Effects of high-oxygen-pressure annealing on transport properties for $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals

Takao Watanabe, Kyoichi Kinoshita, and Azusa Matsuda
NTT Basic Research Laboratories, 3-9-11 Midori-cho, Musashino-shi Tokyo 180, Japan
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We have measured in-plane resistivities $\rho_{ab}(T)$, out-of-plane resistivities $\rho_c(T)$, and Hall coefficients $R_H(T)$ of $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals as a function of temperature for various O_2 annealing pressures. As-grown $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals which are semiconducting become superconducting if they are annealed under high oxygen pressures of more than 100 atm. In each metallic sample, the Hall angles reasonably fit Anderson's formula $\cot\theta_H = \alpha T^2 + C$ (α and C are constants and T is temperature). The phenomenological analysis using this relationship showed that the increase in T_c produced by the annealing mainly results from a reduction in the impurity scattering, while the metallic conduction itself is achieved by an increase in the carrier concentration.

The only electrical active constituent in the $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ compound is a pair of pyramidal Cu-O planes facing each other,[1] whereas $YBa_2Cu_3O_{7-\delta}$ has both pyramidal planes and a square planar chain. Because of the simplicity of this crystal structure, the $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ system is expected to provide essential information about the transport properties of the double pyramidal Cu-O plane. We have recently succeeded in growing single crystals and making them superconducting by annealing them under a high O_2 pressure of 300 atm.[2,3] In our previous paper, we also reported a very small resistive anisotropy of $\rho_c/\rho_{ab} \cong 35$ (at 300 K) for the superconducting sample. To examine more precisely whether this is an intrinsic property or not, and to detect the key parameter causing superconductivity, we systematically studied the anisotropic transport properties of the crystals after various high-pressure oxygen treatments.

On the other hand, the temperature dependence of the Hall coefficient R_H has been one of the most striking but least understood anomalies in high-T_c superconductors. Recently, Anderson explained this problem in connection with the essence of high-T_c superconductivity.[4] He theorized that the Hall angle ($\cot\theta_H \equiv \sigma_{xx}/\sigma_{xy} = 1/\omega_c\tau_H$) has the formula

$$\cot\theta_H = \alpha T^2 + C \tag{1}$$

(where α and C are constants). Thus, the temperature dependence of the Hall coefficient R_H ($=\rho_{ab}/B\cdot\cot\theta_H$, where B is the magnetic field) can be naturally explained for an impure system as well as for a pure system, assuming that C is linearly related to the impurity concentration. Chien, Wang, and Ong[5] demonstrated the validity of Eq. (1) in the single-crystal $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ system. It would be very interesting to know the generality of Eq. (1) for both the variation of high-T_c materials and their carrier doping level at least from the phenomenological point of view.

This paper reports measurements of in-plane resistivities ρ_{ab}, out-of-plane resistivities ρ_c, and Hall coefficients R_H for the $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals as a function of temperature for various O_2 pressures during annealing. We demonstrate here the applicability of Eq. (1) to the $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ system and discuss the possible consequences, which relate to the appearance of superconductivity.

Single crystals were grown in air from a CuO-rich melt, as reported previously.[2,3] The La:Ca ratio of the crystals was determined by electron-probe microanalysis (EPMA) to be 1.89±0.01:1.11±0.01. The bulk single crystallinity was confirmed from an x-ray precession photograph over an average sample size of 0.7×0.7×0.2 mm^3. To investigate the effects of high O_2 pressure annealing on transport properties, crystals were annealed at 1040–1080 °C for 200 h in 20% O_2 +80% Ar at a total pressure between 100 and 1500 atm (effective O_2 pressure between 20 and 300 atm) using a furnace for hot isostatic pressing (HIP). The oxygen content $6\pm\delta$ was not determined. The long annealing time of 200 h, however, ensured that the samples had reproducible and also reversible electrical properties.

The electrical transport properties were measured by a combination of Montgomery's method[6] (ρ_{ab},ρ_c) and van der Pauw's method (ρ_{ab}, R_H). Gold wires were attached to six corners of the crystal with Au-paste. Then, the crystal was annealed at 850 °C for 30 min to reduce the contact resistance. This heat treatment for the electrodes did not affect the properties of the HIP treated sample. For ρ_{ab}, we checked the consistency between the two methods. The Hall coefficient R_H was measured in a magnetic field of 6 T, applied parallel to the c axis. (In the Hall angle analysis described below, however, the magnetic field B is set to 8 T for comparison with the result for $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ obtained by Chien, Wang, and Ong.[5])

Figure 1 shows the temperature dependence of the in-plane resistivities ρ_{ab} for $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals for various O_2 pressures during annealing. The value of ρ_{ab} for an as-grown sample is as high as about 80 mΩcm at room temperature and is almost constant down to 50 K. When these crystals were annealed in the high O_2 pressures, ρ_{ab} decreased rapidly and became metallic

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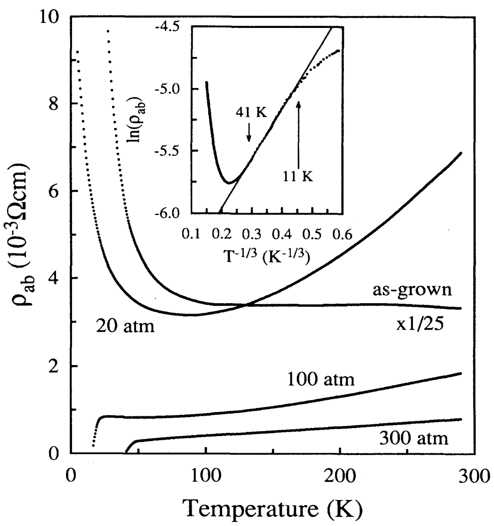

FIG. 1. In-plane resistivities ρ_{ab} of $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals vs temperature for various O_2 pressures during annealing. The inset shows the logarithm of resistivity as a function of $T^{-1/3}$ for the 20-atm O_2 annealed sample. The straight line is a guideline for convenience.

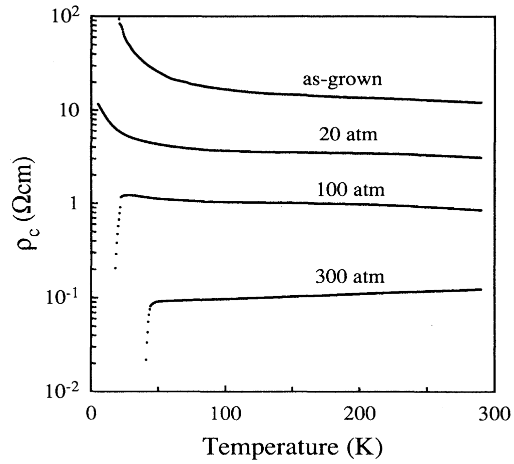

FIG. 2. Out-of-plane resistivities ρ_c of $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals vs temperature for various O_2 pressures during annealing. ρ_c is plotted on a logarithmic scale.

($d\rho_{ab}/dT>0$). In the as-grown and the 20-atm O_2 annealed sample, the ρ_{ab} increased rapidly below 50 K. These results suggest electron localization driven by disorder. The inset shows the plot with two-dimensional variable-range-hopping (VRH) parametrization for the 20-atm O_2 annealed sample. The straight line fits the data between 11 and 41 K. At other temperatures, however, the deviation from the straight line is apparent. Electrical conduction in this system at low temperatures may be dominated by a localization effect, but the precise temperature dependence cannot be interpreted by a simple model. Superconductivity was detected at more than 100 atm. When the pressure was 100 atm, the sample showed a T_c end of 13 K, while 300 atm gave a T_c end of 40 K. The bulk nature of superconductivity, for both samples, was confirmed by magnetic susceptibility measurements. Furthermore, a typical T-linear temperature dependence of ρ_{ab} appeared in the 300-atm O_2 annealed sample. The absolute value, however, was still high compared with other optimally doped systems. Residual resistivities ρ_0 of the metallic samples were estimated by assuming the formula $\rho_{ab}=\rho_0+aT^{\beta}$ in the temperature range from 125 to 300 K. The parameter values ρ_0, a, and β thus obtained are listed in Table I. Carrier concentrations n estimated from $1/eR_H$ in Fig. 3 at 100 K and normalized residual resistivities $\rho_0'=n\cdot\rho_0$, which can be a measure of a disorder, are also shown in the table. ρ_0' decreased with increasing O_2 pressure, suggesting that disorder was reduced as the annealing pressure of O_2 increased.

Figure 2 shows the temperature dependence of out-of-plane resistivity ρ_c for the same crystals as shown in Fig. 1. The early data of ρ_c scattered from sample to sample.[2,3] This was shown to be caused by the existence of misaligned domains along the c-axis in the crystal-by-crystal structure analysis using a precession camera. Therefore, the present data were taken for crystals that did not show any evidence of multidomain structure. The value of ρ_c decreased monotonically with increasing O_2 pressure. The anisotropy ρ_c/ρ_{ab} was 1×10^3 for 20-atm and 100-atm O_2 annealed samples at 150 K, and 200 for the 300-atm O_2 annealed sample, which is comparable to the value for the $La_{2-x}Sr_xCuO_4$ system having the same La_2O_2 insulating layer as a constituent unit.[7] Although the temperature dependence was slightly metallic ($d\rho_c/dT>0$) in the 300-atm O_2 annealed sample, the magnitude of ρ_c seems to violate the Mott-Ioffe-Regel criterion for metallic conductivity $\rho_{ab}\cdot\rho_c<\rho_M^2(\rho_M\sim h/e^2k_F)$, if the carrier concentration is assumed to be about $1\times10^{21}cm^{-3}$. That is, the electrical conduction in our new $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ system can

TABLE I. Transport parameters for metallic $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals. Parameters ρ_0, a, and β were obtained from the fit by $\rho_{ab}=\rho_0+aT^{\beta}$. Carrier concentration n was estimated at 100 K from the Hall coefficients assuming a single band. Constants α and C were obtained from the fit by $\cot\theta_H(=\rho_{ab}/B\cdot R_H)=\alpha T^2+C$, where B was set to 8 T for comparison with the result for $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$. The samples are labeled by their effective O_2 pressure during annealing.

Sample (atm)	ρ_0 (Ω cm)	a (Ω cm/K^{β})	β	n (100 K) (cm^{-3})	$\rho_0'(\equiv n\cdot\rho_0)$ (Ω/cm^2)	α	C
20	2.41×10^{-3}	5.32×10^{-8}	2	2.70×10^{20}	5.78×10^{17}	1.38×10^{-3}	144.3
100	6.05×10^{-4}	2.52×10^{-7}	1.5	8.89×10^{20}	5.38×10^{17}	3.23×10^{-3}	116.4
300	1.98×10^{-4}	2.07×10^{-6}	1	1.08×10^{21}	2.14×10^{17}	3.23×10^{-3}	28.7

be regarded as essentially two-dimensional, like most other high-T_c materials.[7]

Figure 3 shows the temperature dependence of $1/eR_H$ for the same crystals as in Figs. 1 and 2. With increasing O_2 pressure, the magnitude of $1/eR_H$ increases and the temperature dependence becomes apparent above 100 atm. Since $1/eR_H$ is temperature dependent, it cannot simply be considered as a carrier concentration. However, the magnitude of $1/eR_H$ at a fixed temperature may represent a measure of carrier concentration, at least as long as the temperature dependence is weak. From this point of view, the annealing primarily increases the mobile carriers for oxygen pressures of less than 100 atm. A tentative estimate of the number of holes per Cu is 0.08 at 100 K for the 300-atm annealed sample, which is much smaller than 0.38 obtained for the $YBa_2Cu_3O_{7-\delta}$ system.[8] This indicates that the system studied here is in the so-called underdoped region.

The dominant effect of the annealing between 100 and 300 atm is to reduce disorder, according to the estimation of ρ_0'. This point can be more clearly revealed by considering the temperature dependence of the Hall angle. According to Eq. (1), Fig. 4 shows the plot of $\cot\theta_H$ vs T^2 for the metallic samples, where the applied magnetic field B is set to 8 T. All the data can be fitted to straight lines in the temperature range from 150 to 300 K, although a slight upward curvature is seen. This indicates that the T^2 dependence of $\cot\theta_H$ may be a universal property in a wide variety of high-T_c materials and carrier doping levels. In the following analysis, we use Eq. (1) as a phenomenological one, and consider the material-annealing condition dependence of parameters α and C. They are obtained from the straight-line fits as in Table I. The intercept C decreases with increasing O_2 pressure from 100 to 300 atm. The α value of 3.23×10^{-3} for 100- and 300-atm O_2 annealed samples is comparable or slightly smaller than 5.11×10^{-3} of $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$,[5] suggesting that α is not strongly dependent on the precise structure of each high-T_c material as long as the sample shows superconductivity. This seems to be consistent with

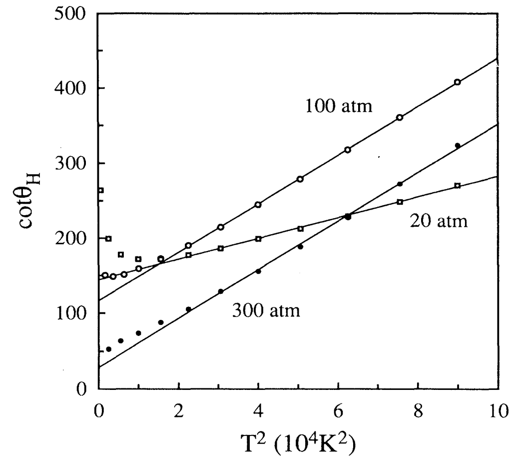

FIG. 4. Temperature dependence of the Hall angle with Anderson's parametrization for metallic $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals for various O_2 pressures during annealing. In the range from 150 to 300 K, the results fit straight lines.

Anderson's explanation that α is related to the spin exchange energy J through $\alpha=m_s/eBJ$, where m_s is the spinon mass. The observed decrease in α for the 20-atm O_2 annealed sample may be related to a decrease in the carrier concentration. This is because, according to Anderson's theory, with decreasing carrier concentration, the effective J (and hence the bandwidth for spinons) may increase and m_s may decrease. On the other hand, our results also show apparent deviations from the straight line in the low-temperature region, which may be due to localization. The magnitude of the deviations becomes more pronounced and the onset temperature shifts to higher temperatures (80 and 100 K in the 100- and 20-atm samples) with decreasing O_2 annealing pressure. This may also indicate a reduction in disorder with higher O_2 pressures.

It is interesting to discuss the relationship between T_c and C. Figure 5 plots T_c vs C for $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$

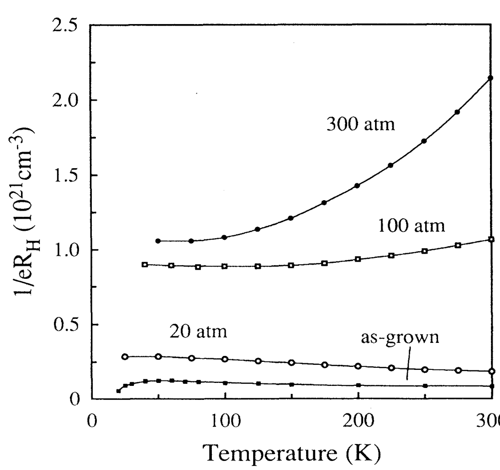

FIG. 3. Temperature dependence of $1/eR_H$ for $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals for various O_2 pressures during annealing.

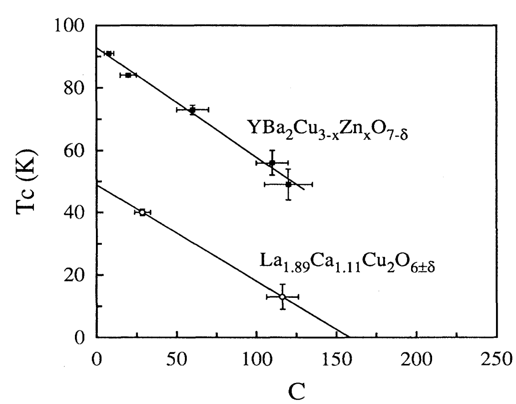

FIG. 5. T_c vs impurity contribution C estimated from the T^2 fit for Hall angles in Fig. 4. The data for $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ are taken from Ref. 5. Here, dT_c/dC is estimated to be -0.35 and -0.31 for the $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ and $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ systems, respectively.

single crystals and $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ single crystals. Here, the straight line for the $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals is drawn with the data of 100- and 300-atm O_2 annealed samples. The slope dT_c/dC is about the same for both systems, suggesting that the mechanism that reduces T_c in the $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ system also works in the present $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ system, although no impurities are artifically added in the present system. Here, the carrier concentration of the system is thought to be constant for the O_2 pressure region considered. We did not determine the oxygen content $6\pm\delta$ for the single crystals. However, a neutron-diffraction study for a sintered sample of $La_{1.82}Ca_{1.18}Cu_2O_{6\pm\delta}$ showed very little difference between superconducting ($O_{6.014\pm0.007}$) and nonsuperconducting ones ($O_{5.99\pm0.02}$).[9] In addition, the invariance of parameter α in Eq. (1) between the two samples may imply the invariance of the carrier concentration. Thus, the decrease in T_c from the 300-atm sample to the 100-atm one is mainly due to the increase in the impurity scattering, which produces an increase in C, rather than a decrease in carrier concentration. The microscopic origins of C may be an in-plane oxygen vacancy and/or an increase in La and Ca disordering between a $4e$ site and a $2a$ site, as revealed by x-ray- and neutron-diffraction analyses.[9,10] It should be noted that these origins of C are not the magnetically active impurities that appear in Anderson's theory. In fact, we did not observe any evidence for the existence of magnetic impurities from our static susceptibility measurements. In a conventional superconductor, the normal impurities or disorder have little or no effect on T_c, which is well known from Anderson's theorem.[11] Hence, the strong sensitivity of T_c on the impurity contribution C revealed here and by the many studies on impurity doping[5,12] is an important issue for understanding high-T_c superconductivity. Actually, the $\cot\theta_H$ vs T^2 plot for published $La_{2-x}Sr_xCuO_4$ data[13] shows a rather large residual C of about 130, even in optimum doping. This may explain why the T_c of $La_{2-x}Sr_xCuO_4$ is so low.

In conclusion, we have measured transport properties ρ_{ab}, ρ_c, and R_H for $La_{1.89}Ca_{1.11}Cu_2O_{6\pm\delta}$ single crystals, whose properties change from semiconductor to superconductor, for various O_2 pressures during annealing. From the measurements of anisotropic properties for ρ_{ab} and ρ_c, the electrical conduction can be considered to be essentially two dimensional, like most other high-T_c materials. The analysis of residual resistivity and Hall angle showed that the reduction of disorder (or impurities) produced by the high O_2 pressure annealing plays an important role in creating superconductivity as well as the hole doping. In addition, the T^2 dependence for the Hall angles proposed by Anderson was satisfied for all metallic samples, suggesting that it is generally applicable for both variations in materials and carrier doping level, at least in the phenomenological sense. However, a literal interpretation of Anderson's theory, which ascribes the origin for the impurity contribution only to magnetic impurities, may encounter difficulties explaining some experimental data.

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[1] N. Nguyen, L. Er-Rakho, C. Michel, J. Choisent, and B. Raveau, Mater. Res. Bull **15**, 891 (1980).
[2] T. Ishii, T. Watanabe, K. Kinoshita, and A. Matsuda, Physica C **179**, 39 (1991).
[3] T. Watanabe, T. Ishii, K. Kinoshita, and A. Matsuda, Physica C **185-189**, 1235 (1991).
[4] P. W. Anderson, Phys. Rev. Lett. **67**, 2092 (1991).
[5] T. R. Chien, Z. Z. Wang, and N. P. Ong, Phys. Rev. Lett. **67**, 2088 (1991).
[6] M. C. Montgomery, J. Appl. Phys. **42**, 2971 (1971).
[7] T. Ito, H. Takagi, S. Ishibashi, T. Ido, and S. Uchida, Nature **350**, 596 (1991).
[8] T. R. Chien, D. A. Brawner, Z. Z. Wang, and N. P. Ong, Phys. Rev. B **43**, 6242 (1991).
[9] K. Kinoshita, F. Izumi, T. Yamada, and H. Asano, Phys. Rev. B **45**, 5558 (1992).
[10] K. Kinoshita, H. Shibata, and T. Yamada, Physica C **176**, 433 (1991).
[11] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
[12] For example, see G. Xiao, M. Z. Cieplak, J. Q. Xiao, and C. L. Chien, Phys. Rev. B **42**, 8752 (1990).
[13] M. Suzuki, Phys. Rev. B **39**, 2312 (1989).