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Temperature dependence of the in-plane resistivity in underdoped $Bi_2Sr_2CaCu_2O_y$ single crystals

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A number of underdoped $Bi_2Sr_2CaCu_2O_y$ single crystals have been obtained by two different ways: (1) substitution of Y for Ca, and (2) removing oxygen from crystals by vacuum annealing. The in-plane resistivity (ρ_{ab}) measurements reveal different transport properties between these crystals. For the Y-doped crystals, $\rho_{ab}(T)$ exhibits metallic behavior until the crystal reaches a doping level where the metal-insulator transition should occur. An S-like T-dependent $\rho_{ab}(T)$ in the underdoped samples, similar to the observations in underdoped $YBa_2Cu_3O_{7-y}$ and $La_{2-x}Sr_xCuO_4$, was observed. However, for vacuum-annealed crystals, $\rho_{ab}(T)$ becomes nonmetallic. We analyze the data and argue that the disorder introduced by vacuum annealing is much greater than that by Y doping as long as the crystals have the same T_c. [S0163-1829(96)04634-6]

I. INTRODUCTION

The understanding of high-temperature superconductivity requires the careful study and understanding of the unusual normal-state properties of these materials. A promising way towards this goal is to perform a systematic study so as to establish how these properties evolve as a function of doped carrier concentration. Previous studies on underdoped $YBa_2Cu_3O_{7-x}$ (Ref. 1) and $YBa_2Cu_4O_8$ (Ref. 2) have provided evidence that the charge transport in the CuO_2 planes is determined by spin scattering. Similar systematic studies on charge transport have also been done on $La_{2-x}Sr_xCuO_4$ at different doping levels.[3,4] In this work, we present measurements of the temperature dependence of in-plane resistivity in underdoped $Bi_2Sr_2CaCu_2O_y$ (Bi2212) single crystals.

As in other high-T_c cuprate systems, there are two ways to reduce the carrier concentration and, thus, prepare samples out of the underdoped region in $Bi_2Sr_2CaCu_2O_y$. One is to substitute an element in the crystal structure by another one with a higher valence state. In this case the substitution of Y^{3+} for Ca^{2+} has been found to be most efficient in Bi2212.[5] It should be mentioned that although a lot of work has been done on this substituted system, only a few experiments were performed on single crystals.[6–8] Another way is to remove oxygen from the pure samples. This can be achieved by annealing the samples in an atmosphere with low partial oxygen pressure.[9] Though both methods have been adopted to adjust the carrier concentration and prepare samples out of the underdoped region in the past, there has, so far, been no careful comparison and discussion about whether or not the normal-state properties evolve in a similar way. We shall show here that, when the superconducting transition has been depressed to about the same temperature by the different methods, the normal-state resistivity behaviors become completely different.

II. EXPERIMENTAL DETAILS

As mentioned above, we used two ways to get underdoped $Bi_2Sr_2CaCu_2O_y$ single crystals: By (i) growing Y-doped $Bi_2Sr_2CaCu_2O_y$ crystals and (ii) annealing the crystals in a vacuum state. The $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ single crystals were grown from a bismuth-oxide-rich melt in Al_3O_3 crucibles. We chose $Bi_{2.5}Sr_2Ca_{1-x}Y_xCu_2O_y$ with $x=0$, 0.07, 0.11, and 0.17 as the nominal compositions of the melt. The mixture of the starting materials of Bi_2O_3, $SrCO_3$, $CaCO_3$, Y_2O_3, and CuO was ground and fired at 800 °C for 17 h 2 or 3 times. The products were melted at 970–1000 °C (depending on the Y concentration) for 4 h, then cooled down slowly to 820–835 °C at a rate of 1.5 °C/h, followed by a furnace cooling down to room temperature. The crystals were removed mechanically after breaking the crucible. To improve the homogeneity of oxygen content, some crystals were annealed in an O_2 atmosphere at 620 °C for 18 h. Vacuum annealing was carried out in a constantly pumped quartz tube at, approximately, $\sim 5\times10^{-6}$ mbar and 400 °C.

X-ray-diffraction (XRD) measurements were performed in an effort to determine the possible presence of secondary phases and to demonstrate the effect of Y doping and oxygen concentration on the c-axis lattice parameter. The resistivity was measured via an ac ($f=43$ Hz) four-probe method using a lock-in amplifier. The typical dimensions used to determine the resistivity were 1.5 mm × 0.7 mm × 8 μm. Contact was made using silver paint. These silver contact pads were painted on samples before annealing. Normally the contact resistance was below 3Ω for oxygen-annealed samples. However, for vacuum-annealed samples, the contact resistance, which depends on the Y concentration in the crystal, increases strongly.

III. RESULTS AND DISCUSSIONS

By means of XRD we could verify the crystals, which grow preferentially along the ab plane, to be of the proper 2212 phase. No trace of secondary phases could be identified. As examples, Fig. 1 shows the (0,0,1) x-ray-diffraction patterns for a pure 2212 crystal both before and after vacuum-annealing and also for a Y-doped crystal with $x=0.11$. We see that there is an opposite trend for the effect of Y doping and vacuum annealing on the c-axis lattice pa-

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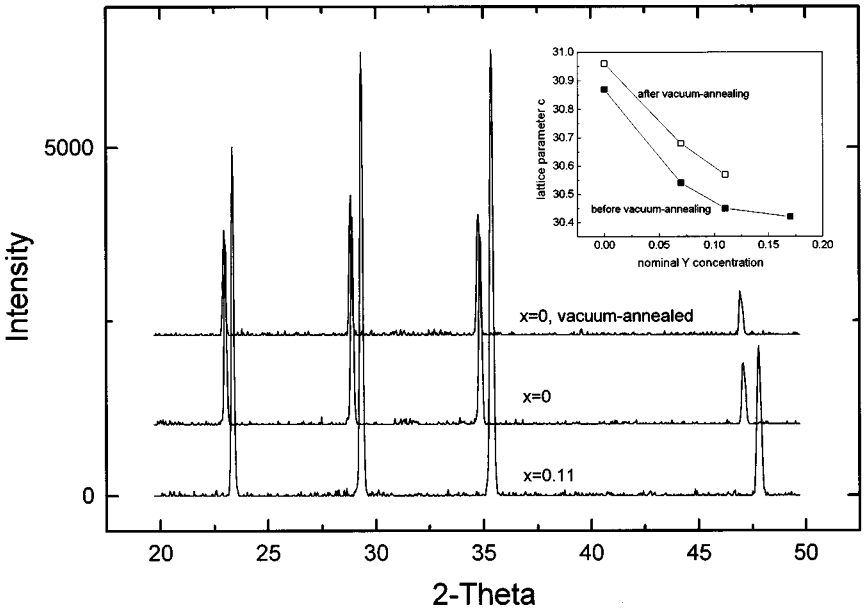

FIG. 1. X-ray-diffraction patterns for a pure 2212 crystal both before and after annealing in a vacuum $\sim 5\times 10^{-6}$ mbar at 400 °C for 14 h and for a Y-doped 2212 crystal with $x=0.11$, measured using 1.54 Å Cu $K\alpha$ radiation. There is no indication of secondary phase material. The inset shows the c-axis parameter as a function of nominal Y concentration both before and after vacuum annealing.

rameter. The lattice parameter c decreases with the increase of Y concentration. However, vacuum annealing results in an increase of the lattice parameter c. The inset of Fig. 1 illustrates the lattice parameter c, before and after annealing in vacuum, as a function of Y concentration. The dependence of the c-axis parameter on nominal Y concentration in unannealed crystals is in good agreement with previous publications.[6,8] The increase of the lattice parameter c after vacuum annealing is apparently due to the loss of oxygen in the crystal structure so that the repelling force amongst cations becomes relatively large. As we shall see below, the vacuum-annealed pure 2212 crystal has nearly the same superconducting transition temperature as the Y-doped crystal with nominal composition $x=0.11$. While the lattice parameter c of the vacuum-annealed crystal is increased compared to pure unannealed sample, it is reduced for the Y-doped crystal. From this observation, we conclude that the superconducting transition temperature is not directly related to lattice parameters.

Figure 2 shows ρ_{ab} vs T curves for an undoped and several Y-doped Bi2212 crystals. The latter ones were annealed in an O_2 atmosphere. There are several features worth mentioning. Firstly, the superconducting transition temperature T_c (defined as the onset of the sharp transition) precipitously drops as Y is added. T_c for undoped 2212 is 87 K, 70 K for nominal $x=0.07$, 32 K for $x=0.11$ and 14 K for $x=0.17$, respectively. This shows clearly that the crystals evolve from optimally doped to underdoped as a result of hole filling due to the substitution of Y^{3+} for Ca^{2+}. Secondly, the crystals still show metallic behavior with $d\rho_{ab}/dT>0$ up to $x=0.11$, even though the magnitude of the resistivity increases rapidly. The metal-insulator transition occurs when the nominal Y concentration approaches 0.17. Thirdly, the underdoped sample exhibits an S-like T-dependent resistivity in the normal state. This is evident in Fig. 2 for the $x=0.11$ sample. This $\rho_{ab}(T)$ dependence is similar to the one observed in underdoped $YBa_2Cu_3O_{7-y}$ (Ref. 1) and $La_{2-x}Sr_xCuO_4$.[3,4]

The increase of the resistivity with Y doping is apparently due to the reduction of the carrier concentration. The disorder introduced as a result of substitution of Y^{3+} for Ca^{2+} also contributes to this increase. The $x=0.17$ sample can be considered to be close to the critical doping level where the metal-insulator transition should occur in the well-established phase diagram for high-T_c cuprates. Concerning the S-like temperature dependence of the in-plane resistivity in the underdoped sample (we shall focus here on the $x=0.11$ sample), there could be two explanations. One is that the accelerated decrease in the resistivity at around 200 K can be related to the opening of a gap in the spin-

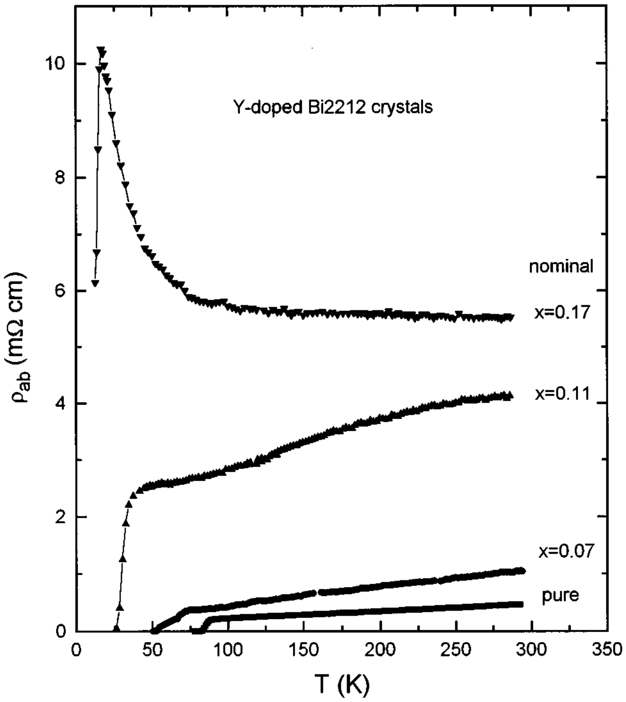

FIG. 2. Temperature dependence of the in-plane resistivity for pure and Y-doped $Bi_2Sr_2CaCu_2O_y$ single crystals. x gives the nominal Y concentration.

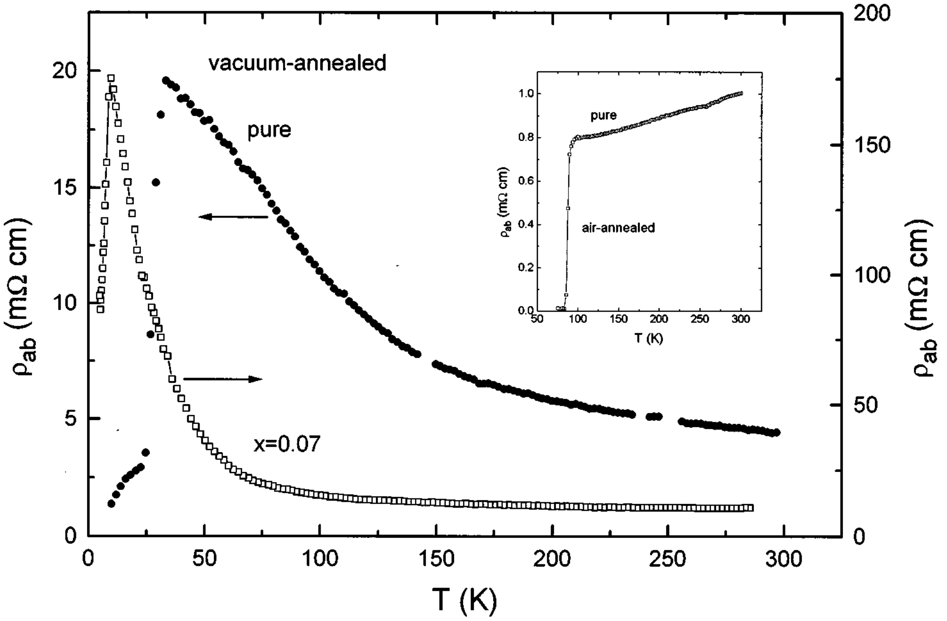

FIG. 3. Temperature dependence of the in-plane resistivity for both a pure and an Y-doped $x=0.07$ $Bi_2Sr_2CaCu_2O_y$ single crystal after vacuum annealing. The inset shows the $\rho_{ab}(T)$ curve normalized at 300 K for the same vacuum-annealed pure 2212 crystal, but after having been reannealed in air at 400 °C for 1 h.

excitation spectrum, a situation similar to other bilayered cuprates like $YBa_2Cu_3O_{7-y}$ (Ref. 1) and $YBa_2Cu_4O_8$.[2] However, the available experimental data concerning the spin excitation for Bi2212 do not yield a consistent picture, though it may be expected that the bilayer-coupling systems should have similar excitation spectra. For example, Ishida *et al.*[10] reported that even for a slightly overdoped Bi2212 crystal, the T-dependent Knight shift, $^{63}K(T)$, as well as the spin-lattice relaxation rate, $(T_1T)^{-1}$, resemble the behavior established for underdoped $YBa_2Cu_3O_{7-y}$: $^{63}K(T)$ decreases upon cooling and $(T_1T)^{-1}$ vs T has a peak above T_c. In contrast to this, no distinct features have ever been observed in ρ_{ab} vs T for undoped Bi2212 crystals.

An alternative approach is to consider the S-like shape of $\rho_{ab}(T)$ as an indication of resistivity saturation at high temperature. We noticed that Takagi *et al.*[3] analyzed their experimental results for underdoped $La_{2-x}Sr_xCuO_4$ following this idea. From simple Drude model for a quasi-two-dimensional (2D) system $\rho_{ab}=(h/e^2)d_c/k_Fl$, where $d_c=c/2$ is the periodic length in the c axis, k_F is the Fermi wave vector, and l is the mean free path, it is easy to estimate the saturated value ρ_M of the resistivity by application of the Mott-Ioffe-Regel criterion $k_Fl\sim1$. This yields $\rho_M\sim4$ m Ω cm for 2212. From Fig. 2, we find that the resistivities for $x=0.11$ for $T>270$ K and 0.17 samples already exceed this value. As the mean free path l cannot be less than the minimum scattering length $a/2$ (a is the in-plane lattice parameter), this may imply that k_F is much smaller than π/a. In other words, this could imply that the underdoped materials have a small Fermi surface.

Figure 3 shows the $\rho_{ab}(T)$ curves for two crystals after annealing in a high vacuum ($\sim5\times10^{-6}$ mbar) at 400 °C for 14 h: i.e., a pure 2212 and a Y-doped one with nominal composition $x=0.07$. We find that vacuum annealing depresses the superconducting transition temperatures strongly. T_c is reduced from 87 to 30 K for the pure 2212 crystal, and from 70 to 10 K for the Y-doped ($x=0.07$) crystal. This rapid depression in T_c is undoubtedly caused by the loss of oxygen content which shifts the sample towards the underdoped region. The increase of the c-axis parameters provides additional evidence for the loss of oxygen. However, we refrained from performing a quantitative determination of the oxygen content before and after the annealing.

The large change in T_c allows us to compare how the normal-state properties evolve upon reducing the doping levels caused either by Y doping or by oxygen removal via vacuum annealing. The vacuum-annealed pure 2212 sample has almost the same superconducting transition temperature (~30 K) as the Y-doped $x=0.11$ crystal. However the normal-state in-plane resistivities behave completely differently. The Y-doped one shows metallic behavior with

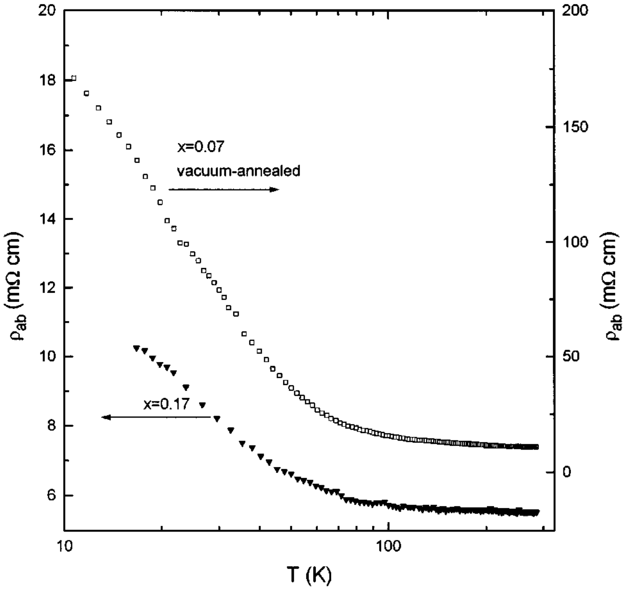

FIG. 4. ρ_{ab} vs T curves for both the Y-doped $x=0.17$ crystal and the vacuum-annealed Y-doped $x=0.07$ crystal in a semilogarithmic plot.

$d\rho_{ab}/dT>0$, while the vacuum-annealed crystal shows a semiconductinglike behavior. For the vacuum-annealed Y-doped $x=0.07$ crystal, the in-plane resistivity increases by more than one order of magnitude as temperature drops from 300 to 10 K, while the increase of resistivity of the oxygen-annealed Y-doped $x=0.17$ crystal with $T_c\sim 14$ K is much smaller in nearly the same temperature interval. For our vacuum-annealed Y-doped samples with $x\geqslant 0.11$, we did not obtain reliable data due to very large contact resistances. However, we are confident that the resistivity must be larger than in all the other samples measured, as a high sample resistance also results in a high contact resistance.

The above results indicate that the vacuum annealing affects the normal-state properties more strongly than substitution of Y for Ca does. This implies that the disorder introduced by vacuum annealing must be greater than that caused by Y doping provided that the crystals have the same T_c. This can be understood by assuming that substitution of Y^{3+} for Ca^{2+} mainly introduces disorder in the Ca layers sandwiched between the CuO_2 planes, while vacuum annealing removes oxygen from different layers. Considering the significant difference of the in-plane resistivities in these two cases and also the fact that the in-plane transport is dominated by the scattering within the CuO_2 layers, we argue that at least some of the oxygen atoms have to be removed from CuO_2 layers by vacuum annealing.

Realizing that the semiconductinglike behavior of $\rho_{ab}(T)$ for vacuum-annealed samples may be mainly caused by the disordering effect, we have tried to fit the $\rho_{ab}(T)$ data in the normal state to Mott's formula of variable-range-hopping conduction: $\rho_{ab}(T)=\rho_0\exp(T_0/T)^\alpha$ with $\alpha=1/3$ for 2D and $\alpha=1/4$ for 3D systems. Unfortunately, the data can not be reproduced well by this formula. Instead, we find that for both the Y-doped $x=0.17$ sample and the vacuum-annealed Y-doped $x=0.07$ sample, the resistivities increase approximately as $\rho_{ab}(T)\sim-(h/e^2)\ln T$, typical for a 2D carrier system in the weak-localization regime, as shown in Fig. 4. The results suggest that all the crystals belong to the weak-localization regime.

Finally, we show that the vacuum-annealed samples can be, reversibly, transformed to superconductors with high transition temperatures after annealing in air or in oxygen. As an example, the inset of Fig. 3 shows a normalized $\rho_{ab}(T)$ curve for the vacuum-annealed pure 2212 crystal displayed in the main part, having been reannealed in air at 400 °C for only 1 h. The transition temperature T_c returns from 30 to 90 K. Though the residual resistivity is higher compared to the original as-grown sample, the in-plane resistivity becomes metallic after reannealing in air. Considering the rather short annealing period and the relatively low annealing temperature, we believe that the oxygen addition during the air-annealing starts to fill up O vacancies within the CuO_2 layers.

In summary, we have successfully obtained underdoped $Bi_2Sr_2CaCu_2O_y$ single crystals by using two different methods: (i) growing Y-doped crystals and (ii) removing oxygen from crystals by vacuum annealing. We find that there are strong differences in the in-plane transport properties between these crystals. In case of Y doping, the in-plane resistivities exhibit metallic behavior until the crystal reaches a doping level where the metal-insulator transition ought to occur. Particularly, we find a complicated S-like T-dependent ρ_{ab} in underdoped $Bi_2Sr_2CaCu_2O_y$ single crystals, similar to previous observations in underdoped $YBa_2Cu_3O_{7-y}$ and $La_{2-x}Sr_xCuO_4$. However, for vacuum-annealed crystals, the in-plane resistivity becomes nonmetallic. Our analysis illustrates that the disorder introduced by vacuum annealing is much higher than that introduced by Y doping, as long as the crystals have the same T_c. We emphasize that these differences should be taken into account also when explaining other experimental data for underdoped $Bi_2Sr_2CaCu_2O_y$ samples.

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