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Concentration dependence of oxygen diffusivity in $GdBa_2Cu_3O_{6+y}$ films

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Oxygen diffusion in the perovskite-related nonstoichiometric oxide $GdBa_2Cu_3O_{6+y}$ has been investigated *in situ* on thin films using high-temperature resistive measurements. Except for a step change in the vicinity of the orthorhombic-tetragonal structural transition, the diffusivity shows no concentration dependence over a wide interval $(0.3<y<0.8)$. The activation energy is constant in the whole measured interval $(E_o \approx 1.2\ \mathrm{eV})$. It is proposed that oxygen diffusion propagates via vacancy mechanism, involving the oxygen atoms at the extremes of the -O-Cu-O- chains in the basal plane. [S0163-1829(98)07309-3]

Recently, investigations on oxides have evoked a considerable interest due to their unusual electrical, magnetic, and structural properties. In this context, the nonstoichiometric oxides, in which the oxygen content can be easily changed in some interval, are particularly intriguing: the oxygen variations lead to drastic changes of the material properties. It follows that the control of the oxygen content, i.e., the oxygen diffusion properties, is crucial for the understanding and applications of these materials.

The triple perovskites $MBa_2Cu_3O_{6+y}$ ($M=\mathrm{Y}$, rare earth) are convenient model objects for studying the general trends of oxygen diffusion in nonstoichiometric oxides. Due to a very strong dependence of the electrical resistance on oxygen content, one can investigate the diffusion process by performing simple resistive measurements. Furthermore, high quality epitaxial films of $MBa_2Cu_3O_{6+y}$, which are routinely available now, provide samples with the geometrical definition and chemical homogeneity necessary to perform such measurements.

In spite of a number of articles on the subject published in the last years (see, for example, Ref. 1) some important features of oxygen diffusion mechanism in $MBa_2Cu_3O_{6+y}$, such as the nature of the barrier E_o or the oxygen paths' probabilities, remain unclear. In our opinion, the dependence of oxygen diffusivity D on oxygen concentration is one of the keystones to understand the diffusion process. A few experimental groups reported a linear Arrhenius behavior of D with temperature at constant oxygen pressure.[2–4] This is a strong, though indirect, proof of the independence of D versus oxygen content, which varies along the Arrhenius line. In fact, the Arrhenius equation can be expressed as

$$D=D_0 \exp(-E_0/kT). \tag{1}$$

A linear dependence between $\ln D$ and $1/T$ in the Arrhenius plots can be seen only if both D_o and E_o are independent of temperature and consequently of oxygen content, which is a strong function of temperature and pressure. Other experimental works as well as theoretical calculations indicate, on the contrary, a concentration-dependent diffusivity.[5–7]

This contradiction can be solved only by direct measurements of oxygen diffusion parameters at fixed temperature and variable concentration. We present here a study of oxygen diffusivity in $GdBa_2Cu_3O_{6+y}$ films deposited epitaxially on $NdGaO_3$ (110) substrates. Diffusivity evaluation was based on electrical resistance measurements performed: (a) at fixed temperature $T=880$ K and variable oxygen pressures $P=2\times10^0-10^5$ Pa; (b) at fixed pressure $P=100$ Pa and variable temperature $T=750-950$ K. The investigated pressure and temperature intervals correspond to the oxygen concentrations of 6.3–6.8.

Details on film deposition, their structure and morphology are given elsewhere.[8,9] After film deposition, four gold contacts were deposited by thermal evaporation to which gold wires were directly bonded. The diffusion measurements were performed in a vacuum chamber filled with pure oxygen using a low-mass stainless steel sample holder/heater. Its thermal response was carefully calibrated at any given working pressure by means of thin-film gold thermometers deposited on identical substrates. We estimate the temperature variation during each series of measurements to be lower than ± 2 K, while the absolute error can be higher (± 5 K) due to variations of the thermal contact between sample and heater.

It is well known that in the 123 system any variation of the oxygen content y changes the sample resistivity via a charge transfer from the oxygen deficient CuO_y plane, characterized by the presence of the -O-Cu-O- linear chains or fragments of linear chains, to the CuO_2 planes. It should be noted that the isolated oxygen atoms cannot be detected by resistive measurements, as only the finite length chains contribute to the charge transfer.[10] On this basis, a method of oxygen diffusivity evaluation from simple resistive measurements has been developed (for a detailed description, see Yamamoto *et al.*[3]). The oxygen content y depends on temperature and oxygen pressure, varying from 0 (high temperature/low pressure) to 1 (low temperature/high pressure). All our data points were measured in isobaric conditions by imposing small and rapid temperature changes inducing slight y variations. At any given pressure P and temperature T, the sample was heated to $T+30$ K, kept a few hours for its equilibration, and then rapidly cooled to T. The electrical resistance variation in time has been measured by four-point dc technique, and the oxygen relaxation time has been evaluated with the procedure briefly described as follows.

The relaxation time is connected to the diffusion coefficient through the diffusion length L by the relation

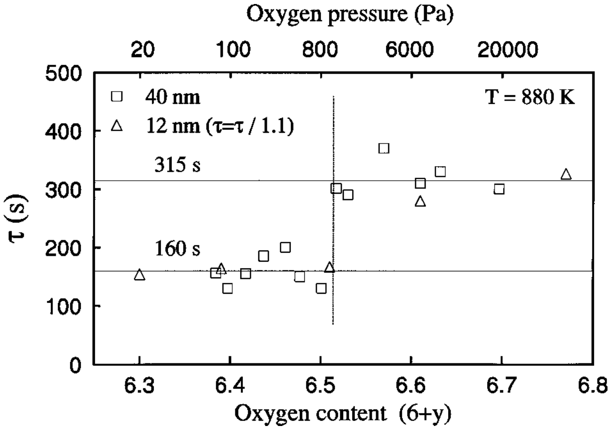

FIG. 1. Diffusion relaxation time τ for two films with different thickness measured at constant temperature $T = 880$ K.

$A(D/L^2) = \tau^{-1}$, where A is a geometrical factor. As resistivity (conductivity) depends exponentially on oxygen content,[3] the value of $\ln R$ as function of time has to be evaluated $[\ln R \sim \exp(-t/\tau)]$. The decay curves consist of two components: fast resistance variations due to the finite heater transition time constant τ_H (about 20 s, slightly changing with pressure), and slower changes caused by oxygen in-diffusion. Therefore, the curves should be fitted by the expression

$$\ln R = A_0 + A_1 \exp(-t/\tau_H) + A_2 \exp(-t/\tau). \qquad (2)$$

The direct fit of data using Eq. (2) is quite dangerous, as different sets of A_1, A_2, τ_H, τ provide roughly similar fitting, the only stable value being A_0. Thus, we use Eq. (2) only to calculate A_0, as the direct substitution of the saturation resistance value is less accurate due to noise. Plotting $\ln(\ln R - A_0)$ vs t, τ is found from the slope of the linear portion of the curve at long times.

Figure 1 shows the dependence of the diffusion relaxation times on oxygen concentration and pressure for a 40 nm-thick (squares) and a 12 nm-thick (triangles) film measured at $T = 880$ K. The relaxation times of the 12 nm sample are divided by a factor of 1.1 to superimpose to the 40 nm sample data. The oxygen concentration has been calculated using data taken from experimental $y = y(P,T)$ phase diagrams for bulk material:[11] the corresponding equilibrium oxygen concentration in thin films might deviate from the bulk value. Such a possible difference, however, should only slightly distort the concentration axis in Fig. 1, not influencing our results to a great extent.

The relaxation time has a distinct steplike behavior with nearly constant, but different values at high and low oxygen concentrations with a sharp change at $y \sim 0.5$, near the orthorhombic-tetragonal (O-T) structural transition.[12,13] The values of the relaxation times in the two sides of the step differ by a factor close to 2, indicating that across the breakpoint the ion diffusivity becomes twice as fast.

To our knowledge the data presented in Fig. 1 are so far the only available data for the diffusivity at constant temperature measured on the same samples throughout a range of y wide enough to cross the O-T transition. For large y values, our data are in agreement with the tracer diffusion coefficient found roughly constant in the pressure range $3 \times 10^3 - 10^5$ Pa.[2]

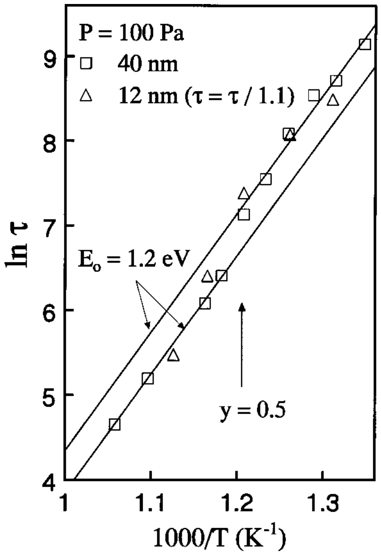

FIG. 2. The Arrhenius plot of τ for the same two films measured at constant pressure $P = 100$ Pa.

Figure 2 shows the Arrhenius plot for the same two films measured at $P = 100$ Pa and different temperatures. The data points may be fitted by a single line, consistent with our previous results.[14] However, assuming that the discontinuity seen at $1000/T \approx 1.2$ is not an artifact, a meaningful linear fit is given by two parallel lines with slope of 1.2 eV and separated by a factor of 1.8. The step discontinuity is observed at $T = 835 \pm 5$ K, which corresponds again to $y \sim 0.5$. The analogy with the results shown in Fig. 1 gives confidence that the two lines' fit is more accurate and the activation energy should be evaluated separately in the two phases leading to a constant value of ~ 1.2 eV. This value is in a good agreement with results reported in literature.[3,15,16] In the P,T phase diagram, the two discontinuity points shown in Figs. 1 and 2 are situated in the tetragonal phase just above the error bar of the O-T transition line detected by neutron diffraction.[12] The constant value of E_o across the structural change is consistent with the observation that at high temperature ($T \geqslant 800$ K) the O-T transformation is a second-order transition with no discontinuity of the cell parameters.[12]

From the results shown in Figs. 1 and 2, it follows that oxygen diffusion in 123 epitaxial films is concentration-independent unless the O-T phase transition occurs. We believe that such a statement can be generalized to bulk samples since what differentiates c-axis oriented films grown on single crystal substrates and any other kind of 123 sample is mainly related to microstructural features and should not affect the intrinsic mechanism of oxygen diffusion. The regularity and stability of the crystal defect system in epitaxial films simply allows precise and reproducible measurements of oxygen diffusion parameters in homogeneous sets of films that would not be possible using other kinds of samples.

Even if our data are by far inadequate to attempt any rigorous microscopic interpretation, it is possible to suggest a

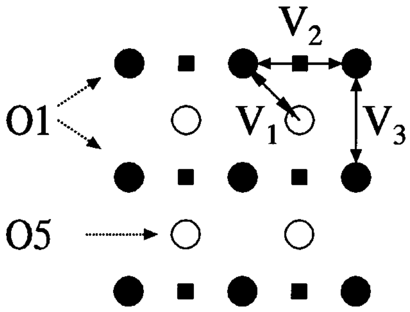

FIG. 3. Visualization of the main O-O interactions in the CuO_y plane ($y=1$, orthorhombic symmetry). Squares indicate Cu atoms, solid circles are for occupied oxygen sites while open circles are for vacant oxygen sites.

qualitative model that accounts for the main results of the experiments: constant activation energy, step discontinuity of diffusivity near transition, and concentration-independent diffusivity in each structural phase.

The constant value of E_o at the two sides of the step indicates that the mechanism of the single oxygen ion jump remains the same. The observed increase of diffusivity by a factor of 2 can be explained on a macroscopic scale by taking into account that in tetragonal phase the oxygen atoms are dynamically distributed on all the possible oxygen sites, while only half of the sites can be occupied in the orthorhombic configuration. In Fig. 3 the interactions of the oxygen ions in the CuO_y plane are indicated. The oxygen distribution is accounted for by three main O-O interactions: strong repulsion V_1 (nearest-neighbor O-O interaction), attraction V_2 (copper mediated O-Cu-O interaction), and weak repulsion V_3 (next-nearest-neighbor O-O interaction). Due to strong V_1 repulsion, the system avoids to place two oxygens on nearest adjacent sites while, due to V_2 attraction, a vacant oxygen site at one end of the -O-Cu- chain is a minimum energy position for a moving oxygen atom. V_1 and V_2 are responsible for the -O-Cu-O- chains' creation, while V_3 favors their orientation along some given axis b, originating the orthorhombic distortion.[17]

The structural transition from the orthorhombic to the tetragonal phase does not necessarily need the complete destruction of chains: for example, at $y=0.5$ the copper and oxygen ions can be arranged in short chain fragments oriented parallel to the b axis in orthorhombic phase [Fig. 4(a)] and randomly oriented along a or b in tetragonal phase [Fig. 4(b)]. The existence of short chain fragments is confirmed by high-resolution electron microscopy studies[18,19] and by room-temperature structural relaxation of quenched tetragonal samples.[20]

Defining a single oxygen jump as a motion into a nearest-neighbor empty site, due to high V_1 repulsive energy, the most convenient jumps are those ending in final sites with no occupied nearest neighbors. In dilute enough cases, decreasing y the number of possible jumps of this kind increases. The arrows in Figs. 4(a) and 4(b) indicate all these jumps in the idealized orthorhombic and tetragonal CuO_y planes, respectively. It is reasonable to consider that the barrier energy responsible for the jump probability is the same in both cases. However, the total number of jumps is rather different in the two configurations: in the orthorhombic plane the number of available stable adjacent sites is strongly reduced in comparison with the tetragonal phase. In a simple random-walk model, the diffusion coefficient is given by[21]

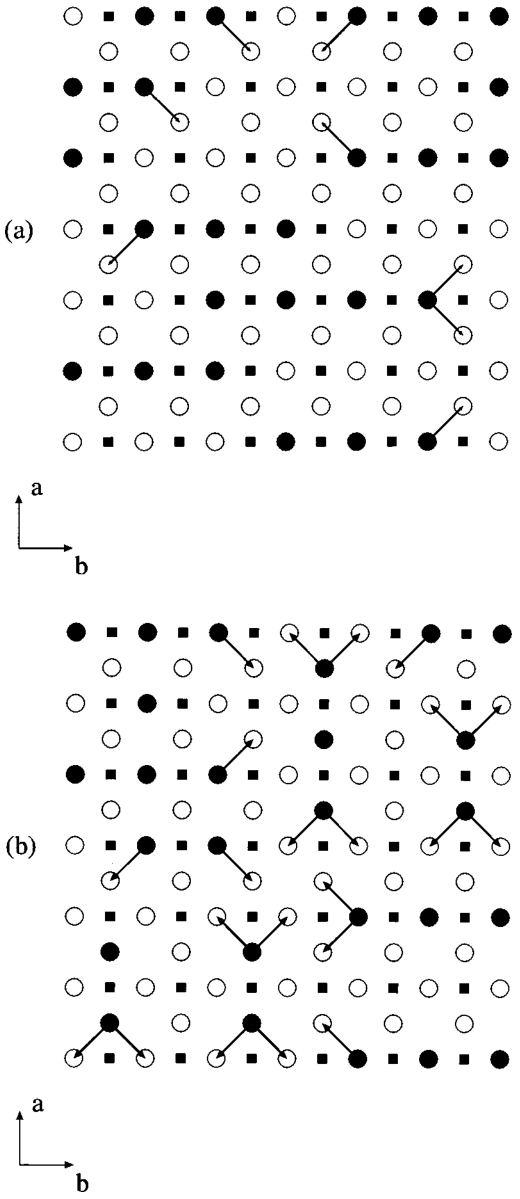

FIG. 4. Schematic view of the $CuO_{0.5}$ plane with short chains fragments: (a) orthorhombic configuration, (b) tetragonal configuration. Arrows indicate energetically favored elementary jumps for oxygen atoms. Format is the same as for Fig. 3.

$$D=C\alpha^2N_v w, \tag{3}$$

where α is the jump length, N_v is the density of sites available for jumps, w is the probability for an atom to jump on a vacant position, and C is a coefficient accounting for the system dimensionality. Since α is constant and w is continuous across the structural transition, the observed (in Fig. 1) steplike behavior is driven by a change in N_v. Of course, Figs. 4(a) and 4(b) present a very simplified picture mainly due to the low number of the atoms considered. A simple Monte Carlo simulation, in which the only condition imposed was the prohibition to place simultaneously two oxygens on the nearest adjacent sites, gives an increase of N_v by a factor of 1.5 in tetragonal phase (all oxygen positions permitted) with respect to orthorhombic phase (half of oxygen positions permitted) for a matrix of 400×400 copper atoms. It is difficult to expect a better quantitative agreement between these simulations and experiment. More accurate evaluation of N_v would imply a detailed knowledge about the chain's length distribution. To our knowledge, such data are not yet available.

The observed constant oxygen diffusivity in the two phases is in contradiction with the general theory of vacancy diffusion.[21] For example, during the in-diffusion process the oxygen atoms occupy and ''cancel'' the former vacancies, decreasing the permitted paths of motion. Nevertheless, as it results from the proposed scenario for the oxygen motion, and in accordance with a model proposed by Rothman and co-workers[2] to explain tracer diffusion data, the only mobile oxygens are those placed at the chain's ends (any single jump of an ''internal'' oxygen would create an energetically unfavorable O1-O5 segment). The assumption that variations of oxygen content will mainly lead to changes of chains length while the chains number should remain nearly constant looks quite realistic and provides a good explanation for the observed constant diffusivity. The working interval of such a mechanism should be restricted to ''intermediate'' concentrations: for very low concentrations the chain number is negligible, while at high enough concentrations the atoms at the extremes of the chains will be blocked by the adjacent chains.

In conclusion, oxygen diffusivity in $GdBa_2Cu_3O_{6+y}$ thin films was investigated by resistivity measurements in the concentration interval $0.3<y<0.8$ and temperatures 750–950 K. Contrary to the general theory of vacancy diffusion, the diffusivity in this oxide is concentration-independent at both sides of the structural phase transition. The phase transition changes the process statistics, increasing the density of available vacancies in tetragonal phase, while the single jump energy E_o remains unchanged and can be attributed to the break of the -Cu-O bond at any end of a chain.

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