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Transformation of in-plane $\rho(T)$ in $YBa_2Cu_3O_{7-\delta}$ at fixed oxygen content

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This paper reveals the origin of a variation in magnitude and temperature dependence of the normal-state resistivity frequently observed in different $YBa_2Cu_3O_{7-\delta}$ (YBCO) single-crystal or thin-film samples with the same T_c. We investigated temperature dependence of resistivity in $YBa_2Cu_3O_{7-\delta}$ thin films with $7-\delta$ between 6.80 and 6.95, which were subjected to annealing in argon at 400–420 K (120–140 °C) or aging at room temperature in air. Before annealing (or aging) these films exhibited a nonlinear $\rho_{ab}(T)$, with a flattening [superlinear $\rho_{ab}(T)$] below 220–230 K, similar to $\rho_b(T)$ and $\rho_{ab}(T)$ observed in untwinned and twinned YBCO crystals, respectively. For all films the annealing causes an increase of resistivity and a transformation of $\rho_{ab}(T)$ from a nonlinear (superlinear) dependence towards a more linear one (less flattening). For films annealed in argon with $7-\delta=6.90$ the increase of resistivity is also associated with an increase in T_c. We proposed a model that provides an explanation of these phenomena in terms of thermally activated redistribution of residual O(5) oxygens in the chain layer of YBCO. A good agreement between the experimental data for $\rho_{ab}(t,T)$, where t is the annealing time, and numerical calculations was obtained.

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I. INTRODUCTION

Right after the discovery of high-temperature superconductivity (HTSC), it was observed that temperature dependence of the normal-state resistivity $\rho(T)$ is linear in many samples over a wide range of temperatures. Phillips[1] explained this result (believed to be universal for all optimally doped HTSC) using two-carrier percolation model. Later, the observation of a linear $\rho(T)$ was also used to support the argument that non-Fermi liquid states are responsible for the normal-state properties of HTSC.[2]

The analysis of the experimental data for $\rho(T)$ obtained on untwinned and twinned $YBa_2Cu_3O_{7-\delta}$ (YBCO) single crystals and YBCO thin films revealed however that the pure linear temperature dependence of resistivity is not a characteristic feature of $\rho(T)$ in HTSC. In fact, it has been found that $\rho_b(T)$ measured along the chain direction in untwinned crystals of YBCO (Refs. 3–6) exhibits a nonlinear behavior with a flattening (superlinear behavior) at temperatures below 220 K [see Fig. 1(a)]. On the other hand, $\rho_a(T)$ measured in a direction perpendicular to the chains increases linearly with an increasing temperature over a wide temperature range. The magnitude of $\rho_a(T)$ is about 2–2.5 times larger than that of $\rho_b(T)$ at the corresponding temperatures. An exception is the result of Welp *et al.*,[7] who observed a linear temperature dependence of both ρ_a and ρ_b. However, the absolute values of these resistivities are about two times higher than those reported elsewhere for untwinned YBCO crystals.[3–6]

The in-plane resistivity $\rho_{ab}(T)$ measured in twinned YBCO crystals with $T_c=93$ K, $\Delta T_c=0.2$ K, and low resistivity $\rho_{ab}(300\text{ K})=130\ \mu\Omega\text{ cm}$[8] displays a nonlinear temperature dependence similar to that observed in many untwinned YBCO crystals along the chain direction [see Fig. 1(b)]. Surprisingly, other YBCO twinned crystals with the same T_c and ΔT_c and higher room-temperature resistivity $\rho_{ab}(300\text{ K})=160\ \mu\Omega\text{ cm}$[8] are characterized by ρ_{ab} with a linear dependence on temperature [Fig. 1(b)]. This value of resistivity is close to that of a nonlinear $\rho_b(T)$ measured at 300 K along the chain direction in some untwinned YBCO crystals.[6]

Temperature dependence of ρ_{ab} measured in c-axis oriented epitaxial YBCO thin films shows features similar to those observed in twinned YBCO crystals.[9,10] Optimally doped films with resistivity as low as 150 $\mu\Omega$ cm at 300 K have a nonlinear $\rho_{ab}(T)$ with a flattening at temperatures below 230 K (Ref. 9) (see Fig. 2). However, it appears that the linear temperature dependence of $\rho_{ab}(T)$ characterizes films with higher resistivity (above $\approx 250\ \mu\Omega$ cm at 300 K). Underdoped films with $T_c\simeq 84$–85 K exhibit $\rho_{ab}(T)$ similar to that observed in optimally doped films[10] (see Fig. 2).

Two different theoretical approaches were used so far to explain the observed nonlinear $\rho(T)$. The first one is based on the classical electron-phonon Bloch-Grüneisen (BG) theory of metallic conductivity.[9] It predicts a nonlinear $\rho(T)$ for temperatures less than the characteristic temperature $T^*=\eta\Theta_D$ (where Θ_D is the Debye temperature and $\eta\sim 1-2$), and a linear $\rho(T)$ for temperatures above T^*. The other theoretical approach employs the thermal Frenkel disorder of long-range-ordered chains of oxygen, a process during which an oxygen atom jumps from its O(1) chain site to a nearby O(5) interstitial (interchain) vacant site.[11]

Poppe *et al.*[9] attempted to explain the nonlinear $\rho(T)$ observed in YBCO thin films by assuming that the resistivity is the sum of the temperature independent residual resistivity ρ_r due to impurities or defects, and the Bloch-Grüneisen resistivity $\rho_{BG}(T)$. They found that BG theory can be applied only if one assumes very high values of Debye temperature between 650 and 950 K. Martin *et al.*[12] were able to obtain good theoretical fits to a nonlinear $\rho(T)$ measured in YBCO(124) films at temperatures up to 600 K, using the BG theory and an effective transport Debye temperature $\Theta_D^*=(2k_F/G)\eta\Theta_D$ of 500 K. They argued that Θ_D^* can be substantially smaller than $T^*=\eta\Theta_D$ if the Fermi vector k_F is

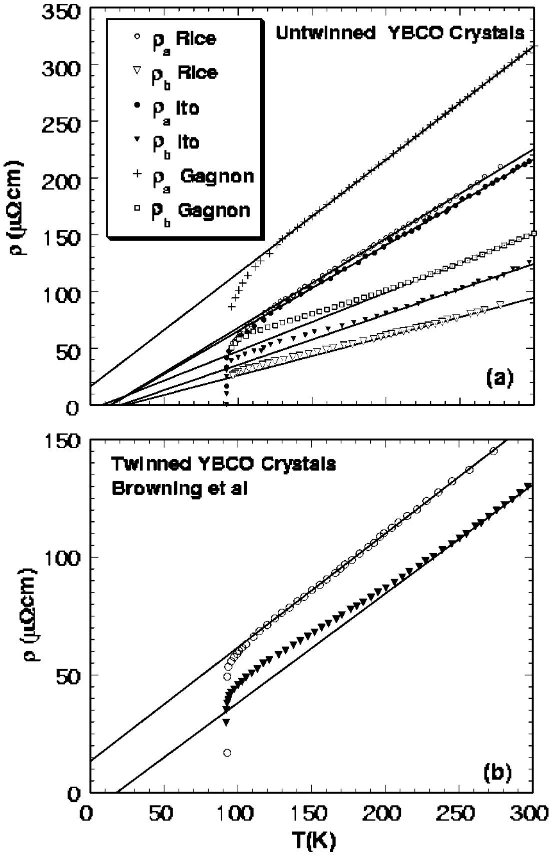

FIG. 1. (a) Temperature dependence of resistivities $\rho_b(T)$ and $\rho_a(T)$ measured in untwinned YBCO crystals along the chain direction (b direction) and along the a direction perpendicular to the chains, respectively. Note the flattening of $\rho_b(T)$ below 220 K and the linearity of $\rho_a(T)$ over a wide range of temperatures for all three samples (Refs. 4–6). (b) Temperature dependence of the in-plane resistivity $\rho_{ab}(T)$ for twinned YBCO crystals. Note that in this case $\rho_{ab}(T)$ exhibits either a nonlinear temperature dependence (with flattening) below 220 K or a linear dependence in the sample with higher resistivity (Ref. 8).

sufficiently smaller than the reciprocal-lattice vector G.

Goldschmidt *et al.*[11] interpreted the nonlinear temperature dependence of resistivity in fully oxygenated polycrystalline YBCO in terms of a thermally activated process of Frenkel pair formation, during which a chain oxygen jumps from an O(1) site to a nearby O(5) site. According to Goldschmidt *et al.* this process accounts for an excess electron scattering with an increasing temperature. Each Frenkel pair creates an intrinsic defect resistivity ρ_d which represents an excess resistivity connected in series to the perfect chain resistivity. The upturn in resistivity that occurs at temperatures above 200 K, is explained as being due to an increase of Frenkel pair density with an increasing temperature. The excess resistivity is defined as $\rho_{excess}=\rho_{chain}-(\rho_o+aT)=\rho_d C_d(T)$, where $C_d(T)$ is the temperature-dependent fractional defect pair occupancy. Temperature dependence of C_d was taken as $C_d\simeq\exp(-E_d/kT)$ which corresponds to that for a two-level system with the energy barrier E_d between the final O(5) and the initial O(1) oxygen sites. Consequently $\rho_{excess}\simeq\rho_d\exp(-E_d/kT)$. Goldschmidt *et al.* obtained a good fit to $\rho(T)$ data measured for a granular YBCO taking the activation energy $E_d\simeq 120$ meV and defect resistivity $\rho_d\simeq 2$ mΩ cm. Measurements performed on untwinned YBCO crystals by Gagnon *et al.*[6] revealed however that the temperature dependence of the excess resistivity above 300 K is linear and not at all exponential.

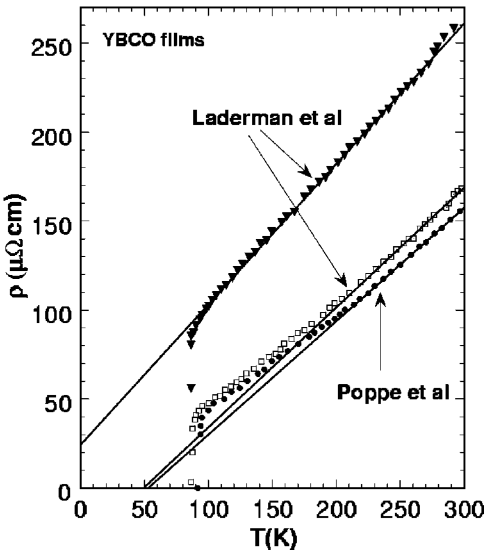

FIG. 2. Temperature dependence of the in-plane resistivity ρ_{ab} measured in c-axis oriented epitaxial YBCO thin films. The data indicate that films with low resistivity exhibit a deviation from the linear temperature dependence at temperatures below ≈230 K (Refs. 9,10).

The experimental results obtained on untwinned and twinned YBCO crystals and YBCO thin films could be summarized as follows: Although $\rho(T)$ for many untwinned crystals shows a nonlinear $\rho_b(T)$ and a linear $\rho_a(T)$, with the magnitude of $\rho_a(T)$ being higher than that of $\rho_b(T)$, these two forms of $\rho(T)$ have also been randomly observed in twinned YBCO crystals and thin films. Surprisingly, the absolute values of resistivity of twinned YBCO crystals and films are often lower than those measured in some untwinned YBCO crystals along the b direction. Also, there is some correlation between the magnitude of resistivity and the specific form of $\rho(T)$ (nonlinear or linear) in twinned YBCO crystals and in YBCO films. In these cases the resistivities of a linear $\rho(T)$ are in general higher than the corresponding ones for a nonlinear $\rho(T)$. In untwinned YBCO crystals, a nonlinear and a linear $\rho(T)$ has been attributed to the chain and plane conductivities, respectively.[6] Therefore, the random appearance of a nonlinear and a linear $\rho(T)$ in twinned YBCO crystals or films of similar T_c is surprising and should be investigated.

This paper provides alternative explanation of the presence of a nonlinear (superlinear) and a linear dependence of resistivity ρ_{ab} on temperature in YBCO. Our studies were focused on YBCO c-axis oriented thin films, both optimally doped ($7-\delta\simeq 6.95$, $T_c\simeq 90$–91 K) and underdoped ($7-\delta\simeq 6.80$–6.90, $T_c\simeq 81$–85 K), with a nonlinear $\rho_{ab}(T)$. We investigated the effect of oxygen ordering (redistribution) on $\rho_{ab}(T)$ in those films. The applied experimental procedure included a systematic annealing of the samples in argon at

400–420 K (120–140 °C) or a long-time aging at room temperature in air, followed by the measurements of $\rho_{ab}(T)$ at temperatures between T_c and 300 K.

The results revealed a transformation of $\rho_{ab}(T)$ from a nonlinear temperature dependence towards a more linear one (less flattening). This transformation is accompanied by an increase in the absolute value of resistivity. In underdoped samples, annealing causes also a small increase in T_c. We present a possible explanation of this phenomenon, which is based on thermally activated redistribution of oxygen in the chain layer of YBCO.

II. EXPERIMENTAL PROCEDURE

We investigated *c*-axis oriented YBCO thin films, which were deposited on different substrates: $SrTiO_3$, $LaAlO_3$, and sapphire (with a CeO_2 buffer layer) using the standard off-axis rf magnetron and laser ablation techniques. The standard photolithography was used to produce 60-μm wide and 6.4-mm long thin-film bridges with four measurement probes. The distance between the voltage probes was 0.4 mm. Silver contacts were sputter deposited using rf-magnetron technique. The samples (films 11–13) were annealed in argon at temperatures 120–140 °C several times for a total time between 8 and 24 h. The measurements of $\rho_{ab}(T)$ (in the a-b planes of the films) at temperatures between T_c and 300 K were conducted after each 2–5 h annealing period. During these measurements a dc current of 5–10 μA was applied to the sample in the form of short pulses (of a duration less than 200 ms) in order to reduce Joule's heating. The current was applied in two opposite directions in order to eliminate the effects of thermal emf in the leads. The voltage was measured using a Keithley 2182 nanovoltmeter connected to a Keithley 236 current source, with the nanovoltmeter working as a triggering unit for the current source. The nanovoltmeter operated in a "Δ" mode, which allows one to perform very fast multiple measurements of the voltage from two voltage measurements for two opposite directions of the current. Temperature was monitored by a carbon-glass thermometer and stabilized (using an inductance-less heater and a temperature controller) within ± 10 mK.

In addition, we performed measurements of resistivity versus temperature on underdoped YBCO sample (film 4) which was subject to a long-time aging (742 days) in air at room temperature.

Oxygen content was determined from x-ray-diffraction measurements of the *c*-axis lattice parameters before aging or annealing for underdoped films 4 and 12. These parameters are 11.70 Å and 11.67 Å which correspond to an oxygen content of 6.8 and 6.9 for films 4 and 12, respectively.[13]

III. EXPERIMENTAL RESULTS

Temperature dependence of resistivity $\rho_{ab}(T)$ measured for slightly underdoped YBCO films with $T_c(R=0) = 85$–86 K is shown in Figs. 3(a) and 4(a) as a function of annealing time in argon at 120–140 °C. $\rho_{ab}(T)$ for unannealed samples exhibits a flattening [superlinear behavior: an upward deviation from a linear temperature dependence; see straight solid line in Figs. 3(a) and 4(a)] at temperatures between T_c and $\approx$220–230 K. The annealing causes a small increase in T_c [see Figs. 3(b) and 4(b)], an increase in resistivity, and a transformation of the temperature dependence of resistivity from a nonlinear behavior to a linear one. The increase in T_c depends on the sample, i.e., it is about 1 K after 8-h annealing at 120 °C for film 12, but only 0.5 K after 24-h annealing at 140 °C for film 13. Temperature dependence of resistivity $\rho_{ab}(T)$ measured for optimally doped YBCO film with $T_c(R=0)$ about 90 K is shown in Fig. 5(a) as a function of annealing time in argon at 120 °C. Annealing of this sample leads to an increase in the magnitude of $\rho_{ab}(T)$ and a reduction of the flattening between T_c and 230–240 K. However, no change of T_c was observed in this case [see Fig. 5(b)]. Temperature dependence of $\rho_{ab}(T)$ at temperatures above $\approx$220 K is linear (see solid lines in Figs. 4 and 5). A deviation from the linear dependence at temperatures below 220 K is shown in Fig. 6 as a function of tem-

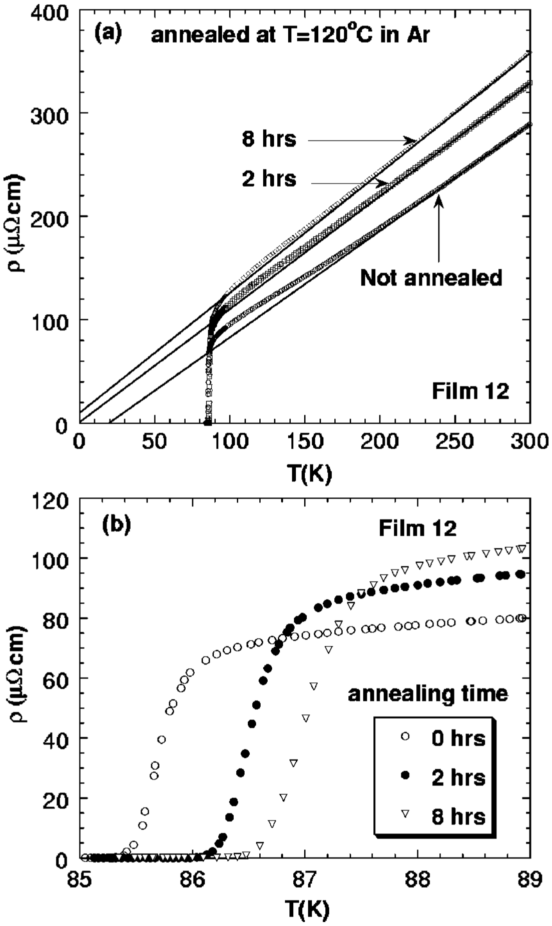

FIG. 3. (a) Temperature dependence of the in-plane resistivity ρ_{ab} measured in the *c*-axis oriented slightly underdoped YBCO thin film 12 with $T_c = 85.4$ K, before and after annealing for 2 and 8 h in argon at 120 °C. Note a systematic increase in resistivity and a reduction of a deviation from a linear temperature dependence of ρ_{ab} with an increasing annealing time. (b) Temperature dependence of resistivity close to T_c measured before and after annealings. Note a small systematic increase in T_c with an increasing annealing time.

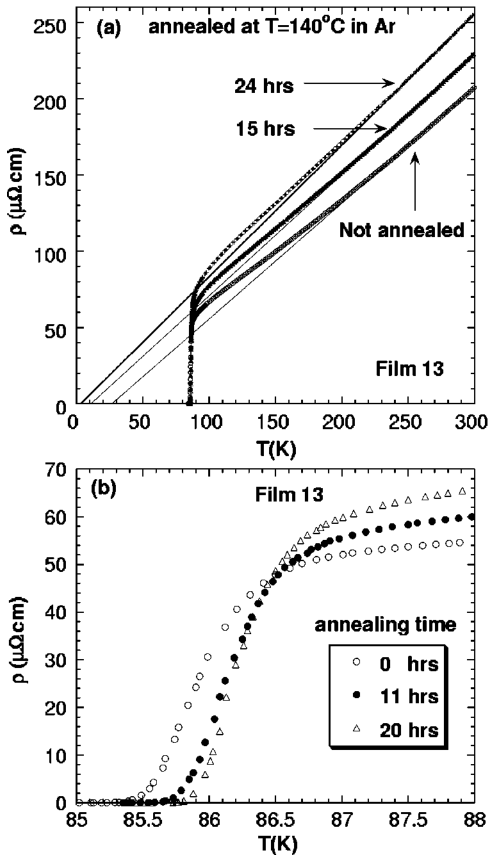

FIG. 4. (a) Temperature dependence of the in-plane resistivity ρ_{ab} measured in the c-axis oriented slightly underdoped YBCO thin film 13 with $T_c = 85.4$ K before and after annealing for 15 and 20 h in argon at 140 °C. Note a systematic increase in resistivity and a reduction of a deviation from a linear temperature dependence with an increasing annealing time. (b) Temperature dependence of resistivity close to T_c before and after annealings. Note a small systematic increase in T_c with an increasing annealing time.

perature for different annealing times. Deviation is defined as $[\rho_{ab}(T) - \rho_{linear}(T)]/\rho_{ab}(T_1)$, where T_1 is the temperature at which a maximum upward deviation of $\rho_{ab}(T)$ from $\rho_{linear}(T)$ occurs. This deviation initially decreases with an increasing annealing time, however it reaches saturation at longer annealing times. The magnitude of resistivity $\rho_{ab}(T)$ for all samples studied was found to increase gradually with an annealing time [see Figs. 4– 6].

Figure 7 shows a transformation of the temperature dependence of resistivity from a superlinear to a perfectly linear one for film 4 with $T_c = 81$ K due to long-time aging at room temperature in air for 742 days. After aging, the resistivity of this sample at 300 K increased 2.5 times but the corresponding increase in T_c was only about 0.1 K.

IV. DISCUSSION

According to Jorgensen, annealing of YBCO at 120–140 °C causes redistribution of oxygen in the chain layer, without any change in the overall concentration of oxygen in the sample.[14] Low-temperature annealing was performed previously by Jorgensen *et al.*[15] and Shaked *et al.*[16]

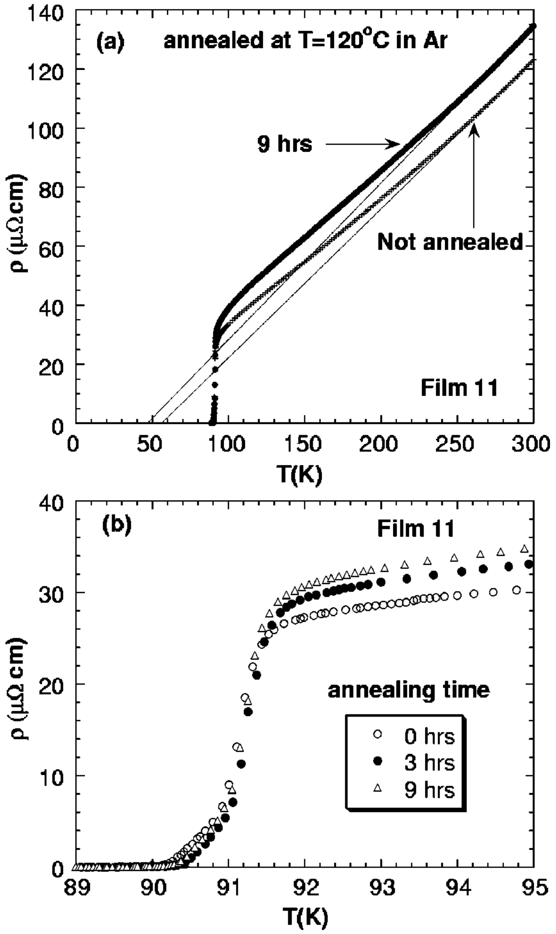

FIG. 5. (a) Temperature dependence of the in-plane resistivity ρ_{ab} measured in the c-axis oriented optimally doped YBCO thin film 11 with $T_c = 90.4$ K before and after annealing for 9 h in argon at 120 °C. The resistivity increases with an increasing annealing time. Deviation from a linear temperature dependence at temperatures below 230–240 K decreases with an increasing annealing time (see Fig. 6 for more details). (b) Dependence of resistivity on temperature close to T_c measured before and after annealing. T_c was found to be independent of the annealing time.

They carried out room-temperature annealing of sintered samples of underdoped YBCO (with $7-\delta = 6.41$ and 6.25) which were quenched first from a temperature of 100–150 °C down to a liquid-helium temperature. Room-temperature annealing led to a dramatic change of the transport and structural properties of this compound, i.e, an increase in T_c and a decrease in lattice parameters with annealing time. This behavior was explained in terms of a local ordering of oxygen atoms at room temperature, which causes formation of oxygen supercells (alternating partial and full chains) in the chain layer. Veal *et al.*[17] reported observation of a time-dependent behavior at room temperature in the superconducting and structural properties of $YBa_2Cu_3O_x$ single crystals, with stoichiometries controlled within the range $6.3 < x < 6.6$ by quenching the samples from 520 °C down to a liquid-nitrogen temperature. They proposed two explanations of this behavior. One interpretation was that oxygens, quenched into O(5) sites, move to neigh-

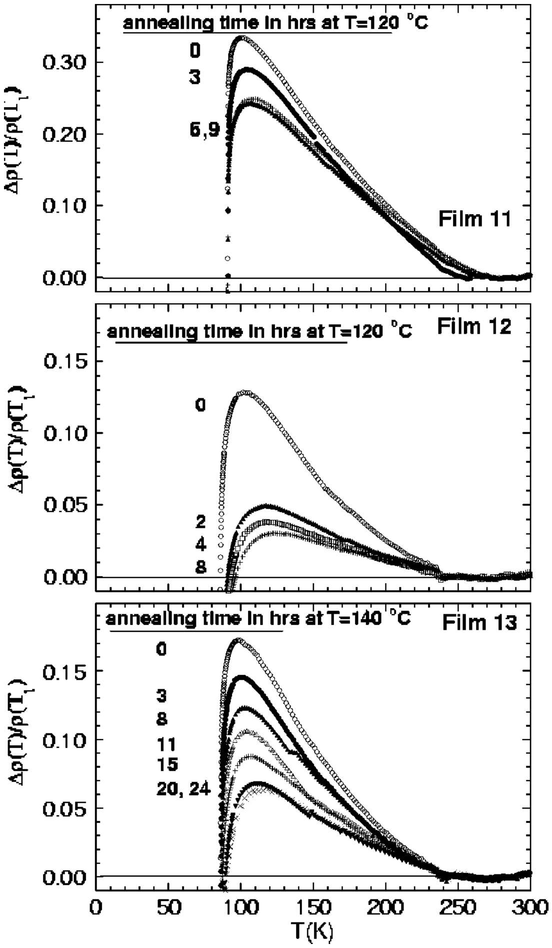

FIG. 6. Upward deviation of $\rho_{ab}(T)$ (measured for films 11, 12, and 13) from the linear temperature dependence of resistivity $\rho(T)$, defined as $\Delta\rho(T)/\rho(T_1)=[\rho_{ab}(T)-\rho(T)]/\rho_{ab}(T_1)$, where T_1 is the temperature at which the maximum upward deviation of $\rho_{ab}(T)$ from a linear $\rho(T)$ occurs. Note the saturation of $\Delta\rho(T)/\rho(T_1)$ after annealing times of 6 h for film 11, and 20 h for film 13, respectively.

boring O(1) chain sites thus enhancing the order in the O(5) oxygen vacancy array in the chain layer. The other one suggested that the ordering associated with a low-temperature annealing likely involves formation of alternating full and empty (oxygen-free) chains in the chain layer. Andersen *et al.*[18] investigated ordering kinetics of ortho-superstructures in the chain layers of YBCO single crystals as a function of temperature up to about 150 °C and an oxygen doping level over a range between 6.3 and 6.8. They provided a structural phase diagram of the superstructure ordering in YBCO (see Fig. 5 in Ref. 18). According to this diagram, our samples with an oxygen content of about 6.90 and 6.95 should have the ortho-I structure with no sign of a superstructure formation between room temperature and 150 °C.

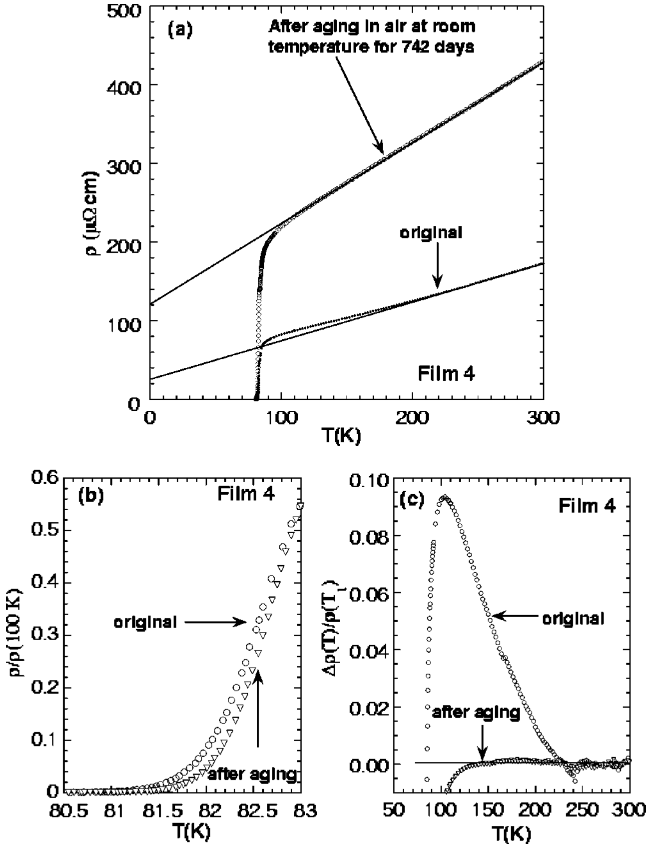

FIG. 7. (a) Temperature dependence of the in-plane resistivity ρ_{ab} measured in the *c*-axis oriented underdoped YBCO thin film 4 with $T_c=81$ K before and after aging for 742 days in air. Note the transformation of $\rho_{ab}(T)$ from a superlinear to a perfect linear temperature dependence after aging. (b) Temperature dependence of resistivity close to T_c before and after aging. (c) Upward deviation of $\rho_{ab}(T)$ from a linear temperature dependence of resistivity $\rho(T)$, defined as $\Delta\rho(T)/\rho(T_1)=[\rho_{ab}(T)-\rho(T)]/\rho_{ab}(T_1)$, where T_1 is the temperature at which the maximum upward deviation of $\rho_{ab}(T)$ from a linear $\rho(T)$ occurs. Note that $\Delta\rho(T)/\rho(T_1)$ is independent of temperature after aging, which indicates a perfect linear behavior.

The data presented in Figs. 3 and 4 for underdoped films 12 and 13 with $T_c(R=0)\simeq 85.4$ K show an increase of resistivity and T_c with an increasing annealing time in argon. This behavior may appear to be similar to that of an overdoped sample whose oxygen content is decreasing during annealing in argon. There are several arguments against this interpretation. The lowest T_c reported for an overdoped $YBa_2Cu_3O_7$ is not less than 89–90 K (Refs. 19,20) (which is about 3 K less than that of an optimally doped YBCO with $T_c=92$–93 K). This includes recent measurements on an overdoped YBCO single crystal of $7-\delta=6.99$ by Sutherland *et al.*[21] Film 12 with $T_c\simeq 85.4$ K has an oxygen content of 6.9, corresponding to a *c*-axis lattice constant of 11.67 before the first annealing and therefore cannot be considered overdoped. Furthermore, in order to strengthen this argument we measured $\rho_{ab}(T)$ for an additional YBCO thin film 4 with $T_c=81$ K (oxygen content 6.8, corresponding to a *c*-axis lattice constant of 11.70), which was subject to an aging in air at room temperature for 742 days (see Fig. 7). The result of this aging is a large increase of resistivity accompanied by a very small increase in T_c (about 0.1 K) and a transformation of $\rho_{ab}(T)$ from a superlinear to a perfect linear dependence on temperature. These changes are similar to those observed for the corresponding quantities for films 12 and 13. The transformation from a superlinear to a linear temperature dependence appears to be independent of T_c.

According to Veal *et al.*[17] room-temperature annealing of oxygen-deficient YBCO in air causes redistribution of oxygen in the chain layer and is unlikely to produce a change in the oxygen content of the sample. Following these facts we assumed that redistribution of oxygen during annealing at temperatures of 120–140 °C in argon or room-temperature aging in air takes place in the chain layers of YBCO. It is known that even optimally doped $RBa_2Cu_3O_x$ (RBCO) (including YBCO) contains a few percent of an interchain oxygen O(5) in the chain layers.[14,20,22] Therefore, we assume that O(5) oxygens form links (bridges) between the partially occupied chains of oxygen O(1). These links could be formed by O(5) oxygens during cooling of the films from a high deposition temperature (usually around 650–750 °C). The links allow the transport current in the chain layer to zigzag between the chains via O(5) sites, thus reducing the overall resistivity in the chain layer. For a twinned sample, the overall resistivity ρ_{ab} is an average of ρ_a and ρ_b in the a and b directions, respectively, i.e., $\rho_{ab}=(\rho_a+\rho_b)/2$. It is also equal to the plane- and the chain-layer-resistivities connected in parallel according to the formula

$$\frac{1}{\rho_{ab}}=\frac{1}{\rho_{plane}}+\frac{1}{\rho_{chain\text{-}layer}} \tag{1}$$

or

$$\rho_{ab}=\frac{\rho_{plane}}{1+\dfrac{\rho_{plane}}{\rho_{chain\text{-}layer}}}. \tag{2}$$

According to the experimental results obtained on untwinned YBCO crystals,[4–6] the temperature dependence of resistivity in the planes is linear, i.e.,

$$\rho_{plane}(T)=a_1+a_2T, \tag{3}$$

where a_1 and a_2 are constants. On the other hand, according to Refs. 4,5, temperature dependence of the chain resistivity in untwinned YBCO crystals contains both linear and quadratic components. The latest reference[6] revealed however that on average the chain resistivity of four untwinned YBCO crystals follows almost pure T^2 dependence over a temperature range between 130 and 300 K, i.e,

$$\rho_{chain}(T)=b_1+b_2T^2, \tag{4}$$

where b_1 and b_2 are constants. In Eqs. (3) and (4), resistivity and temperature are in units of $\mu\Omega$ cm and K, respectively.

T^2 dependence of resistivity was observed in quasi-one-dimensional (1D) organic conductors (see, for example, Weger *et al.*[23]). Abrikosov and Ryzhkin[24] developed a theory of the temperature dependence of resistivity in quasi-1D metals. According to this theory in quasi-1D metals with a long mean free path, electron-phonon scattering produces T^2 dependence of resistivity. Such model may be applied to the chains of YBCO, since in a pure YBCO the mean free path should be much larger than the lattice constant. So far however no calculations of $\rho_{chain}(T)$ have been performed using the relevant phonon frequencies for YBCO.

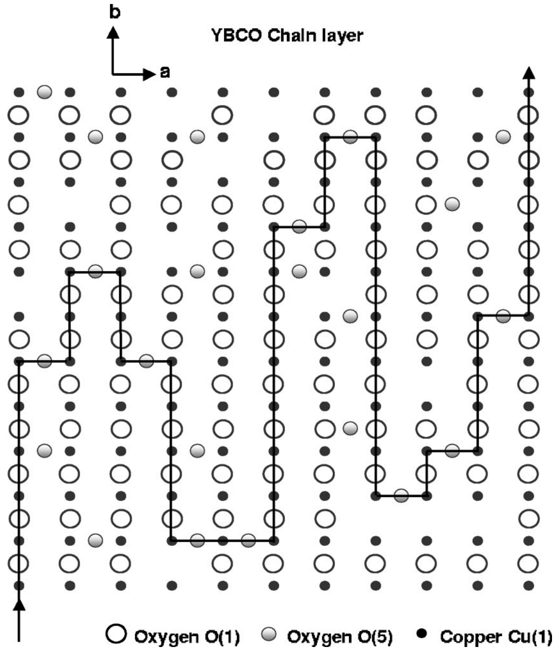

FIG. 8. Representation of the proposed local structure of the chain layer. Chain oxygen O(1) ions are represented by open circles, interchain oxygen O(5) by shaded circles, and copper ions by black dots. Black solid line represents a possible zigzag path of the transport current through O(5) sites in the chain layer.

In an underdoped YBCO, and even in an optimally doped YBCO, the chains are not fully occupied. As mentioned above, in the presence of an interchain O(5) oxygen, the transport current could therefore zigzag between the chains in the chain layer via O(5) bridges along a path of the lowest resistance (see Fig. 8). In this case, electrical transport would still be quasi-1D and the resistivity should be proportional to T^2. One also could expect that O(5) bridges lower the overall resistance in the chain layer. The activation energy for the motion of O(5) oxygen between the chains in the b direction is very small,[25] and during annealing at relatively low temperatures of 120–140 °C, oxygen O(5) should be highly mobile in this direction. High mobility of O(5) during annealing could change the electrical properties of the chain layer. O(5) can fill some O(1) vacancies in the chains, which leads to a higher T_c. On the other hand, the motion of O(5) between the chains in the chain direction could interrupt the paths of the lowest resistance, causing an overall increase of resistivity in the chain layer. One could make a counterargument that even in the absence of an interchain O(5) oxygen, annealing could cause more disorder in the chains, resulting in an increase of resistivity. This however should be accompanied by a decrease in T_c.

We considered a model that could explain an increase in resistivity with annealing time in twinned YBCO thin films. In the presence of oxygen O(5), the electrical transport in the chain layer is determined by the resistance of the chain fragments and the interchain bridges through O(5) sites. The resistance of the interchain bridges R between any two neigh-

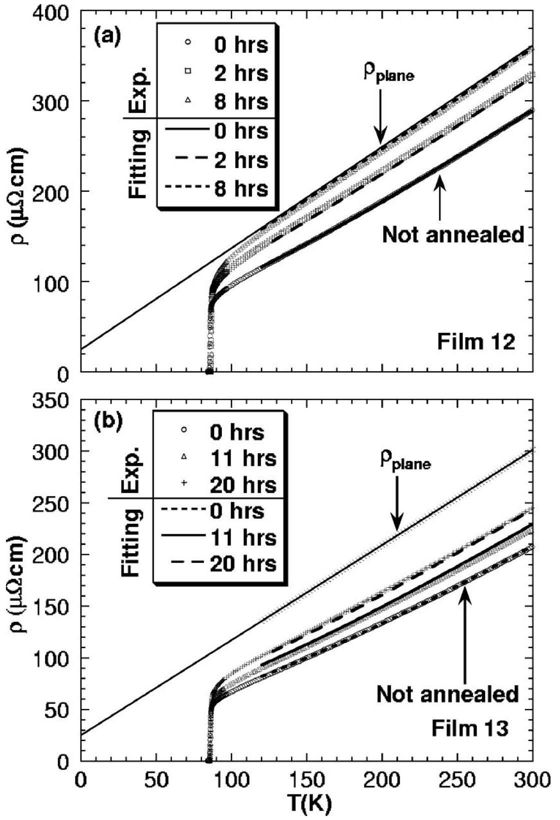

FIG. 9. Experimental data and theoretical fitting curve obtained between 120 and 300 K, using the proposed model described in the text, for $\rho_{ab}(t,T)$ measured in slightly underdoped films 12 and 13. The assumed resistivity of the planes $\rho_{planes}(T)$ in Eq. (9) is represented by the solid line marked ρ_{plane} at temperatures between 120 and 300 K.

boring chains could be considered as that of "effective" bridges (through which the current flows) connected in parallel, i.e., $R = R_0/N$, where R_o is the resistance of a single effective bridge and N is an average number of effective bridges. During annealing at 120–140 °C in argon or aging at room temperature in air, due to high mobility of oxygen O(5), the number of effective bridges N could be reduced. We assumed that this process is completely random and the number of effective bridge disintegrations that occur is proportional to the number of effective bridges present, i.e.,

$$\frac{dN}{dt} = -\alpha N, \tag{5}$$

where α is a decay constant. Dependence of N on time is then

$$N = N_0 \exp(-\alpha t), \tag{6}$$

where t is annealing time and N_0 is the number of effective bridges at $t=0$. The resistance R should then increase with time t according to the expression

$$R = R_0/N = (R_0/N_0)\exp(\alpha t). \tag{7}$$

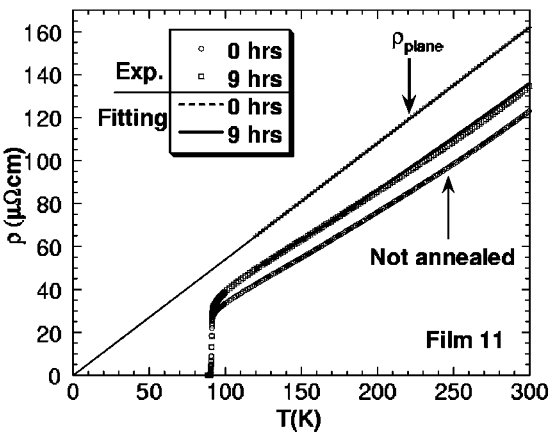

FIG. 10. Experimental data and theoretical fitting curves obtained between 120 and 300 K, using the proposed model described in the text, for $\rho_{ab}(t,T)$ measured in the optimally doped film 11. The assumed resistivity of the planes $\rho_{planes}(T)$ in Eq. (9) is represented by the solid line marked ρ_{plane} at temperatures between 120 and 300 K.

The total average resistance offered to the current by any two chains could be written as the sum of the resistances due to chain fragments (which we consider time independent) and that due to the time dependent O(5) bridges [Eq. (7)]. Therefore, the overall resistivity in the chain layer as a function of annealing time t and temperature T can be expressed in the following form:

$$\rho_{chain\text{-}layer}(t,T) = \rho_0(T)\,\frac{1 + C\exp(\alpha t)}{1+C} = \frac{b_1 + b_2T^2}{1+C}[1 + C\exp(\alpha t)], \tag{8}$$

where $\rho_0(T) = b_1 + b_2T^2$ is the total chain-layer resistivity at temperature T and annealing time $t=0$ [which includes contributions due to both chain fragments and O(5) bridges], and C is the normalization constant which ensures that at $t=0$ the total chain-layer resistivity equals $\rho_0(T)$.

Then the overall resistivity $\rho_{ab}(t,T)$, including the contribution due to the planes, could be written as

$$\rho_{ab}(t,T) = \frac{\rho_{plane}(T)}{1 + \dfrac{\rho_{planes}(T)}{\rho_{chain\text{-}layer}(t,T)}}. \tag{9}$$

We assumed that $\rho_{plane}(T)$ in this equation depends on temperature according to Eq. (3) and not on annealing time, so all changes in resistivity due to annealing occur in the chain layers.

We performed computer calculations of $\rho_{ab}(t,T)$ and compared them with the data obtained for twinned c-axis oriented YBCO films. The fits to the experimental data are shown in Figs. 9 and 10. The fitting parameters are a_1, α, and C. Constants a_1 and a_2 in the equation $\rho_{plane}(T) = a_1 + a_2T$ are shown in Table I for films 11, 12, and 13 and for untwinned YBCO crystals. The slopes of ρ_{plane} curves in Figs. 9 and 10, which are represented by constants a_2, were

TABLE I. Parameters a_1, a_2, α, and C, which were used in the calculation of $\rho_{ab}(t,T)$ for YBCO films 11, 12, and 13. For untwinned YBCO crystals, experimental values of a_1 and a_2 are shown. Note: a_1 and a_2 for untwinned YBCO crystals 1–4 (Ref. 6) represent the average values for all four crystals. a_1, α, and C are the fitting parameters.

Material	a_1	a_2	α	C	Ref.
YBCO film 11	0	0.54	0.066	5	This work
YBCO film 12	25	1.12	0.442	10	This work
YBCO film 13	25	0.92	0.042	2	This work
YBCO untwinned crystal 1	16.5	1.00			[6]
YBCO untwinned crystals 1–4	0	1.00			[6]
YBCO untwinned crystal	−10.5	0.79			[4]
YBCO untwinned crystal	−10.3	0.76			[5]

assumed to follow roughly the slope of the experimental data for $\rho_{ab}(t,T)$ at temperatures above 250 K. Constants b_1 and b_2 for $\rho_{chain}(T)$ [see Eq. (4)] were calculated using Eqs. (2) and (3) and the experimental data for $\rho_{ab}(t=0,T)$ in unannealed YBCO films. A good agreement between the experimental data and the proposed model was obtained for both optimally doped and slightly underdoped YBCO films.

According to Eq. (9) the total resistivity $\rho_{ab}(t,T)$ approaches that of the planes (which increases linearly with an increasing temperature) if the chain-layer resistivity is very high (i.e., it exhibits a semi-insulating or an insulating behavior). This could happen after a long annealing time t if the decay constant α [which describes the process of disintegration of O(5) bridges between O(1) chains] is independent of time. On the other hand, if the chain-layer resistivity is small (i.e., metalliclike), then the chain layer contributes substantially to the total resistivity. In this case, one could expect a deviation of $\rho_{ab}(t,T)$ from a linear temperature dependence towards a quadraticlike one, due to a T^2 dependence of $\rho_{chain}(T)$. Equation (9) shows that the change of resistivity from a small towards a large one in the chain layer (which corresponds to a transition from a metal-like to an insulating behavior) causes an increase in the total resistivity $\rho_{ab}(T)$ and a transformation of its temperature dependence from a nonlinear towards a linear one. This could explain why so many YBCO single-crystal samples (or YBCO thin-film samples) with similar T_c have very different magnitudes and temperature dependencies of resistivity.

V. CONCLUSIONS

Our investigation of the temperature dependence of resistivity of twinned YBCO thin films as a function of annealing time at 120–140 °C led us to conclude that the resistive properties of the chain layer (located between two CuO_2 double planes) could have a dramatic effect on the magnitude and the temperature dependence of the total resistivity $\rho_{ab}(T)$. We suggest that the resistive properties of the chain layer could be modified by a residual amount of the interchain oxygen O(5) which allows a current to flow between the chains along a path of the lowest resistance. Following this suggestion, annealing at 120–140 °C in argon or aging in air at room temperature causes a redistribution of oxygen O(5) and a resulting disruption of low-resistance paths and an increase of the chain-layer resistivity. Distribution of oxygen O(5) in the chain layer could therefore be responsible for the change of the resistive state of this layer from a metalliclike state to an insulating one. Halbritter[26] argued that the resistivity of the chain layer in YBCO affects the resistivity along c axis and consequently the anisotropy of the normal-state resistivity. Small conductivity in the chain layer should therefore cause higher anisotropy (and higher c-axis resistivity) than that expected for YBCO with metalliclike chain layers. Our recent measurements of the angular dependence of resistivity in the a-b planes close to the superconducting transition temperature revealed larger than expected changes of resistivity in some YBCO thin films, when the angle between the direction of an external magnetic field and the a-b planes was changed from 0° to 90°.[27] These large changes suggest large anisotropy (and strong pinning of magnetic flux between the CuO_2 planes), which could be caused by an insulating state of the chain layers in these samples. On the other hand, the changes of the chain-layer resistivity may be also responsible for different temperature dependencies of the c-axis resistivity observed in different YBCO single crystals. Surprisingly, the c-axis resistivity of YBCO crystals studied so far exhibits either a $1/T$ dependence[28,29] or a linear temperature dependence.[3,30,31] A small increase in T_c of underdoped samples during annealing in argon at 120–140 °C or long-time aging in air could result from a large activation energy for a jump of an interchain O(5) oxygen into the site of a chain oxygen O(1).

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