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Anisotropy of oxygen tracer diffusion in single-crystal $YBa_2Cu_3O_{7-\delta}$

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Oxygen tracer diffusion has been measured in single-crystalline $YBa_2Cu_3O_{7-\delta}$ from 300 to 650 °C in the *c* direction, at a few temperatures in the *ab* plane of twinned crystals, and in the *b* direction of an untwinned crystal. The diffusion coefficient in the *c* direction, D_c, is $\approx 10^6$ lower than the diffusion coefficient in polycrystals at 400 °C and diffusion in the *b* direction is at least 100 times faster than diffusion in the *a* direction at 300 °C. The oxygen diffusion coefficient in polycrystals is, within an experimental uncertainty of a factor of 2, independent of oxygen partial pressure at 400 °C, in agreement with previous results measured at 600 °C. Some suggestions are presented on the mechanism of diffusion, the relation of diffusion and internal friction in $YBa_2Cu_3O_{7-\delta}$, and on the meaning of the activation energy.

I. INTRODUCTION

This paper deals with the details of atomic motion of oxygen in $YBa_2Cu_3O_{7-\delta}$, and we approach this by measurements of the anisotropy of the tracer diffusion of oxygen in $YBa_2Cu_3O_{7-\delta}$ single crystals. The kinetics of oxygenation, so important to the technical applications of $YBa_2Cu_3O_{7-\delta}$ and described by many workers,[1-12] are not the subject of this paper.

Diffusion in $YBa_2Cu_3O_{7-\delta}$ can be anisotropic because the $YBa_2Cu_3O_{7-\delta}$ lattice is orthorhombic; diffusion in a crystal with this symmetry is described by three independent diffusion coefficients, one parallel to each principal crystallographic axis. The anisotropy can be very large because the structure of the CuO plane (the "chain" plane) differs so strongly from the other planes in the crystal. The oxygen ion vacancies in the $YBa_2Cu_3O_{7-\delta}$ structure (Fig. 1) occur almost exclusively on the CuO planes;[13] thus, diffusion in the *c* direction is expected to be much slower than it is in the *ab* plane.

Oxygen ion vacancies are distributed equally on the O(1) and O(5) sites in the high-temperature tetragonal phase [there are a few on O(4) as well]. As the temperature is lowered, the vacancies tend to order on the O(5) sites. The stoichiometry and site occupancy depend on the temperature and oxygen partial pressure, P_{O_2}.[13-22] For $\delta = 0$, all the O(1) sites are occupied and all the O(5) sites are unoccupied. The minimum value of δ attained in practice is a subject of debate: Lindemer *et al.*[19] find $\delta = 0.003$ at $P_{O_2} = 1$ atm and 300 °C, whereas Anderson *et al.*[21] find $\delta = 0.08 \pm 0.02$ in the fully oxidized state.

A number of thermodynamic treatments have been given of the nonstoichiometry in $YBa_2Cu_3O_{7-\delta}$.[17-22] A possibly apropos one is that of Hong and co-workers,[22] who find that the equilibrium constant for the defect reaction

$$V_{\ddot{O}} + \tfrac{1}{2}O_2 \Longleftrightarrow O_O + 2h^{\cdot}$$

fits perfectly to an Arrhenius expression if the data of Lindemer *et al.*[19] are used. Here $V_{\ddot{O}}$ represents an oxygen-ion vacancy, charged +2 with respect to a normally occupied O^{2-} site, and $h^{\cdot}$ represents an electron hole. This would appear to indicate that the solution of oxygen in $YBa_2Cu_3O_{7-\delta}$ is ideal, i.e., the energy gained (lost) by adding an oxygen ion is independent of stoichiometry.

Further ordering of the oxygen ions at lower values of δ is found both experimentally (see, e.g., Refs. 23–27) and from phase diagram calculations (see, e.g., Refs. 28 and 29). The general features are that for all values of δ, the oxygen ions are ordered into chains, and that the

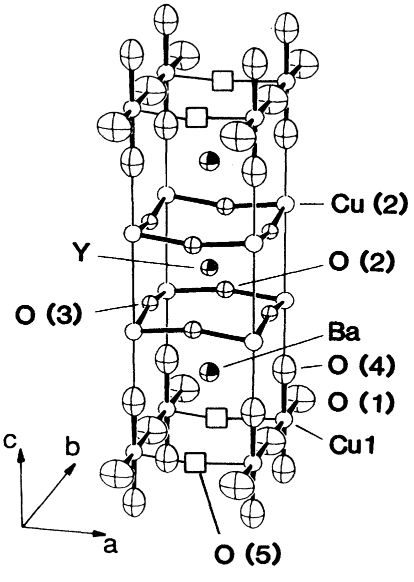

FIG. 1. Structure of $YBa_2Cu_3O_{7-\delta}$ (Ref. 13).

spacing between the chains depends on the stoichiometry, e.g., for $\delta=0.5$, every second row of O(1) sites is occupied, or for $\delta=0.33$, the sequence is two rows occupied, one row empty, etc. Thus the arrangement of oxygen ions into rows is preserved. At high temperatures in the orthorhombic phase, where some O(5) sites are occupied, or in the tetragonal phase, the ions on the O(5) sites are not randomly located, but are arranged in rows on the O(5) sites. A possible explanation of the result[22] that the addition/removal of an oxygen ion involves the same energy change regardless of stoichiometry is then that oxygen ions are added or removed at the ends of the chains, since the number of chains does not change significantly with δ.

Diffusion coefficients for oxygen in $YBa_2Cu_3O_{7\text{-}\delta}$ have been calculated theoretically. Many of these calculations are based on the statistical mechanics of vacancy arrangements in $YBa_2Cu_3O_{7\text{-}\delta}$, computed on the basis of various models, and they yield a wide variety of results. There appears to be general qualitative agreement that diffusion in the *ab* plane is much faster than in the *c* direction, but not much agreement on the details of the diffusion path, or of the activation energies.

The tracer diffusion coefficient of oxygen in $YBa_2Cu_3O_{7\text{-}\delta}$ calculated[30] from a thermodynamic model which in turn was based on two energy parameters calculated from the temperature dependence of the oxygen site occupancy[30,31] showed a slight P_{O_2} dependence and a break at the orthorhombic-tetragonal transformation. Addition of a Monte Carlo calculation of the Bardeen-Herring correlation factor[32] yielded somewhat lower values of the diffusion coefficient, but did not change the qualitative aspects of the variation of the diffusion coefficient with P_{O_2} or temperature.

Calculation of tracer and chemical diffusion coefficients by Monte Carlo simulations of an asymmetric next-nearest-neighbor Ising model yielded a strongly stoichiometry-dependent value of D which also displayed significant anisotropy in the *ab* plane.[33] A lattice-gas model qualitatively reproduced the oxygen ordering in the *ab* plane, but no diffusion coefficients were calculated.[34] A calculation of oxygen tracer diffusion coefficients using the cluster variation method in conjunction with the path probability method yielded activation energies of 0.8 and 1.2 eV in the tetragonal and orthorhombic phases, respectively, with a stoichiometry-dependent D, and a break in the Arrhenius plot at the orthorhombic-tetragonal transformation.[35] A migration energy of 0.3 eV has been calculated for oxygen ions using a shell model and associated two- and three-body short-range interaction potentials.[36] In another model,[6] it was assumed that the force between two neighboring oxygen ions was repulsive for an O(1) and O(5) site, repulsive for two O(1) sites in the *a* direction and attractive in the *b* direction. A strong anisotropy of the diffusion coefficient in the *ab* plane and a strong stoichiometry dependence of the diffusion coefficient were obtained.

All the above theoretical calculations of diffusion were based on the assumption that diffusion occurs via oxygen vacancy motion in the CuO planes and that diffusion in the *c* direction is negligible. A mean-field calculation[37] suggested that oxygen could move interstitially over the O(5) sites (along channels parallel to the *b* direction) with an almost zero activation energy for motion, whereas the activation energies for diffusion in the *a* and *c* directions were ≈ 1.7 eV. Another calculation[38] showed that vacancy diffusion via the O(1)-O(4)-O(1) path was energetically the most favorable. None of these theoretical results are completely supported by the experimental results described in this paper.

On the experimental side, many measurements of the chemical diffusion of oxygen in $YBa_2CuA_3O_{7\text{-}\delta}$ have been carried out because of the technological importance of the in- and out-diffusion of oxygen.[1-12] However, the chemical diffusion coefficient, $\tilde{D}$,

$$\tilde{D}=\tfrac{1}{2}a^2\omega f_v\left[1+\frac{\partial\ln\gamma}{\partial\ln c}\right] \tag{1}$$

contains the thermodynamic factor

$$\left[1+\frac{\partial\ln\gamma}{\partial\ln c}\right], \tag{2}$$

which is calculated to be large and strongly temperature dependent,[33,39] although this contradicts the finding of an ideal solution by Hong *et al.*[22] If the solution is nonideal, $\tilde{D}$ differs from the tracer diffusion coefficient D^*,

$$D^*=\tfrac{1}{2}a^2\omega fp\ . \tag{3}$$

(Here a is the jump distance, ω the jump frequency, f_v and f the correlation factors for vacancy and oxygen ion diffusion, respectively, γ and c the activity coefficient and concentration, respectively, of oxygen ions, and p the vacancy availability factor.) A comparison of the chemical diffusion coefficients with the tracer diffusion coefficient measured here thus yields only the thermodynamic factor.

We have measured the tracer diffusion of oxygen in $YBa_2Cu_3O_{7\text{-}\delta}$ polycrystals from 300 to 850 °C, using secondary-ion mass spectrometry, SIMS, to obtain ^{18}O diffusion profiles.[40] The main points of our results are the following.

1. The volume diffusion coefficient in untextured polycrystals is given by

$$D^*=1.4\times10^{-4}\exp[(-0.97\pm0.05)\ \text{eV}/kT]\ \text{cm}^2\,\text{s}^{-1}\ . \tag{4}$$

2. The Arrhenius line is straight, within the experimental uncertainty of a factor of 2, over the temperature range 300–850 °C. There is neither break nor bend at the orthorhombic-tetragonal transformation.

3. The diffusion coefficient at 600 °C does not depend strongly on the oxygen partial pressure.

The values of D_{poly} have been confirmed by Sabras *et al.*[41] and Turrillas *et al.*[42] using the same technique. Diffusion coefficients deduced from measurements of dc[42] and ac[43-45] oxygen ion conductivity are rather scattered and sometimes seem to agree with the chemical diffusion coefficient,[42] although the values of D calculated from a recent study[43] agree with our tracer results within a factor of 5. The values of the tracer diffusion coefficients obtained by Ikuma and Akiyoshi[46] are in strong disagreement with our data; we have pointed out possible flaws in their methodology.[40] Preliminary work on the anisotropy of tracer diffusion of ^{18}O in single crystalline $YBa_2Cu_3O_{7-\delta}$ has been reported by us.[47] Anisotropy has also been observed in chemical diffusion.[48]

Another measurement on $YBa_2Cu_3O_{7-\delta}$ polycrystals that may be related to oxygen ion motion is that of internal friction. We have plotted the frequencies corresponding to the internal friction peaks versus the reciprocal absolute temperature of the peak, observed by a number of workers,[49–55] in Fig. 2. Results on anelastic relaxation[56–57] and the relaxation of T_c (Ref. 26) are also shown. The points fall on a reasonably good Arrhenius line, with an activation energy of about 1 eV, suggesting that the same jump is responsible for the internal friction as for the long-range diffusion of oxygen, and therefore that whatever defect is responsible for diffusion must also fulfill the symmetry conditions for giving rise to an internal friction peak.

The objectives of the present investigation were to explore further the anisotropic diffusion of oxygen and to separate D_a and D_b by making measurements on untwinned single crystals. The plan of the paper is as follows. We first present our results for the tracer diffusion of oxygen in $YBa_2Cu_3O_{7-\delta}$ single crystals. We then discuss related experimental observations, the P_{O_2} dependence of the oxygen diffusion coefficient, internal friction results, and observations on low-temperature ordering of oxygen in $YBa_2Cu_3O_{7-\delta}$. Finally, we attempt to describe a possible basis for a model of the atomic jumps of oxygen in $YBa_2Cu_3O_{7-\delta}$.

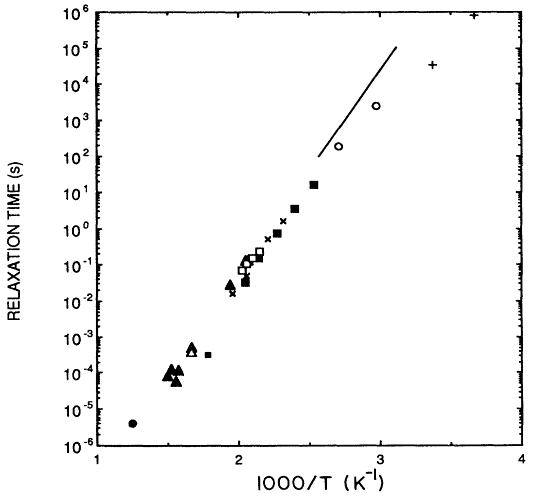

FIG. 2. Relaxation time obtained from internal friction, anelastic relaxation, and time-dependent T_c measurements vs $1/T$. Data is from filled circles—Ref. 49, crosses—Ref. 50, filled squares—Ref. 51, open triangles—Ref. 52, filled triangles—Ref. 53, open squares—Ref. 54, small filled square—Ref. 55, square cross—Ref. 26, and open circles—Ref. 56. The line is the fit to 26 data points from the anelastic relaxation experiments of Ref. 57.

II. EXPERIMENTAL TECHNIQUES

The single crystals of $YBa_2Cu_3O_{7-\delta}$ used in this study were obtained from the sources listed in the acknowledgments. They were grown by a flux growth technique, but with different individual recipes. The surfaces were prepared either by sputtering (ion implantation of ^{18}O at 5 keV) or by etching in a solution of Br in ethyl alcohol.[58] The etching treatment was carried out before an equilibration anneal to set the stoichiometry. The sample was not exposed to air after etching until after the diffusion anneal. The samples were sealed in quartz tubes under ^{16}O for the equilibration anneals or ^{18}O for the diffusion anneals. The P_{O_2} during the diffusion anneal was determined from the initial pressure and the perfect gas law. The equilibration anneal was at the same temperature and P_{O_2} as the diffusion anneal, but for a much longer time, so the gradient of chemical potential during the diffusion anneal was minimized. Annealing temperatures were controlled to ±1 °C. Depth profiling was carried out in a SIMS using 17-keV Cs^+ ions. The final crater depth was measured by a profilometer.

Most of the measurements on single crystals were of diffusion in the c direction. A few of the crystals were thick enough to allow depth profiling in the ab plane. Several of these crystals were detwinned[59] and stress relieved at the detwinning temperature of 420 °C, and in one of them depth profiles were measured in both the a and b directions. Several attempts to repeat this experiment were only partially successful because the sample either fractured or retwinned.

To study the effect of stoichiometry on the tracer diffusion coefficient, an experiment was carried out on diffusion in a polycrystal at 400 °C under 0.01 atm P_{O_2}. This depth profile was obtained by stepping the beam along a tapered surface.[60]

In all of these experiments, the concentration of in-diffused ^{18}O

$$c_{18}=\frac{N(^{18}O)-N(BG)}{N(^{16}O)+N(^{18}O)} \tag{5}$$

where N is the number of counts, was fitted to the complementary-error-function solution of the diffusion equation

$$c_{18}=c_0\operatorname{erfc}(x/[2(Dt)^{1/2}]) \tag{6}$$

by means of the statistical analysis system (SAS) nonlinear-least-squares routine[61] in order to obtain values of D. Here, N(BG) refers to the natural background of ^{18}O, usually obtained by averaging the ^{18}O counts at the end of the depth profile, and the number of counts are from the raw data obtained in the SIMS. We estimate the accuracy of the measured values of D to be about a factor of 2. Measurement of the crater depth in the ab

plane was particularly difficult, and the uncertainty of the values of D in these directions may be larger.

III. RESULTS

The anisotropy between diffusion in the c direction and the ab plane is indicated by the two depth profiles in Figs. 3 and 4. (Irregularities near $x=0$ in the SIMS data are not due to diffusion but represent equilibration of the sample under sputtering.) The former (Fig. 3) indicates a diffusion zone about 0.1 μm deep after 24 h diffusion in the c direction at 430 °C, while the latter (Fig. 4) shows a diffusion zone 3 μm thick after 17 h at 300 °C. A plot of c_{18} versus x (penetration) obtained from the latter plots (Fig. 5) fits nicely to $c_0\mathrm{erfc}(x/[2(Dt)^{1/2}])$ with a value of D of 2.4×10^{-13} cm^2 s^{-1}.

The anisotropy of diffusion in the ab plane is shown by the two depth profiles taken in the a and b directions in a detwinned single crystal annealed 0.5 h at 300 °C (Fig. 6). The depth profile for the b direction shows a diffusion zone ~ 1 μm deep, whereas the depth profile for the a direction shows a narrow surface peak that is probably an artifact due to equlibration of the surface, followed directly by background. The diffusion zone on the a direction profile is certainly <0.1 times the diffusion zone on the b-direction profile. Hence $D_a < 0.01D_b$, although we have not succeeded in obtaining a value for the diffusion coefficient in the a direction at 300 °C. The c_{18} versus x plot for the b-direction depth profile fits a complementary error function with $D=2.0\pm0.15\times10^{-12}$ cm^2 s^{-1}. Another experiment at 450 °C also showed that the penetration in the b direction was considerably greater than in the a direction, i.e., $D_b \gg D_a$, but the b-direction plot was definitely non-Fickian, so no value of D_b was obtained. An attempt to measure D in the b direction at 400 °C resulted in the crystal retwinning during the anneal. In this instance, selected area imaging was used in the SIMS analysis, and five values of D were obtained from the same crater (crosses in Fig. 7). Examination of the crystal in polarized light suggested that the crater was mostly in an area that had retwinned, so the majority direction was a, not b.

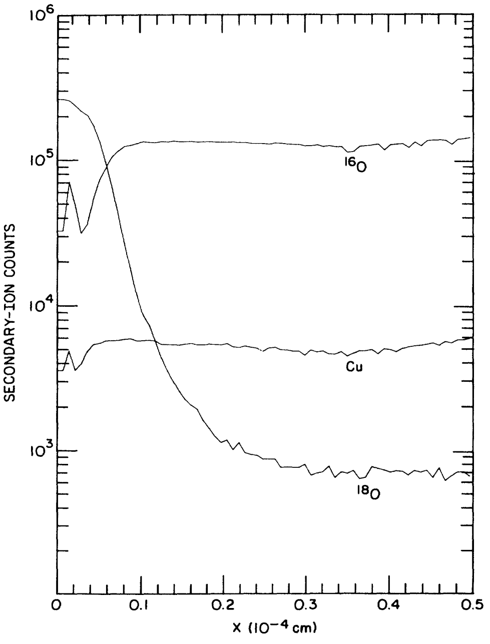

FIG. 3. Secondary ion counts of ^{16}O, ^{18}O, and Cu vs penetration depth obtained for a c-axis single crystal annealed 24 h at 430 °C at $P_{O_2}=10^5$ Pa.

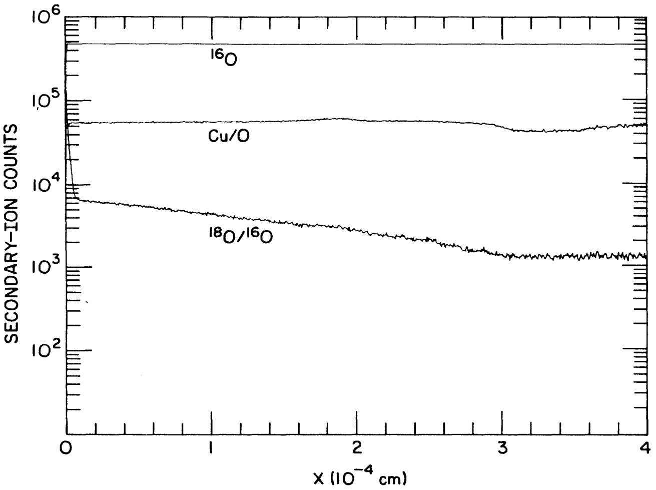

FIG. 4. Normalized secondary ion count vs penetration depth after diffusion for 17 h at 300 °C in ab plane of a twinned crystal. The relative positions of the lines are as shown but the numbers on the ordinate refer to ion counts before normalization.

The diffusion coefficient in a polycrystal at 400 °C and 0.01 atm P_{O_2} ($\delta=0.1$)[19] is $4.4\pm0.7\times10^{-12}$ cm^2 s^{-1}. This is in the middle of the range of values obtained under 1 atm P_{O_2} (Ref. 40) ($\delta=0.015$)[19] and within a factor of 2 of the value of 7.6×10^{-12} cm^2 s^{-1} calculated from Eq. (4),

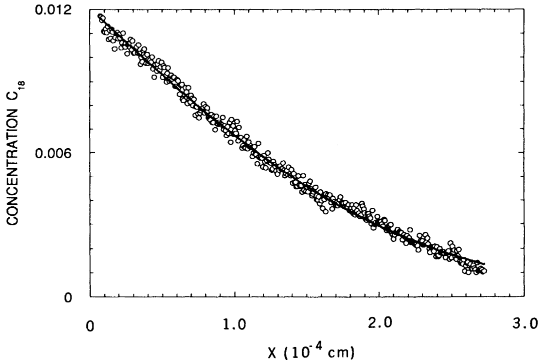

FIG. 5. Fit to the solution of the diffusion equation (solid line) for the experimental data of Fig. 4.

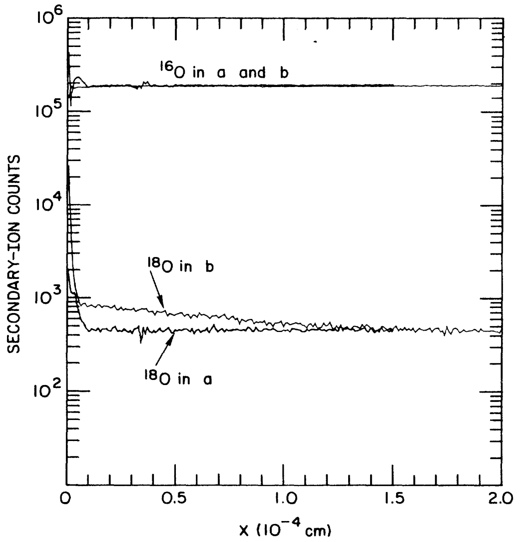

FIG. 6. Secondary ion counts for ^{16}O and ^{18}O for both *a* and *b* directions obtained after diffusion for 0.5 h at 300 °C and $P_{O_2}=10^5$ Pa.

indicating that the diffusion coefficient is independent of P_{O_2} within the experimental uncertainty of about a factor of 2.

An Arrhenius plot (Fig. 7) of all our data on the tracer diffusion of oxygen in $YBa_2Cu_3O_{7-\delta}$ single crystals, as well as a line representing diffusion in polycrystals [Eq. (4)], all at 1 atm P_{O_2}, shows the following features.

(1) The diffusion is highly anisotropic: $D_{ab}>10^4-10^6$ D_c.

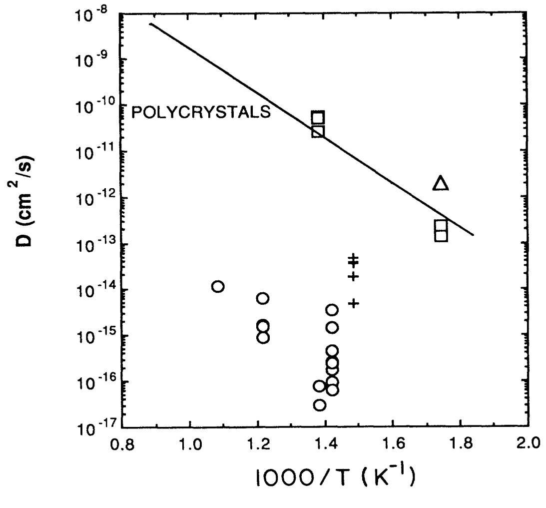

FIG. 7. Arrhenius plot for oxygen diffusion in $YBa_2Cu_3O_{7-\delta}$ at $P_{O_2}=10^5$ Pa. The solid line represents data on polycrystals, the open squares—diffusion in the *ab* plane (the points at each temperature represent multiple craters), open triangle—*b* direction, open circles—*c* direction, and crosses—*a* direction obtained from selected area imaging of one crater.

(2) The values of D_c are scattered over 2 orders of magnitude, far outside any reasonable experimental uncertainty.

(3) $D_{ab}\approx D_{\text{poly}}$.

(4) $D_b\approx 10D_{ab}$.

IV. DISCUSSION

A. P_{O_2} dependence of D

Our measurements of the P_{O_2} dependence of the tracer diffusion coefficient are shown in Fig. 8 (most of the data are tabulated in Ref. 40). It is clear that there is no strong dependence of the tracer diffusion coefficient on the stoichiometry (δ changes from 0.015 to 0.1^{19} at 400 °C). Since the concentration of both the oxygen ion vacancies and the oxygen ions on O(5) increases with decreasing P_{O_2},[31] the lack of dependence of D on P_{O_2} suggests either that the diffusion coefficient is independent of the defect concentrations, or that two different factors in the diffusion coefficient have opposite dependence on defect concentration.

B. Internal consistency and anisotropic diffusion in single crystals

The first of the four features mentioned above, the large anisotropy of diffusion with $D_c \ll D_{ab}$, is expected from both the vacancy concentrations on the different oxygen sites, and from the structure of the lattice itself. If only thermal vacancies occur on O(2) and O(3) sites, the vacancy concentration on these sites, and hence the probability of an oxygen ion jumping to one of these sites, is much smaller than the vacancy concentration, and hence the probability of a jump in the "chain" planes. In addition, the jump from an O(1) to an O(5) site is probably easier than the jump from an O(4) site to an O(2) or O(3) site, because the distance is less.

The large scatter in the values of D_c can be explained by a consideration of the tensor properties of the

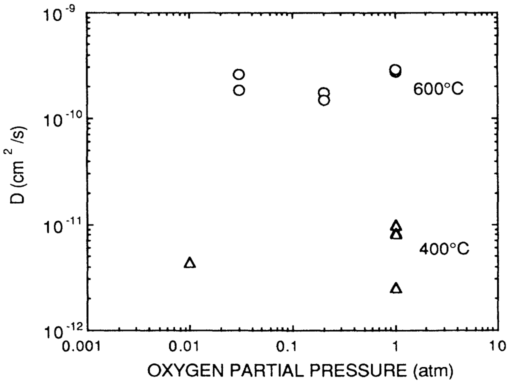

FIG. 8. Variation of D as a function of oxygen partial pressure measured on polycrystalline samples at 400 and 600 °C.

diffusion coefficient.[62] Since $YBa_2Cu_3O_{7-\delta}$ is orthorhombic, there are three independent diffusion coefficients in the structure, one parallel to each of the principal axes, and the diffusion coefficient in an arbitrary direction is given by

$$D_\theta = D_a\cos^2\theta_a + D_b\cos^2\theta_b + D_c\cos^2\theta_c \ , \tag{7}$$

where the θ's are the angles between the diffusion direction and the principal axes. Since these measurements were made on twinned crystals, diffusion is isotropic in the *ab* plane, so Eq. (7) can be rewritten as

$$D_\theta = D_{ab}\sin^2\theta + D_c\cos^2\theta \ , \tag{8}$$

where θ is the angle between the diffusion direction and the *c* axis. Because $D_{ab} \gg D_c$, the *ab* contribution can dominate this expression if $\theta \neq 0$. That is, if $D_{ab} \geq 10^6 D_c$, the *ab* contribution will equal the *c* contribution if $\theta = 0.001$ radians. Such a value of θ can easily be found due to mosaic misorientations in the single crystals. Thus the scatter in the measured values of D in the *c*-axis crystals represents not a scatter in D_c, but in $\sin^2\theta$, and the minimum value measured is likely to be the maximum possible value of D_c. The minimum anisotropy is therefore the ratio between D_{ab} and the minimum values of D_c, resulting in $D_{ab} \geq 10^6 D_c$ at 400 °C. Since the activation energy for diffusion in the *c* direction is surely greater than for diffusion in the *ab* plane, the anisotropy will decrease with increasing temperature.

The near equality of D_{ab} and D_{poly} can also be explained on the basis of Eq. (8). If the grains in the polycrystalline sample are randomly oriented,

$$D_{\text{poly}} \approx D_{ab}\langle \sin^2\theta \rangle = \tfrac{2}{3} D_{ab} \ , \tag{9}$$

where the average is taken over a hemisphere.

The fact that $D_b \approx 10 D_{ab}$ is easily understood by considering the paths traveled by an atom diffusing in a twinned or in an untwinned crystal (Fig. 9), respectively, and the fact that $D_b \gg D_a$. Both atoms will take, say, N jumps in time t. However, the atom diffusing in the untwinned crystal takes all N jumps in the direction of the analyzing beam, whereas the atom diffusing in the twinned crystal takes N_b jumps in that direction, and N_a jumps perpendicular to that direction. These N_a jumps do not contribute to the displacement of the atom along the depth profile, so $D_b/D_{ab} = (N_a + N_b)/N_b = (A^2 + B^2)/B^2$ where A and B are the distances traveled in the twin lamellae with the *b* direction perpendicular or parallel, respectively, to the analyzing beam. For randomly twinned samples, $A = B$ and, therefore, $D_b/D_{ab} = 4$. The five values of D from the selected area imaging, obtained from the same crater (crosses in Fig. 7), show the scatter that can be obtained as a function of amount of twinning.

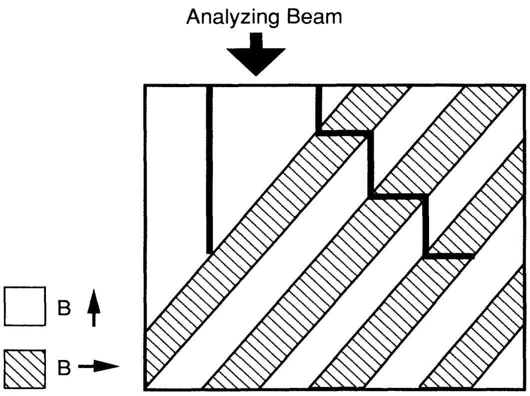

FIG. 9. Model indicating the differences between diffusion in an untwinned and twinned single crystal.

C. Agreement with theory

The theories of the tracer diffusion coefficient mentioned above[30,32,34–39] all describe some aspects of our results correctly, but contradict at least one of our experimental findings. The theories of Bakker *et al.*[30,32,39] do not predict a large pressure dependence, but do predict a bend at the orthorhombic-tetragonal transformation. The calculation of Salomons and de Fontaine[33] predicts $D_b \gg D_a$, but predicts a strong P_{O_2} dependence. Choi *et al.*[35] also predict a strong P_{O_2} dependence. Further, they predict preferential diffusion along twin boundaries; this is in direct contradiction to our result that D_b in a detwinned crystal is greater than D_{ab} in a twinned crystal. Ronay and Nordlander[37] also predict $D_b \gg D_a$, but their theory cannot be compared to other aspects of our data.

D. Diffusion mechanisms

The experimental facts that any diffusion mechanism must be consistent with are

(1) the Arrhenius plot is straight;

(2) the diffusion coefficient is independent of P_{O_2};

(3) $D_b \gg D_a, D_c$, at least at 300 °C; and

(4) the defect configuration involved in diffusion is of a type that would also give rise to an internal friction peak.

The first two of these criteria apply, of course, only within the experimental uncertainty of a factor of 2.

The first of these criteria suggests that diffusion in both the orthorhombic and tetragonal phases takes place by the same type of jump. The second suggests that the diffusion coefficient is independent of the concentration of oxygen ion vacancies and interstitials. The third of these criteria is related to the structure in the *ab* plane. The combination of a straight Arrhenius line over the entire temperature range and the finding that $D_b \gg D_a$ at 300 °C suggests at first glance that $D_b \gg D_a$ should hold over the entire temperature range. However, Eq. (7) shows that D_{poly} would increase by only a factor of 2 if D_a were to increase until it was equal to D_b, and this is within our experimental uncertainty.

A basic part of any theory is the view adopted for the change in the arrangement of the oxygen ions and vacancies with temperature and P_{O_2}. The theories of Bakker *et al.*[30,32,39] assume that the vacancies on O(1) and the oxygen ions on O(5) occur randomly. Diffusion via randomly arranged single vacancies at high values of δ would necessarily lead to strong correlation effects and probably a curved Arrhenius plot. We therefore believe that diffusion via isolated vacancies is not the mechanism for the diffusion of oxygen in $YBa_2Cu_3O_{7-\delta}$. The Monte Carlo calculations of Salomons and deFontaine[33] are based on the ordering of oxygen ions at $\delta < 1$, but still yield a strong P_{O_2} dependence of D.

The strong anisotropy of diffusion in the *ab* plane suggests that diffusion may take place parallel to the rows over the O(5) sites, as first suggested by Ronay and Nordlander.[37] The diffusion coefficient for such a mechanism may show only a weak dependence on P_{O_2} for the following reason.[22] If only the oxygen ions at the ends of the chains are mobile, and the number of chains stays constant with stoichiometry, the number of mobile atoms will be independent of P_{O_2}. (The number of chains clearly does change with stoichiometry, but not by much, only a factor of two from $\delta=0$ to $\delta=0.5$.) In this model, the length of the chains changes with stoichiometry, and therefore the jump distance will also change. The mechanism we suggest is that an oxygen ion at the end of a row of O(1) sites jumps into an O(5) site, moves along O(5) sites until it comes to another row end, and attaches itself there. (Recall that the calculation of Ronay and Nordlander[37] showed a near zero activation energy for such motion.) The activation energy is then made up mostly of the energy to move from an O(1) site at the end of a row to a neighboring O(5) site. The defect consisting of an atom in an O(5) site just off the end of a row fulfills the symmetry conditions for giving rise to an internal friction peak. Verification of this model will require detailed calculations of D_{ab} as a function of stoichiometry, taking into account the change of the number and length of rows, and the increase in D_a as rows of oxygen ions on O(5) sites appear. Such a calculation is beyond the scope of this paper.

V. CONCLUSIONS

1. The tracer diffusion of oxygen in $YBa_2Cu_3O_{7-\delta}$ is strongly anisotropic, with $D_b \gg D_a, D_c$.
2. The tracer diffusion of oxygen in $YBa_2Cu_3O_{7-\delta}$ is independent of P_{O_2}.
3. On the basis of these data, we speculate that diffusion in $YBa_2Cu_3O_{7-\delta}$ probably does not take place by the random movement of vacancies in the CuO plane, but rather by the movement of oxygen ion over O(5) sites between the rows of oxygen ions.

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