measurement, we used another sample crystal and painted a pair of Corbino-type electrodes. The current electrodes were annular rings painted on the *ab* face. The voltage contacts were spots painted in the center of the rings.

Figure 1 shows the doping dependence of the resistivity of the $YBa_2Cu_3O_y$ crystals. The SI transition takes place near oxygen content $y \simeq 6.3$. The observed in-plane threshold resistivity is $\rho_{ab}^{\mathrm{SI}} \sim 0.8$ mΩ cm, which corresponds to the critical sheet resistance per the CuO_2 bilayer ($\frac{\rho_{ab}^{\mathrm{SI}}}{d} \simeq \frac{h}{4e^2} \simeq 6.5$ kΩ), as indicated by an arrow shown in Fig. 1(a). The obtained ρ_{ab}^{SI} value is twice as large as that observed in the *disorder-driven* SI transition [11]. Here, we use $d = 11.8$ Å, the unit cell dimension in the c direction, as the interbilayer distance assuming that the nearest

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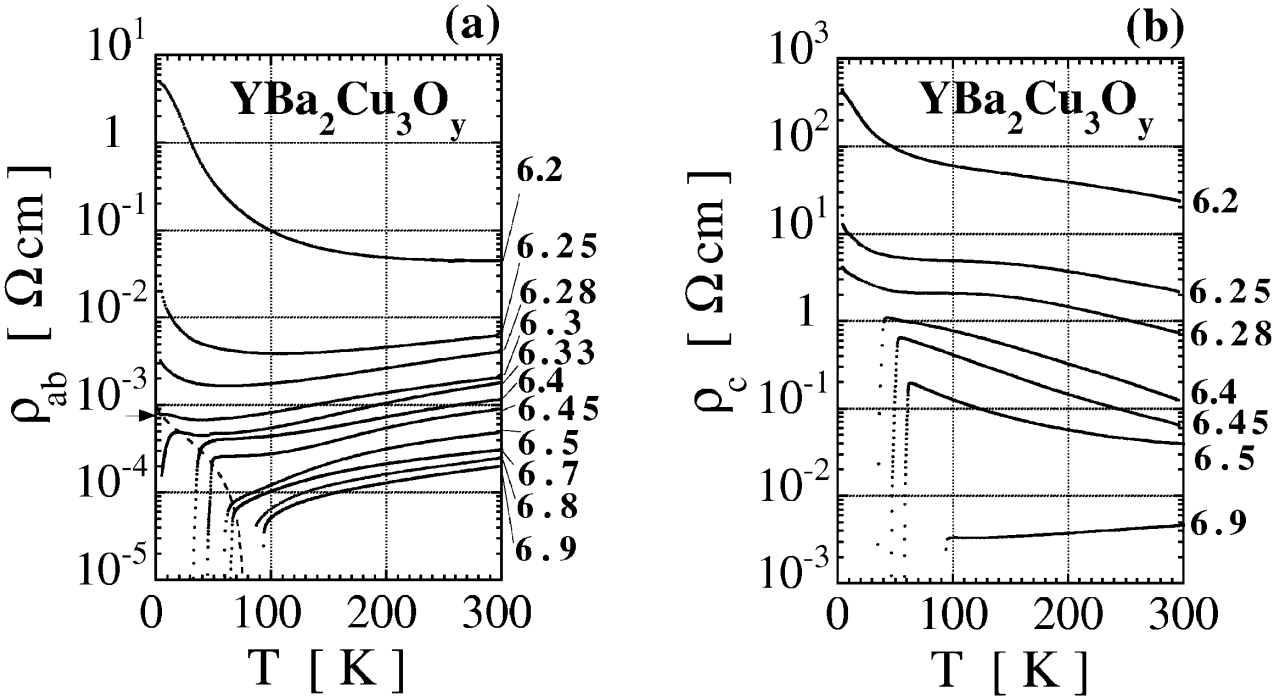

FIG. 1. Temperature dependence of (a) in-plane resistivity, (b) out-of-plane resistivity. The superconductor-insulator transition takes place at $y \simeq 6.3$. The threshold resistivity corresponds to a critical sheet resistance of $\frac{h}{4e^2} \simeq 6.5\ \mathrm{k}\Omega$ per CuO_2 bilayer which is indicated by an arrow in (a). The broken line in (a) is derived from Eq. (1) [24] for $\rho_Q = 1.5\ \mathrm{m}\Omega\,\mathrm{cm}$, $T_\theta^{\max} = 77$ K [25], and $A\hbar\Omega_0 \approx J = 1200$ K. Note that $\rho_{ab}(T)$ of $6.3 < y \leq 6.45$ is quite different from $\rho_{ab}(T)$ of $6.5 \leq y \leq 6.9$. Correspondingly, the Hall number, $n_H(T)$, acquires a strong temperature dependence at $y \simeq 6.5$. The out-of-plane resistivity of $y = 6.9$ is obtained by the Montgomery measurement.

neighbor CuO_2 layers are coherently coupled [17]. Alternatively, if each individual CuO_2 plane is a noninteracting two-dimensional unit, the sheet resistance will be doubled.

On the superconductor side of the SI transition, there is another critical doping level, around $y \simeq 6.5$, which separates $\rho(T)$ in Fig. 1 into two groups. For less doped superconductors ($6.3 \leq y < 6.5$), resistivity tends to saturate at low temperatures and T_c is a sensitive function of doping; $\frac{dT_c}{dy} \simeq 300$ K. The normal state resistivity of these less doped superconductors is similar to resistivity of the insulator samples ($6.25 \leq y < 6.3$) except insulating behavior at lowest observed temperature. In contrast, for more doped superconductors ($6.5 \leq y \leq 6.9$), $\rho(T)$ shows metallic behavior and T_c is less sensitive to doping; $\frac{dT_c}{dy} \simeq 75$ K.

The $6.3 < y < 6.5$ samples are on the border of applicability of the Boltzmann transport theory because the quasiparticle mean free path is considered to be comparable to its de Broglie wavelength; $l \leq \lambda_F = \frac{2\pi}{k_F}$, where k_F is the Fermi wave number and l is the carrier mean free path. Here, we estimated tentative $k_F l$ from the two-dimensional free-electron formula $hd/\rho e^2$, where d is chosen CuO_2 bilayer spacing 11.8 Å. The threshold resistivity ($\rho_{ab}^{\mathrm{SI}} = \frac{hd}{4e^2}$) indicated by an arrow in Fig. 1 corresponds to $k_F l = 4$.

As shown in Fig. 2, for the $y = 6.28$ sample which is just on the insulator side of the transition, both the in-plane resistivity ρ_{ab} and out-of-plane resistivity ρ_c diverge logarithmically down to 4.2 K, while the anisotropy (ρ_c/ρ_{ab}) remains nearly constant below 100 K (Fig. 3). This behavior is similar to that of the anomalous insulator of underdoped $La_{2-x}Sr_xCuO_4$ under a strong magnetic field [19]. One possible interpretation of this insulating behavior is

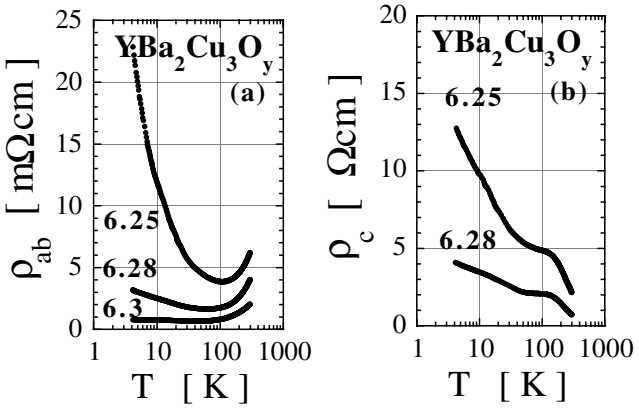

FIG. 2. In-plane (a) and out-of-plane (b) resistivity of $y \leq 6.3$ samples. For the $y = 6.28$ sample which is just on the insulator side of the SI transition, both in-plane resistivity ρ_{ab} and out-of-plane resistivity ρ_c are found to diverge logarithmically as $T \to 0$, while the anisotropy ratio remains nearly constant. Note the close resemblance to the insulating behavior of underdoped $La_{2-x}Sr_xCuO_4$ under a strong magnetic field [19].

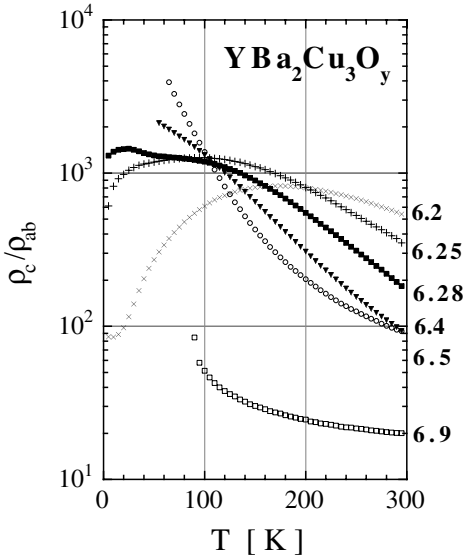

FIG. 3. Anisotropy ρ_c/ρ_{ab} of a $YBa_2Cu_3O_y$ crystal. ρ_c/ρ_{ab} is calculated for different crystals but for the same oxygen content shown in Fig. 1. Note that the temperature dependence changes at the SI transition ($y \simeq 6.3$).

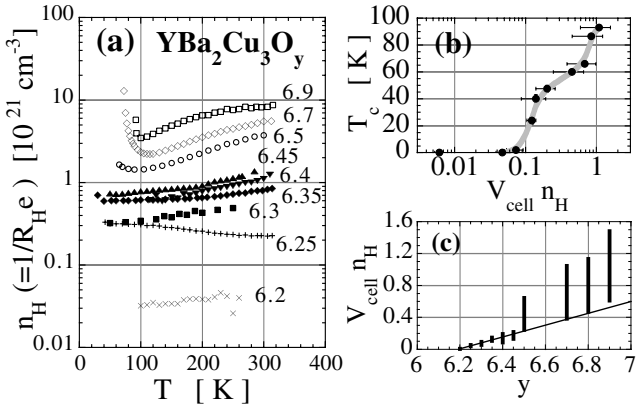

FIG. 4. (a) The temperature dependence of the Hall number ($n_H = 1/R_H e$) of a $YBa_2Cu_3O_y$ crystal. (b) Superconducting critical temperature as a function of the Hall number in a unit cell. (c) Hall number in a unit cell ($V_{\rm cell} n_H$) vs oxygen composition y. The evolution of carrier $V_{\rm cell} n_H \propto y - 6.2$ is clearly observed in the underdoped region ($y < 6.5$). The solid line is a guide for the eyes. The variation in n_H with temperature ($T_c < T < 300$ K) is shown by an error bar. Note that n_H abruptly acquires a strong temperature dependence at $y \simeq 6.5$ which corresponds to the change of $\rho_{ab}(T)$ and the Hall angle. The critical carrier density of the SI transition ($y = 6.3$) is $n_H \simeq 3 \times 10^{20}$ cm^{-3} corresponding to $V_{\rm cell} n_H \simeq 0.05$.

the localization of Cooper pairs, which will be mentioned in the last part of this Letter.

The temperature dependence of the anisotropy also changes at the SI transition. Figure 3 shows the anisotropy ρ_c/ρ_{ab} which is calculated from the resistivity in Fig. 1. As long as the ground state is a superconductor ($y > 6.3$), the normal state resistivity is metallic in plane, semiconducting out of plane, and the anisotropy (ρ_c/ρ_{ab}) increases monotonically with decreasing temperature. In contrast, when the ground state is an insulator ($y < 6.3$), the anisotropy does not show monotonous temperature dependence. It saturates at around 100 K, and decreases at lower temperatures. The saturation temperature increases as doping is reduced.

Hall measurements were performed with a sample inside a superconducting magnet with a maximum field B of 7 T. To obtain reliable Hall signals, B was fixed at 0, 7, and -7 K, and the nanovoltmeter (Keithley 2002) output was averaged. We estimated that the smallest detectable R_H value is $\pm 2 \times 10^{-10}$ m^3/C. Figure 4(a) shows the Hall number $n_H = 1/(R_H e)$ of an $YBa_2Cu_3O_y$ crystal. Below 300 K, there are three types of temperature dependence. (i) $y \geq 6.5$ (open symbols): n_H decreases as the temperature is decreased and reaches a minimum at $T \sim 100$ K before diverging toward T_c. (ii) $6.3 \leq y < 6.5$ (filled symbols): n_H is only weakly temperature dependent. We observed no divergent behavior. (iii) $y < 6.3$ (crossed symbols): we observed $\frac{dn_H}{dT} < 0$ for $y = 6.25$ sample. The n_H of $y = 6.3$ and 6.25 converge at low temperature. So, we can uniquely determine the critical carrier density of the SI transition as $n_H^{\rm SI} \simeq 3 \times 10^{20}$ cm^{-3}. Figure 4(b) shows T_c as a function of carrier concentration. T_c develops rather sharply at $V_{\rm cell} n_H \simeq 0.15$. There is a steplike structure centered at $V_{\rm cell} n_H \simeq 0.4$. Besides the charge reservoir effect of the CuO chain layer, we consider that the suppression of T_c at a carrier concentration of $1/8$ per CuO_2 may also work in $YBa_2Cu_3O_y$ [20]. In Fig. 4(c), we plotted the Hall numbers, n_H, as a function of oxygen content y. Bars indicate its variation over the temperature range $T_c < T < 300$ K. As is clearly seen, the $V_{\rm cell} n_H \propto y - 6.2$ relation is observed for $y < 6.5$. Note that not all the doped carrier ($y - 6.0$) contributes to the transport carrier. This indicates that a certain amount of holes is localized or does not contribute to the Hall signal, though they contribute to destroy AF long range order of the mother insulator. One possible scenario is the microsegregation, i.e., a formation of the spin stripes and the charge stripes as a result of hole doping. In underdoped $La_{2-x}Sr_xCuO_4$, there is a region where the Hall number below room temperature is well described as $n_H \propto x$ [7]. Here, we observed a similar region in $YBa_2Cu_3O_y$, for $y < 6.5$, where the temperature dependence of the Hall coefficient is practically negligible. Above $y \simeq 6.5$, n_H suddenly acquires a strong temperature dependence. The empirical relation of the Hall angle $\cot\theta_H = \alpha T^2 + C$ [21,22] is maintained in this region, $y \geq 6.5$, but it is violated in the slightly doped region $y < 6.5$ as shown in Fig. 5. As far as our knowledge, this kind of doping dependence is not expected in the existing theories.

Next we consider the changes in the temperature dependence of the resistivity and Hall number. Around $y = 6.5$, there should be a radical change in the electronic state. We consider that the effect of the CuO chain is negligible at

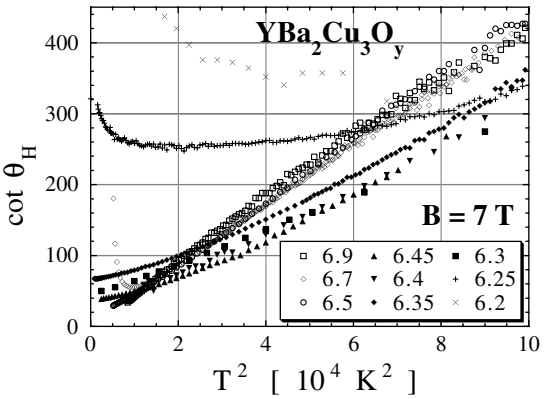

FIG. 5. Temperature dependence of $\cot\theta_H = \frac{1}{B\mu_H}$ of a $YBa_2Cu_3O_y$ crystal. The same symbols are used as in Fig. 4(a). The empirical relation $\cot\theta_H = \alpha T^2 + C$ [21,22] is maintained for $y \geq 6.5$. It is violated in the slightly doped region $6.2 \leq y < 6.5$.

least at around $y \simeq 6.5$ and the above observations reflect the physics in the CuO_2 plane.

One promising model is the theory of "bad metals" proposed by Emery and Kivelson (EK) [23,24], because HTS is a doped insulator with a very low superfluid density. According to EK, a bad metal behaves as if it is a quasiparticle insulator which is rendered metallic by collective fluctuations, moreover, the quantum phase fluctuation of the superconducting order parameter depresses the transition temperature T_c well below its mean field value:

$$\rho(T_c) = \rho_Q \frac{\ln\frac{AV_0}{k_B T_c}}{\ln\frac{A\hbar\Omega_0}{k_B T_c}}, \qquad (1)$$

where $\frac{AV_0}{k_B} = T_\theta^{\max}$ is the classical phase ordering temperature and Ω_0 is the bare cutoff frequency. We set $A\hbar\Omega_0 \approx J = 1200$ K as the antiferromagnetic exchange energy in $YBa_2Cu_3O_y$ [24]. The broken line in Fig. 1(a) is derived from Eq. (1) with $\rho_Q = 1.5$ mΩ cm and $T_\theta^{\max} = 77$ K [25]. The rather good fit with reasonable parameters indicates the quantum phase fluctuation plays a significant role in the slightly doped region.

The sudden change in the transport properties, especially in the Hall signal, around $y \simeq 6.5$ can be corresponded to a crossover from essentially a temperature independent *quantum phase fluctuation* region to a temperature dependent *classical phase fluctuation* region [23,24] or alternatively, the crossover of the major carrier from the local superconducting fluctuation to the quasiparticles.

We are indebted to H. Appelboom for information about the P_{O_2} of $YBa_2Cu_3O_y$ [14]. K. S. thanks M. Naito, H. Shibata, and S. Sasaki for stimulating discussions.

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[25] In fact, $T_\theta^{\max} \simeq \frac{\hbar^2 n_s(0) d}{4m^*}$ [23], $n_s(0)$ is the superfluid density at zero temperature, m^* is the effective mass of a quasiparticle, and d is the interplane distance. Since the exact $\frac{n_s}{m^*}$ value of a sample is unknown, we tentatively assume that the $T_\theta^{\max}$ values of slightly doped samples ($6.3 \leq y < 6.5$) are approximately the same.