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Diffusion of ^{18}O in $Bi_2Sr_2CuO_x$ single crystals

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Tracer diffusion of ^{18}O in the *ab* plane and in the *c* direction in single crystals of $Bi_2Sr_2CuO_x$ has been investigated at one atmosphere oxygen pressure in the temperature ranges 250–350 and 450–700 °C, respectively. The diffusion coefficients determined from penetration profiles measured with secondary-ion mass spectrometry are $D_{ab}=8\times10^{-5}\exp(-1.01\ \mathrm{eV}/kT)$ cm^2/s and $D_c=0.06\exp(-2.11\ \mathrm{eV}/kT)$ cm^2/s. Comparison of the results for $Bi_2Sr_2CuO_x$ with those recently published for $Bi_2Sr_2CaCu_2O_y$ indicates that the differences in structure between these two superconductors do not have a strong effect on the oxygen tracer-diffusion rates.

The pseudotetragonal 10-K superconductor $Bi_2Sr_2CuO_x$ (2:2:0:1) has a layer sequence of Bi-O, Sr-O, Cu-O, Sr-O, and Bi-O parallel to the *ab* plane.[1] In the 90-K superconductor $Bi_2Sr_2CaCu_2O_y$ (2:2:1:2), the Cu-O layer is replaced by a three-layer Cu-O, Ca, Cu-O sequence.[1] The *c*-lattice parameters are 24.6 and 30.6 Å for (2:2:0:1) and (2:2:1:2), respectively. However, both the (2:2:0:1) and the (2:2:1:2) exhibit incommensurate modulations in the Bi-O plane caused by the presence of an oxygen interstitial.[2] Recent x-ray-diffraction studies of (2:2:0:1) suggest that other defects also contribute to the modulations.[3]

A recent investigation[4] of oxygen tracer diffusion in (2:2:1:2) showed that oxygen diffuses much faster in polycrystals than in the *c* direction of single crystals. Hence, diffusion in polycrystals is expected to be primarily due to diffusion parallel to the *ab* planes and $D_{\mathrm{poly}}=\frac{2}{3}D_{ab}$. Runde *et al.*[4] determined the value of the preexponential factor, D_0, and the activation energy for polycrystals from rather scattered data to be 1.7×10^{-5} cm^2/s (corresponding to $D_0=2.5\times10^{-5}$ cm^2/s for diffusion in the *ab* plane) and 0.93 eV, respectively. It was proposed that oxygen diffusion in the *ab* direction in this compound occurs along the Bi-O planes via an interstitial mechanism, and the activation energy represents the migration energy. They also suggested that diffusion along the *c* axes of (2:2:1:2) probably occurs via a vacancy mechanism because the preexponential has a value of 0.6 cm^2/s, and an activation energy of 2.20 eV, which would represent the sum of the vacancy formation and migration energies.

A comparison of the structures of (2:2:1:2) and (2:2:0:1) indicates that diffusion in the *ab* plane should be the same in these two superconductors, whereas diffusion in the *c* direction is expected to depend on the details of the mechanism. If the main activation barrier is in the planes common to the two structures, the diffusion coefficients in the *c* direction should be similar in magnitude, or slightly different due to differences in lattice spacing and in the environment of the oxygen vacancy because of the missing Ca layer. On the other hand, if the activation barrier is in the planes that are present in (2:2:1:2), but not in (2:2:0:1), the diffusion coefficients for the *c* direction could be drastically different.

This paper reports on diffusion of ^{18}O in the *c* direction and in the *ab* plane of (2:2:0:1). The data are compared with those obtained for (2:2:1:2) in order to elucidate more details about the oxygen diffusion mechanisms in these superconductors.

The $Bi_2Sr_2CuO_x$ single crystals were grown by a flux technique. High-purity powders of Bi_2O_3, $SrCO_3$, and CuO, in the cation ratio of 2.0:2.0:(1.5–2.0), were used as starting materials and thoroughly ground in a ball mill. The powders were placed in a Pt crucible and heated in air to 1000 °C at a rate of 100–150 °C/h, held at 1000 °C for about 2 h, and cooled to 950 °C at a rate of 900°C/h. The temperature was held at 950 °C for 3–4 h, then slowly decreased to 800 °C at a rate of 1–3 °C/h. The solidified samples were subsequently cooled to room temperature at 50–100 °C/h. A number of single crystals with dimensions as large as $20\times15\times5$ mm^3 and with black shiny surfaces were obtained. X-ray diffraction revealed the presence of only the (2:2:0:1) phase. Rocking curves indicated that the single crystals were of high quality, having a mosaic spread of $\leq0.5°$. Direct-current susceptibility measurements on both as-grown and annealed crystals showed that the samples were bulk superconductors with an onset of superconductivity at 7 K. The crystals were fully diamagnetic after the diffusion anneals.

The crystals cleaved easily along the *ab* planes, revealing a clean, planar surface. Thus no further surface preparation was required for the samples that were used in the *c*-direction diffusion experiments. For the *ab*-direction experiments, a surface perpendicular to the cleavage plane was polished with diamond paste down to 0.25 μm grit.

The pressure of both the natural oxygen during the preanneal and the ^{18}O during the diffusion anneal was 10^5 Pa. Secondary-ion mass spectroscopy (SIMS) was used to measure the tracer penetration profile, and the concentration of ^{18}O was least-squares fitted to the complementary error function solution of the diffusion equation to obtain values of the tracer-diffusion coefficient *D*. The experimental techniques used in the present work were identical to those used for the single crystals in the (2:2:1:2) study.[4]

Figure 1 shows a typical tracer penetration plot for the *c* direction. The fit of the experimental points, shown as circles, to the complementary error function solution of the diffusion equation, the solid line, is very good and can be taken as evidence that the measured *D* reflects true volume diffusion. The values of *D* obtained from five penetration plots for *ab* diffusion and 11 for *c* diffusion are listed in Table I and are plotted in the usual Arrhenius form in Fig. 2. The data are independent of time and are reproducible from sample to sample or crater to crater to better than 20%.

Several unsuccessful attempts were made to measure the *ab*-direction diffusion coefficient at 450 °C. After being annealed at this temperature, the sample surfaces were usually discolored, indicating that a surface reaction had occurred during the anneal. This observation was supported by the SIMS profiles, which showed that in most of these samples the tracer penetration plot was anomalous near the surface. Even in the cases where no surface reaction was evident from the SIMS profile, it turned out that the tracer concentration did not fit the complementary error function well. Nevertheless, values of *D* were estimated from the deep-penetration part of the profiles. They were centered about the solid line in Fig. 2, but had at least one order of magnitude of scatter.

Least-squares analysis of the data presented in Table I yields the following values for D_{ab} and D_c for diffusion in the *ab* plane and *c* direction of (2:2:0:1) single crystals, respectively:

$$D_{ab}=(8^{+12}_{-5})\times 10^{-5}\exp-[(1.01\pm 0.05)\ \mathrm{eV}/kT]\ \mathrm{cm}^2/\mathrm{s}$$

and

$$D_c=(6^{+5}_{-3})\times 10^{-2}\exp-[(2.11\pm 0.04)\ \mathrm{eV}/kT]\ \mathrm{cm}^2/\mathrm{s}\ .$$

Comparison of these results with those for the (2:2:1:2) (Ref. 4) indicates that diffusion in the *ab* direction is, within experimental uncertainty, the same in both materials; the difference between the diffusion parameters is within the experimental error. For the *c* direction, on the other hand, although the activation energies are nearly the same for (2:2:0:1) and (2:2:1:2) [(2.11±0.04) eV compared to (2.20±0.03) eV], diffusion in the *c* direction in (2:2:0:1) is slower than in (2:2:1:2). If the activation energies are set equal, D_0 for the (2:2:0:1) is about a factor of 4 lower than it is for (2:2:1:2).

TABLE I. Diffusion coefficients for oxygen tracer diffusion in single crystals of $\mathrm{Bi_2Sr_2CuO}_x$.

Sample No.	*T* (°C)	Time (h)	Direction	*D* (cm²/s)
1	250	92	*ab*	1.13×10^{-14}
1	250	92	*ab*	1.63×10^{-14}
1	250	92	*ab*	1.67×10^{-14}
2	350	2	*ab*	5.22×10^{-13}
2	350	2	*ab*	5.36×10^{-13}
3	450	48	*c*	1.53×10^{-16}
3	450	48	*c*	1.56×10^{-16}
4	450	240	*c*	1.17×10^{-16}
4	450	240	*c*	1.51×10^{-16}
5	550	3	*c*	6.62×10^{-15}
5	550	24	*c*	5.43×10^{-15}
5	550	24	*c*	6.07×10^{-15}
6	650	2	*c*	2.17×10^{-13}
6	650	2	*c*	2.55×10^{-13}
7	700	0.75	*c*	7.19×10^{-13}
7	700	0.75	*c*	9.13×10^{-13}

The preexponential factor for diffusion is given by

$$D_0=\gamma\lambda^2 \nu f\exp(\Delta S/k)\ ,$$

where γ is a geometrical factor, λ is the jump distance, ν is the attempt frequency, f is the correlation factor, and ΔS is the entropy of activation.[5] The equality of the activation energies implies that the jump takes place over the same barrier in the (2:2:1:2) and (2:2:0:1). Thus it is likely that the planes of the initial and final positions of the jumping atom, between which the activation barrier

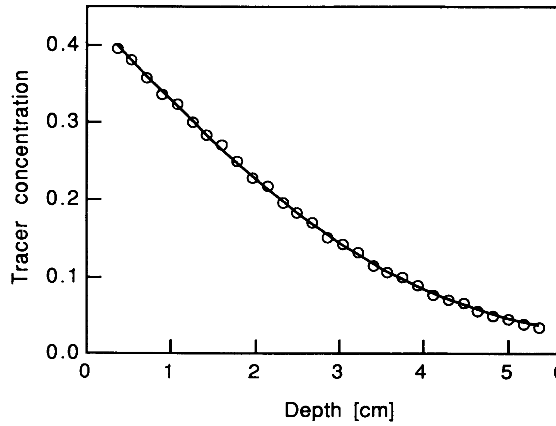

FIG. 1. Penetration plot obtained along the *c* direction of a sample annealed at 550 °C for 24 h. The solid line is the least-squares fit to the complementary error function solution of the diffusion equation.

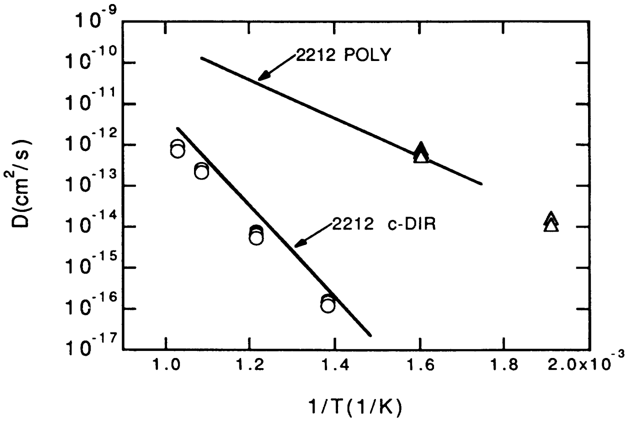

FIG. 2. Arrhenius plot of oxygen tracer-diffusion coefficients parallel to the *ab* planes and in the *c* direction in $\mathrm{Bi_2Sr_2CuO}_x$. The least-squares fits of *D* values from (2:2:1:2) polycrystals and in the *c* direction of (2:2:1:2) single crystals obtained earlier (Ref. 4) are shown as solid lines and included for comparison.

is highest, are the same in the (2:2:0:1) and (2:2:1:2) structures. The neighboring planes that are common to both structures are the two Bi-O, the Sr-O, and the Cu-O planes; thus, the rate-limiting jump must take place between two of these neighboring planes. The values of ν and ΔS are probably the same because the activation energies are equal for the two structures. The difference between the preexponentials is, therefore, due to differences in f or λ^2.

An estimate of the differences in λ can be constructed as follows. Diffusion along the c direction is a sequence of jumps between different planes. The activation energy is the height of the activation barrier for the rate-controlling jump that is the slowest in the sequence. Since the other jumps in the sequence occur more rapidly, the jump distance can be considered to be equal to the lattice parameter. Therefore this contribution to the ratio of the preexponentials for the c direction in the (2:2:0:1) to the (2:2:1:2) should be $(24.6/30.6)^2$ or a factor of 0.6. The rest of the experimental factor of 0.25 ($\frac{1}{4}$) may be due to differences in the correlation factor.

In summary, oxygen tracer diffusion in the ab plane of $Bi_2Sr_2CuO_x$ has been found to be equal to ab-plane diffusion in $Bi_2Sr_2CaCu_2O_y$, as expected from the crystal structure. It is likely, therefore, that diffusion in the ab plane occurs via the same mechanism as in (2:2:1:2), which was suggested to be via an oxygen interstitial.[4] Diffusion in the c direction is about a factor of 4 slower in (2:2:0:1) than in (2:2:1:2) because of the decrease in the preexponential factor. About half of this change can be explained by the decreased jump distance. The rest of the change is probably due to changes in the correlation factor. In both (2:2:0:1) and (2:2:1:2), the activation barrier for oxygen diffusion reaches a maximum between the Bi-O and Sr-O, between the Bi-O and Bi-O, or between the Sr-O and Cu-O planes.

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[5] See, for example, J. R. Manning, *Diffusion Kinetics for Atoms in Crystals,* (Van Nostrand, Princeton, NJ, 1968).