

Effect of oxygen distribution on the resistivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxides ($0 \leq \delta < 0.8$)

N.-C. Yeh, K. N. Tu, S. I. Park, and C. C. Tsuei

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 9 May 1988)

The resistivity variation in ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq \delta < 0.8$) oxides has been studied as a function of δ during the oxygen in-diffusion and out-diffusion processes. The distribution of $\delta = \delta(x, t)$ as a function of the position (x) and time (t) within a grain has been inferred for both processes. We conclude that the oxygen distribution in the oxides is inhomogeneous in the beginning of in-diffusion. This inhomogeneity is due to the fast saturation of oxygen (i.e., $\delta = 0$) in the outer layer of each grain and the high activation energy of diffusion of oxygen through these superconducting "shells" ($E = 1.3 \pm 0.1$ eV), which limit the rate of forming a uniform sample. The shell formation has important effects on the electronic properties of these superconducting oxides, and must be taken into account in attempting to control the oxygen homogeneity in these oxides, especially in single crystals. On the other hand, out-diffusion produces much more homogeneous samples of $\delta > 0$ due to a surface energy barrier $E_{\text{out}} = 1.7 \pm 0.1$ eV.

It is well known that the oxygen deficiency δ in the oxides $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq \delta \leq 1$) plays an important role in determining both the superconducting- and the normal-state electronic properties of these oxides.¹⁻³ A key issue in the studies of the superconducting oxides is how to control the value and the homogeneity of δ . For any meaningful physical measurement, it is crucial to use homogeneous, single-phase samples, so that the discrepancy among sample-dependent experimental results can be resolved. Another important issue is the atomic scale ordering of the oxygen vacancies⁴⁻⁷ which may be related to the normal-state electronic properties and the superconducting mechanisms.

In this work, we began the resistivity experiments on ceramic samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $\delta \approx 0$ and $T_c = 91$ K. The grain size of these samples is typically a few microns. Details of the sample preparation and the resistivity measurements have been given elsewhere.³ To control the oxygen deficiency δ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, we annealed the oxides of $\delta \approx 0$ in 100% He atmosphere at a constant rate ($3^\circ\text{C}/\text{min}$) from room temperature up to a chosen temperature T_f , and then we furnace-cooled the oxides in He ambient back to room temperature. By selecting the final temperature T_f , the oxygen deficiency δ can be controlled for each sample, and the value of δ can be determined from the weight loss measurements. *In situ* He annealing resistivity data for various δ values of one sample ($\delta = 0.18, 0.34, 0.41, 0.52, 0.57, 0.66$, and 0.73), with each run starting from $\delta = 0$, are shown in Fig. 1. The curves show that the resistivity increases linearly with temperature for $T \leq 350^\circ\text{C}$. The departure from the linear temperature dependence for $T > 350^\circ\text{C}$ is indicative of the onset of oxygen out-diffusion.⁸⁻¹⁰ The carrier density decreases with increasing oxygen deficiency, which therefore increases the resistivity.¹⁻³ In the beginning of cooling, since the temperature is still sufficiently high, oxygen keeps diffusing out and the resistivity keeps rising. After the temperature is lower than 350°C , the resistivity for all the curves with $\delta < 0.6$ decreases monotonically with decreasing temperature. In contrast, the cooling curve for

$\delta = 0.73$ exhibits an increase in resistivity with decreasing temperature until $T \approx 70^\circ\text{C}$ where we speculate that an order-disorder transformation occurs. We note that a bend in the resistivity occurs at about 70°C for all the curves with $\delta > 0.2$. More details regarding this anomaly at $T \approx 70^\circ\text{C}$ will be reported separately.

The differences in the resistivity at various temperatures [$\Delta\rho(\delta, T) = \rho(\delta, T) - \rho(0, T)$] before and after the He annealing are shown in Fig. 2. The quantity $\Delta\rho$ is approximately linear with δ for $\delta < 0.4$, and then begins to increase nonlinearly for $\delta > 0.4$. The nonlinear behavior is further enhanced as temperature increases. This obser-

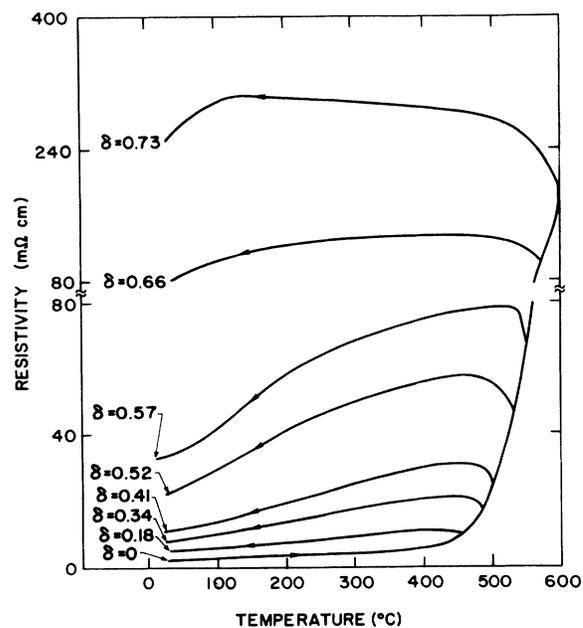


FIG. 1. A series of *in situ* resistivity vs temperature curves for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in He ambient. The heating rate is $3^\circ\text{C}/\text{min}$, and the final δ values were determined from the weight-loss measurements.

vation is consistent with the earlier report on the residual resistivity data extrapolated from the low-temperature resistivity measurements,³ but is significantly different from the results by Cava *et al.* who reported a decrease in the resistivity for $\delta \approx 0.4$ (Ref. 2). It should be emphasized that our measurements were performed on the same sample, and resistivity data for each δ value were taken more than once to assure the reproducibility. The nonlinear increase in the resistivity for $\delta \geq 0.5$ is consistent with the findings of other dramatic changes in the electronic and structural properties of the oxides.^{1-3,6} In considering the resistivity $\rho = m^*/(ne^2\tau)$, where m^* denotes the effective mass, the large enhancement in ρ as δ increases may be attributed to the increase of the defect-scattering rate ($1/\tau$), in addition to the decrease in

the carrier concentration (n). However, details of the transport mechanisms and the temperature dependence of $\Delta\rho(\delta, T)$ are still to be explained.

The out-diffusion of oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is independent of δ and is limited by a 1.7 eV activation energy barrier, which is larger than that of the in-diffusion.^{8,9} Consequently, the final δ distributions in the slow furnace-cooled and He-annealed samples should be uniform because of the fast oxygen diffusion in the CuO planes with $\delta > 0$. Assuming that both the following relations $d\delta \propto \exp(-E_{\text{out}}/k_B T) dt$ and $k_B T_i \ll E_{\text{out}}$ are valid, where $E_{\text{out}} = 1.7$ eV denotes the out-diffusion activation energy^{8,9} and T_i is the initial temperature, we may relate the δ value to the given final temperature T_f by the following formula:

$$\delta \propto \sum_{j=h,c} \int_{T_i}^{T_f} \exp\left(-\frac{E_{\text{out}}}{k_B T}\right) \frac{dT}{a_j} \approx \frac{k_B T_f^2}{E_{\text{out}}} \exp\left(-\frac{E_{\text{out}}}{k_B T_f}\right) \left(\frac{1}{a_h} + \frac{1}{a_c}\right), \quad (1)$$

where a_h and a_c denote the heating and cooling rates, respectively. Equation (1) qualitatively describes the increase of final δ with the increase of the final He-annealing temperature.

Figure 3 shows the resistivity recovery curves in oxygen ambient as a function of temperature for various initial δ values. The resistivity initially increases with the temperature and exhibits a bend at $T \approx 70^\circ\text{C}$ except for the curve with $\delta < 0.2$. At higher temperatures, the increase in the resistivity slows down due to the effect of oxygen in-diffusion, reaches the maximal resistivity T_{max} , and then begins to drop due to a fast oxygen in-diffusion. As oxygen saturates the sample at T_{min} (i.e., $\delta \approx 0$), the resistivity reaches its minimum, and then increases with temperature. We have already reported in a separate paper¹⁰ that the activation energy for the oxygen in-diffusion can be obtained from the rate dependence of both T_{max} and T_{min} , and that T_{min} only depends on the heating rate, not on the initial δ value. As shown in Fig. 3, our data are consistent with the prediction that T_{min} is independent of the initial δ (Ref. 10). Furthermore, the resistivity can al-

ways be reduced to the initial value at $\delta = 0$ for all He-annealed samples by means of the oxygen annealing. The superconducting transition temperature of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxides has also been shown to be totally recovered after the oxygen annealing process.⁸⁻¹⁰

In our previous work,¹⁰ we obtained the same activation energy ($\Delta E = 1.3 \pm 0.1$ eV) from the rate dependence of both the T_{min} and the T_{max} . This result suggests that in the slow oxygen annealing process, the outer shell of a grain can reach its oxygen solubility very rapidly, thereby slowing down the subsequent oxygen in-diffusion process and resulting in an inhomogeneous sample. This finding is extremely important from a processing viewpoint. Thus, we show in Fig. 4(a) a schematic illustration of the oxygen in-diffusion; and we describe in the following the δ

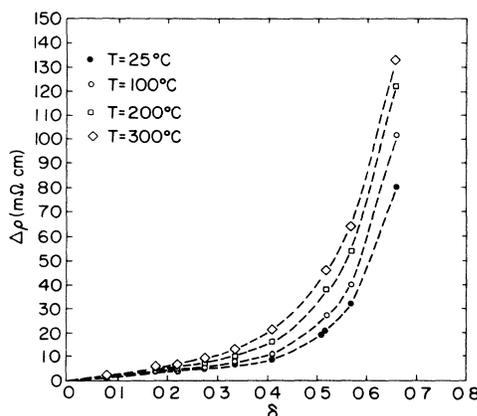


FIG. 2. The resistivity variations $\Delta\rho(\delta, T) = \rho(\delta, T) - \rho(0, T)$ as a function of δ at various temperatures. Note that $\Delta\rho(\delta)$ begins to increase nonlinearly with δ for $\delta > 0.4$.

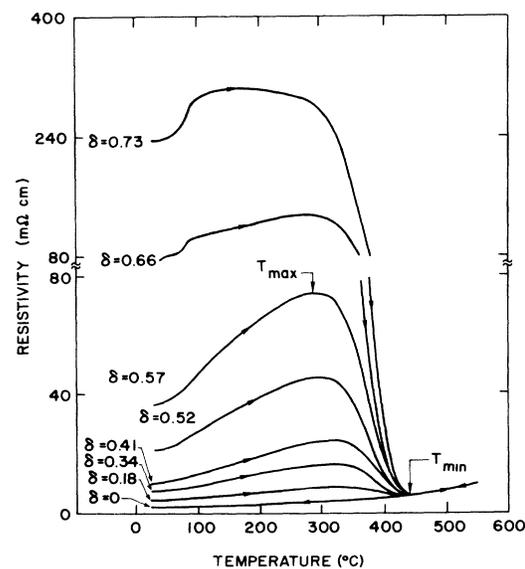


FIG. 3. A series of resistivity recovery curves vs temperature for various initial δ values in oxygen ambient. Note that the temperatures T_{min} where the minimal resistivity occurs are independent of the initial δ values. The heating rate is $3^\circ\text{C}/\text{min}$.

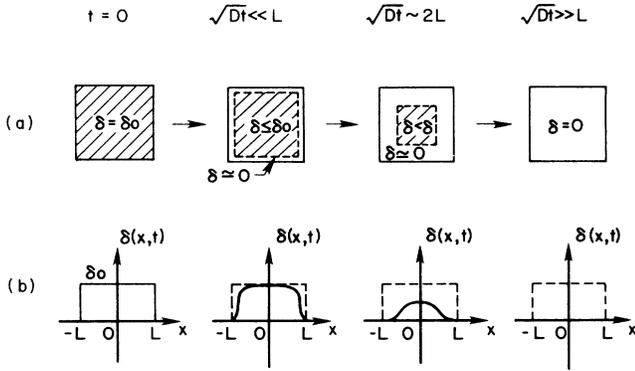


FIG. 4. (a) The time evolution of the oxygen distributions within a grain. Note that the outer portion of the grain reaches its oxygen solubility ($\delta=0$) much faster than the inner region. (b) The spatial variations of the oxygen distribution function $\delta(x,t)$ at a constant temperature.

distribution as a function of the position (x) and time (t) during the in-diffusion process.

Neglecting the in-plane anisotropy effect,^{4,11} we may simplify the oxygen diffusion by a one-dimensional process. The continuity equation for the oxygen deficiency at a constant temperature is

$$\frac{\partial \delta}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \delta}{\partial x} \right), \quad (2)$$

where the diffusion coefficient D is related to the activation energy E by the formula $D = D_0 \exp(-E/k_B T)$, and D_0 is a preexponential factor. The initial conditions for a sample after He annealing and with oxygen deficiency δ_0 are $\delta(x,t=0) = \delta_0$ for $0 \leq |x| \leq L$ and $\delta(x,t=0) = 0$ for $|x| > L$, where L is the average radius of a grain [see Fig. 4(b)]. The solution of Eq. (2) which satisfies the initial conditions is

$$\delta(x,t) = \delta_0 \operatorname{erf} \left(\frac{L - |x|}{\sqrt{Dt}} \right), \quad (3)$$

$$l^2 = \int D dt = \frac{D_0}{a_h} \int_{RT}^{T_{\max}} \exp(-E/k_B T) dT \approx \frac{D_0}{a_h} \frac{k_B T_{\max}^2}{E} \exp(-E/k_B T_{\max}), \quad (4)$$

where l denotes the diffusion length, RT denotes room temperature, and a_h the heating rate. Using $E = 1.3$ eV, $a_h = 3^\circ\text{C}/\text{min}$, $T_{\max} = 319^\circ\text{C}$, and assuming $D_0 \approx 1$ cm^2/sec , we obtain $l = 7 \times 10^{-5}$ cm from Eq. (4), in good agreement with the estimate obtained directly from the weight-loss measurements. It should be noted that for a given averaged grain size, the preexponential factor D_0 can be estimated from the above quenching experiment and using Eq. (4), provided that the shell model is valid.

The picture described above can explain a puzzling phenomenon observed in oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples. Zero resistivity has been obtained in many $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with nominal $\delta \geq 0.5$, yet the diamagnetic (or shielding) signals of these samples were less than 5%

where $\operatorname{erf}(x)$ denotes the error function and is defined as $\operatorname{erf}(x) = (2/\sqrt{\pi}) \int_0^x \exp(-y^2) dy$. It should be noted that the solution in Eq. (3) is obtained under the assumption that the diffusion coefficient D is independent of x . The spatial distributions of δ as time evolves are shown in Fig. 4(b).

The physical significance of Eq. (3) becomes clear as we consider the following x dependence of the error function. For $x = L - \epsilon$, where $0 < \epsilon \ll L$, the oxygen deficiency $\delta(x,t)$ decreases rapidly from $\delta(x,t=0) = \delta_0$ to $\delta(x,t) < 0.1\delta_0$ for $\sqrt{Dt} \geq 10\epsilon$. Since ϵ can be chosen to be arbitrarily small, the fast decrease of δ for the outer portions of a grain which are exposed to oxygen atmosphere gives rise to an inhomogeneous oxygen distribution during the initial period of annealing, as shown in Fig. 4(b). Consequently, for a large grain such as a single crystal with size L normal to the c axis, the central portion of the crystal cannot reach its oxygen solubility (i.e., $\delta=0$) until $\sqrt{Dt} > 2L$. Using the activation energy $E = 1.3 \pm 0.1$ eV from our previous work (Ref. 10), $D_0 \approx 1$ cm^2/sec , and a typical size of $2L \approx 0.5$ mm for a single crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, we can estimate the required annealing condition for producing a uniform $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystal with $\delta=0$; at $T = 450^\circ\text{C}$, the time needed is at least 10 days.

In order to investigate the self-consistency of the above description of the inhomogeneous oxygen distributions during a slow oxygen in-diffusion, we have annealed a sample with $\delta=0.4$ in oxygen ambient up to T_{\max} , and then quickly quenched the sample to room temperature. This procedure is to assure that only the outer portion of the sample is saturated with oxygen, since the temperature range of $T \leq T_{\max}$ is expected to be insufficient for a complete oxygen in-diffusion. After quenching the sample, the weight gain of the sample was 0.06%. Assuming that the outer portions of the grains of the sample formed a "shell" of $\delta=0$, we estimated the thickness of the "shell" to be approximately 8×10^{-5} cm for an average grain diameter of 3×10^{-4} cm. On the other hand, we can estimate the thickness of the shell from the following calculation:

(Refs. 12 and 13). Since the volume fraction 5% is well below the percolation threshold for three-dimensional superconductors,¹⁴ we attribute the observed zero resistivity to the existence of superconducting "shells" of the grains, which are formed even by exposing the oxygen-deficient samples to ambient air. Figure 5 shows a typical example of an oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $\delta \approx 0.6$, in which zero resistivity is achieved at $T_c \approx 4$ K, although the volume fraction of the superconducting material is extremely low.

Although we have discussed the oxygen distribution $\delta(x,t)$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ during a slow oxygen in-diffusion process, the direct relation between the resistivity variation and the δ distribution is still to be unraveled. If, for

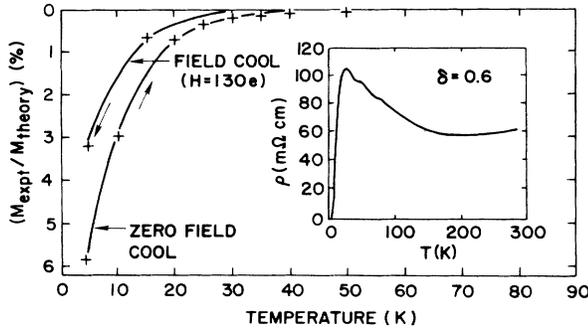


FIG. 5. The diamagnetism of a porous ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxide with $\delta \approx 0.6$ is shown as a function of temperature for both the zero-field cool and the field cool ($H = 13$ Oe) data. The resistivity vs temperature data for the same sample are shown in the inset. Note that although the volume fraction of the superconducting material is very small ($< 6\%$), a complete resistivity transition is achieved at $T_c \approx 4$ K.

simplicity, we take the relation $\Delta\rho \propto \delta$ for small δ , the resistivity may be related to δ by the following formula:

$$\rho = \rho(\delta, T) = \rho_0 + A_0 T + A_1 \delta(T), \quad (5)$$

where A_0 and A_1 are positive constants. Using Eqs. (3) and (5), we may explain the decrease in the resistivity between T_{max} and T_{min} in Fig. 3 from the following consideration: In the limit $(L - |x|)/\sqrt{Dt} < 1$, the temperature dependence of δ in the oxygen in-diffusion process can be simplified by the following expression:

$$\delta(T) \approx \frac{2}{\sqrt{\pi}} \delta_0 \frac{\langle L - |x| \rangle_x}{\sqrt{(D_0 a_h)}} [T^{-1/2} \exp(E/2k_B T)], \quad (6)$$

where $\langle L - |x| \rangle_x$ denotes the spatial average, and δ_0 denotes the initial oxygen deficiency. Thus, the fast decrease in the resistivity from T_{max} to T_{min} and the steeper slope for larger δ_0 can be qualitatively explained from Eqs. (5) and (6).

If we assume that the temperature dependence of $\rho(\delta, T)$ in Eq. (5) is dominated by the electron-phonon scattering, i.e., $\rho(\delta, T) - \rho_0 = (A_0 + A_1 \delta/T)T$, the carriers involved in the conduction mechanism may be decomposed into two types of carriers n_0 and n_δ , where $n_0 \propto A_0^{-1}$ and $n_\delta \propto A_1^{-1} T^{3/2} \exp(-E/2k_B T)$. The "thermally activated" carrier concentration n_δ , which resembles the temperature dependence of the carrier densities in semiconductors, results from filling up the oxygen vacancies during the oxygen in-diffusion; while the "normal" carrier concentration n_0 is associated with the "intrinsic" metallic properties of the originally oxygen-deficient sample. A systematic study of $\rho(\delta, T)$ is now in progress in order to obtain further physical understanding of the temperature coefficients A_0 and A_1 , as well as the relation of $\rho(\delta, T)$ to the superconductivity of these oxides.

In conclusion, we have studied the resistivity behavior of the ceramic oxides $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as oxygen diffuses in and out of the samples. A homogeneous oxygen distribution at a given δ value can be achieved by performing the out-diffusion anneal in He. In contrast, the oxygen distributions during in-diffusion are inhomogeneous in nature. The inhomogeneity has important effects on the electronic properties of these superconducting oxides. Since the oxygen distributions cannot be homogenized without a sufficient anneal, it is very important to be aware of the effects of sample inhomogeneity on any physical measurement.

- ¹J. D. Jorgensen, B. W. Veal, W. K. Kowk, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and P. Paulikas, Phys. Rev. B **36**, 5731 (1987).
- ²R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Phys. Rev. B **36**, 5719 (1987).
- ³S. I. Park, C. C. Tsuei, and K. N. Tu, Phys. Rev. B **37**, 2305 (1988).
- ⁴J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. V. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).
- ⁵G. Van Tendeloo, H. W. Zandbergen, and S. Amelickx, Solid State Commun. **63**, 603 (1988).
- ⁶L. T. Willie, A. Berera, and D. de Fontaine, Phys. Rev. Lett. **60**, 1065 (1988).
- ⁷L. T. Wille and D. de Fontaine, Phys. Rev. B **37**, 2227 (1988).

- ⁸K. N. Tu, S. I. Park, and C. C. Tsuei, Appl. Phys. Lett. **51**, 2158 (1987).
- ⁹K. N. Tu, C. C. Tsuei, S. I. Park, and A. Levi, Phys. Rev. B **38**, 772 (1988).
- ¹⁰K. N. Tu, N. C. Yeh, S. I. Park, and C. C. Tsuei, Phys. Rev. B **38**, 5118 (1988).
- ¹¹S. W. Tozer, A. W. Kleinsasser, T. Penney, D. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1768 (1987).
- ¹²R. Beyers, E. M. Engler, P. M. Grant, S. S. P. Parkin, G. Lim, M. L. Ramirez, K. P. Roche, J. E. Vazquez, V. Y. Lee, and R. D. Jacowitz, Mater. Res. Soc. Symp. Proc. **99**, 77 (1988).
- ¹³R. J. Cava, B. Batlogg, A. P. Ramirez, D. Werder, C. H. Chen, E. A. Rietman, and S. M. Zahurak, Mater. Res. Soc. Symp. Proc. **99**, 19 (1988).
- ¹⁴For example, see D. Stauffer, Phys. Rep. **54**, 3 (1979).