

## Oxygen diffusion in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxides in ambient helium and oxygen

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(Received 22 February 1988)

*In situ* resistivity measurement has been used to monitor diffusion of oxygen in and out of bulk and polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in ambient  $\text{O}_2$  and He atmospheres. The out-diffusion of oxygen from the oxide is found to be independent of  $\delta$  and its rate is surface-reaction limited with an activation energy of 1.7 eV. The in-diffusion depends strongly on  $\delta$ ; the activation energies of the process at  $\delta \cong 0$  and  $\delta = 0.38$  are 1.1 and 0.48 eV, respectively. The latter is taken to be the activation energy of motion and the former, the activation energy of diffusion. On the basis of the kinetic and published structural information, we have proposed a defect mechanism in the CuO plane for the anisotropic diffusion of oxygen in the oxide.

The superconducting properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxide are known to depend on oxygen stoichiometry, e.g.,  $T_c$  decreases with increasing  $\delta$ .<sup>1-3</sup> The normal-state electrical conduction, magnetic behavior, orthorhombic-to-tetragonal transition, and structural twins have also been found to be much affected by varying  $\delta$ .<sup>4-8</sup> The parameter  $\delta$ , however, can be easily changed by a moderate heat treatment in an inert or oxygen atmosphere due to the rapid anion diffusion in the defective structure. It is recognized that to process and to sustain the superconducting state, a tight control of oxygen solution and diffusion in the oxide is crucial. The kinetics of oxygen motion has become a key issue in understanding the structure-properties correlation, chemical stability of interfacial contact to metals, and perhaps the mechanism of superconductivity of the oxide.

Since oxygen is absent in the Y plane in the lattice and the Y-O bond is extremely strong, the diffusion of oxygen normal to the CuO plane is expected to be much slower than in-plane diffusion. Neutron diffraction analysis has shown that vacant oxygen sites in oxygen-deficient oxides are located entirely in the CuO plane between two BaO planes.<sup>1,9</sup> The diffusion of oxygen in the oxide becomes highly anisotropic and is practically two dimensional, so the diffusion mechanism is extremely interesting.

Because of the strong dependence of the normal-state conduction on  $\delta$ ,<sup>4,5</sup> we have chosen *in situ* resistivity measurements to study the oxygen content as well as the dynamics of oxygen diffusing in and out of the oxide. We found that this has sufficient sensitivity for monitoring rapid rate changes of  $\delta$  in response to oxygen partial-pressure changes. The rates of out-diffusion and in-diffusion of oxygen are quite different upon annealing the oxide at temperatures above 350°C, respectively, in ambient He and  $\text{O}_2$ ; the in-diffusion is much faster.<sup>4</sup> This asymmetrical behavior is important concerning the stability of the oxide, since it indicates an irreversible chemical process of oxygen at the oxide surfaces. In this paper we report our study of the activation processes which quantifies this asymmetrical behavior and also the mechanism of anisotropic diffusion of oxygen in the oxide. A defect mechanism of diffusion is proposed. The experimental

procedure of sample preparation and *in situ* resistivity measurement has been reported elsewhere.<sup>4</sup>

In Fig. 1, resistivity changes of a bulk and polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  sample upon heating in He (the solid curve) from room temperature to 530°C and cooling in  $\text{O}_2$  (the dotted curve) from 530°C to room temperature are shown. The broken curve indicates the temperature changes during the annealing. Three quantities, resistivity ( $\rho$ ), time ( $t$ ), and temperature ( $T$ ) were measured simultaneously. The controlled heating rate was about +0.5°C/min. and the uncontrolled cooling rate was initially about -3°C/min and gradually slowed down with temperature. The resistivity drop upon switching from ambient He to  $\text{O}_2$  at 530°C is dramatic; within a couple of minutes in  $\text{O}_2$  the entire resistivity increase due to the annealing in He has essentially been recovered. The rates of resistivity change at the point of switching between the two ambients are asymmetrical. The slow departure of

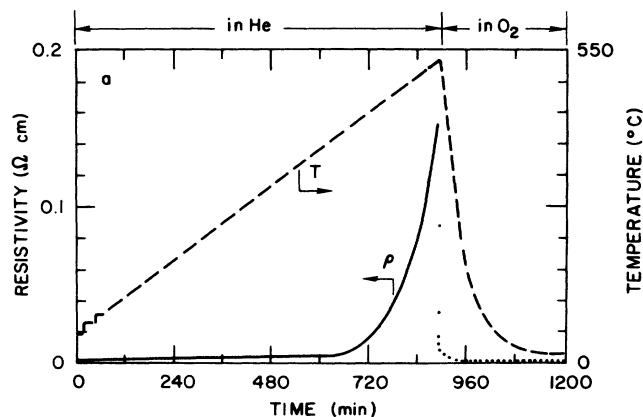


FIG. 1. The solid curve shows the resistivity change as a function of time of a bulk  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxide sample ( $1.3 \times 0.5 \times 0.1 \text{ cm}^3$ ) annealed in He at a heating rate of 0.54°C/min from room temperature to 530°C, and the dotted curve shows the resistivity change upon furnace cooling back to room temperature in ambient  $\text{O}_2$ . Before the annealing, the oxide had a  $T_c = 91 \text{ K}$  ( $\delta = 0$ ). The broken curve shows the temperature change.

oxygen from the oxide in the He annealing was interpreted by assuming a reaction barrier which limits the departure flux at the oxide surface (or grain boundaries). The activation energy of the barrier can be determined by knowing the departure rate as a function of temperature. It has been shown that the rates,  $d\rho/dt$ , as measured by performing isothermal annealing at 370, 390, 410, 425, and 440°C in He are constants, and an activation energy of  $1.7 \pm 0.1$  eV of the barrier has been obtained.<sup>4</sup>

Information on the temperature dependence of  $d\rho/dt$  can also be derived from the curves of constant heating rate shown in Fig. 1 provided that the heating rate is sufficiently slow. The advantage of adopting this procedure is that it is a single measurement as compared to performing several isothermal annealings. In the annealing from room temperature to 350°C as shown in Fig. 1, the resistivity is a function of temperature only,  $\rho = \rho(T)$ , and the temperature coefficient of resistivity,  $d\rho/dT$ , is constant in this temperature range. Hence,  $d\rho/dt$  is also constant when measured during a constant heating rate of  $dT/dt$ . For the annealing at temperatures above 350°C in He, we have  $\rho = \rho(T, t)$  and

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial T} \frac{dT}{dt} + \frac{\partial\rho}{\partial t} \quad (1)$$

The values of  $d\rho/dt$  as a function of  $T$  can be determined by measuring, respectively,  $\partial\rho/\partial T$  and  $\partial\rho/\partial t$  from the data shown in Fig. 1 with a subtraction of the linear temperature coefficient of resistivity. Figure 2 shows a plot of  $\ln(d\rho/dt)^{-1}$  vs  $1/k_B T$  from 350 to 530°C on the basis of the data given in Fig. 1. The average slope of the portion of the curve from 370 to 440°C is 1.75 eV, which is in very good agreement with the earlier measurement of  $1.7 \pm 0.1$  eV. The transition of slope along the curve near 460°C shows the orthorhombic-to-tetragonal phase transition of the oxide.<sup>5-7</sup> Above 460°C, the slope is nearly the same as below, indicating that the activation energy for oxygen to depart from the tetragonal phase is about the same as that from the orthorhombic phase.

We have carried out annealings at 0.3 and 3°C/min in He in order to check the rate dependence of the measure-

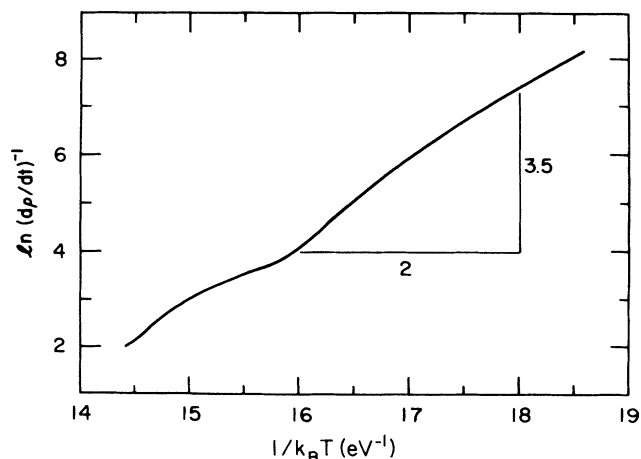


FIG. 2. The plot of  $\ln(d\rho/dt)^{-1}$  vs  $1/k_B T$  based on the data shown in Fig. 1 and the use of Eq. (1).

ment. We have observed a strong dependence of the orthorhombic-to-tetragonal transition on the heating rate; the slower the heating rate, the lower the transition temperature. The latter was observed to be 440 and 510°C for the 0.3 and 3°C/min, respectively. The  $\rho$  vs  $T$  curves for the 0.3°C/min and the 0.5°C/min overlap each other closely and the activation energies obtained by plotting  $\ln(d\rho/dt)^{-1}$  vs  $1/k_B T$  were the same. The 3°C/min curve showed a slower variation of  $\rho$  vs  $T$  and the activation energy obtained was about 1.5 eV, indicating that the rate is not slow enough. We are now extending the measurement to study the effect of oxygen partial pressure and crystal orientation of oxide on the out-diffusion behavior of oxygen in order to understand the origin of the surface barrier and also any factor which might lower the barrier. The desorption of oxygen from an oxide surface in general requires bond breaking, surface diffusion, and the formation of oxygen molecules. The details of the process require a careful study of the surface chemistry of the oxide.<sup>10</sup>

Since in-diffusion of oxygen is rapid, it can be studied at lower temperatures than out-diffusion. We have annealed samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  where  $\delta = 0.38$  in  $\text{O}_2$  at 360, 310, 260, and 210°C and the corresponding rates of resistivity decrease were measured. The samples having  $\delta = 0.38$  were prepared by annealing samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with  $\delta \approx 0$  in He at 3°C/min from room temperature to 500°C, then they were immediately furnace cooled to the annealing temperature of 360°C (or the others) and kept at the temperature. The amount of weight loss before the switching to  $\text{O}_2$  ambient was measured to be 0.91% corresponding to  $\delta = 0.38$ . Since the switching of ambients was performed by turning a valve without interrupting the resistivity measurement or moving the sample, we assume that the sample surface is uncontaminated for in-diffusion. In Fig. 3, the temperature profile and resistivity change of a sample which has experienced the 3°C/min annealing in He and the 310°C isothermal annealing in  $\text{O}_2$  are shown. In  $\text{O}_2$  ambient, the resistivity dropped rapidly in the beginning, yet it slowed down very much at the end. We shall consider these two extreme cases.

At the beginning of in-diffusion of oxygen, where  $\delta = 0.38$ , the oxide has a high concentration of oxygen empty sites in the CuO planes. The crystal lattice approaches the tetragonal symmetry where its  $a$  axis and  $b$  axis become nearly equal so the oxygen sites in the plane are equivalent, and the  $c$  axis expands. Thus, the barrier to diffusion of oxygen in the CuO plane is the activation energy of motion only, i.e., no formation of defects is required. By plotting the initial slopes of resistivity drop at the four annealing temperatures in logarithmic scale against  $1/k_B T$ , we obtained a value of  $0.48 \pm 0.05$  eV as shown in Fig. 4. The difference between the activation energies of 1.7 eV for out-diffusion and 0.48 eV for in-diffusion quantifies the asymmetrical behavior shown here in Fig. 1 as well as Fig. 3 and Ref. 4.

At the end of the annealing (where  $\delta \approx 0$ ), the diffusion of oxygen is much slower than at the beginning. This is because at the end there are few excess vacancies or empty sites in the oxygen sublattice. Besides, the  $c$  axis con-

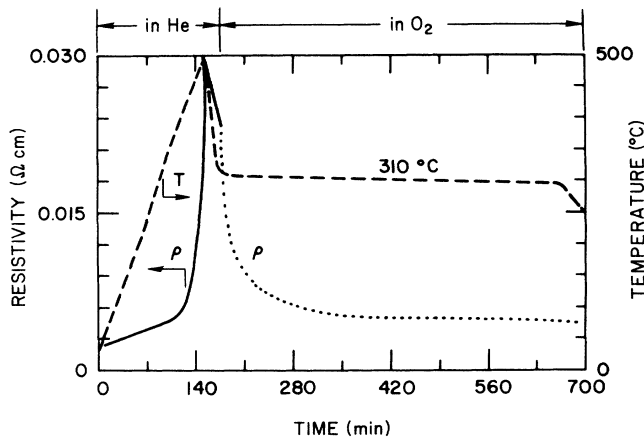


FIG. 3. The broken curve shows the profile of annealing temperature of a bulk sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \approx 0$ ) starting from room temperature to  $500^\circ\text{C}$  at a heating rate of  $3^\circ\text{C}/\text{min}$  and followed by furnace cooling to  $310^\circ\text{C}$  in He. Then the annealing temperature was kept at  $310^\circ\text{C}$  and at the same time the ambient was switched to  $\text{O}_2$ . The solid and dotted curves show the corresponding resistivity changes in He and  $\text{O}_2$ , respectively. In  $\text{O}_2$ , the initial change of resistivity was rapid, but at the end the change was very sluggish.

tracts and  $a$  axis and  $b$  axis are no longer equal. We have determined the activation energy of oxygen diffusion near  $\delta \approx 0$  to be  $1.1 \pm 0.1$  eV by measuring the times needed to reduce a fixed amount of resistivity at the end of the annealings. The value is close to those reported.<sup>11-14</sup>

By taking the difference between 1.1 and 0.48 eV, we obtain 0.6 eV for the formation energy of a defect which mediates oxygen diffusion. A defect mechanism is proposed because the in-diffusion of oxygen consumes empty lattice sites and it is a nonconservative reaction. The diffusion occurs mainly in the CuO plane and is highly anisotropic. The anisotropic behavior is supported by the general observation that it takes a much longer time at the same temperature to deplete (or replenish) oxygen from (or into) epitaxial films or single crystals than polycrystalline oxides. Nevertheless, we note that the diffusion depends strongly on  $\delta$ , similar to other nonstoichiometric oxides.<sup>15</sup> The activation energy of oxygen diffusion in a superconducting oxide with  $\delta = 0$  should be slightly higher than our measured value of 1.1 eV, since our technique is based on kinetic behavior of changing  $\delta$  rather than at  $\delta = 0$ . At  $\delta > 0$ , the effect of excess vacancies will lower the activation energy. However, at  $\delta = 0$ , the activation energy of motion could be slightly higher than 0.48 eV because of the contraction of the  $c$  axis. The measured activation energy agrees with the observation as shown in

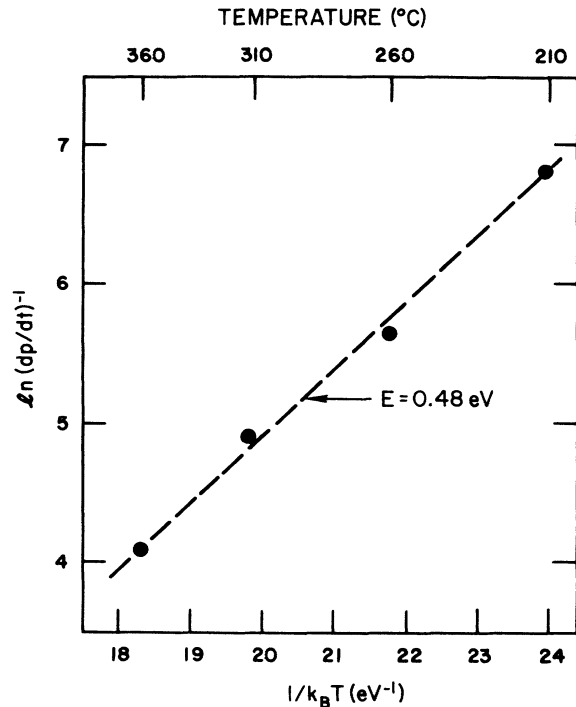


FIG. 4. The plot of  $\ln(dp/dt)^{-1}$  vs  $1/k_B T$  where  $dp/dt$  is the initial rate change of resistivity of a sample  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \approx 0.38$ ) annealed isothermally in  $\text{O}_2$  at 360, 310, 260, and  $210^\circ\text{C}$ .

Fig. 1 that at  $500^\circ\text{C}$  in ambient  $\text{O}_2$ , it takes about 100 sec to replenish all the oxygen lost in the sample of grains of  $5\text{--}10\ \mu\text{m}$  due to the annealing in He.

In conclusion, we have demonstrated that the out-diffusion of oxygen is much faster than the in-diffusion of oxygen in annealing  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxides in ambient He and  $\text{O}_2$ , respectively. The out-diffusion is independent of  $\delta$  and is surface-reaction limited with an activation energy of  $1.7 \pm 0.1$  eV. In-diffusion depends strongly on  $\delta$  and at  $\delta = 0.38$  it is characterized at the beginning by an activation energy of  $0.48 \pm 0.05$  eV, and at the end by an activation energy of  $1.1 \pm 0.1$  eV. The former corresponds to the activation energy of motion of oxygen in the oxide and the latter to the diffusion of oxygen in the oxide, which consists of energies of formation and motion. The diffusion is anisotropic and the mechanism of diffusion of oxygen in the CuO plane has been proposed to occur via a lattice defect.

The authors would like to thank J. Berosh for sample preparation and R. D. Thompson for the automation of the resistivity measurement.

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