Study on Chemical Diffusion of Oxygen in Ba$_2$YCu$_3$O$_{7-\delta}$

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Chemical diffusion in the high-T_c oxide superconductor Ba$_2$YCu$_3$O$_{7-\delta}$ system was thermogravimetrically studied in a temperature range from 550 to 850°C under an oxygen pressure of 1 to 10^{-2} atm, using highly densified polycrystalline specimens. Isothermal weight relaxation after stepwise changes of the oxygen pressure were measured and analyzed in terms of oxygen diffusion-controlled kinetics. The chemical diffusion coefficient was found to be strongly sensitive to the oxygen composition. Its absolute value sharply increased with decreasing oxygen deficiency, δ, although it did not change appreciably at the structural transition between orthorhombic and tetragonal phases. Such a compositional dependence of the chemical diffusion is not expected from a simple vacancy diffusion mechanism. It is interpreted in terms of composition-sensitive activation energy for the two-dimensional motion of oxygen within the unique crystal structure of this oxide system. © 1989 Academic Press, Inc.

I. Introduction

It has been well-established by now that structures and various properties of Cu-based high-T_c oxide superconductors are strongly dependent on their chemical compositions and heat treatments (*1, 2*). In particular, one of the most salient features immediately recognized at the early stage of investigations of Ba$_2$YCu$_3$O$_{7-\delta}$, a prototype compound for a series of 90 K-class superconductors, was that its superconducting transition was quite sensitive to its oxygen content, which was most decisively governed by the cooling speed of specimens after firing at high temperatures. Ba$_2$YCu$_3$O$_{7-\delta}$ specimens slowly cooled under oxidizing atmosphere exhibited a sharp superconducting transition at around 90 K, while those quenched from high temperatures were electrically semiconducting and did not show superconductivity.

These observations quite naturally led to detailed studies of oxygen nonstoichiometry of Ba$_2$YCu$_3$O$_{7-\delta}$ and innumerable accounts of work on its composition-sensitive low-temperature properties. At the same time, the magnitude of oxygen diffusion coefficient became of immediate interest since

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it was one of the most critical parameters in optimization of the heat treatment. Knowledge of the compositional and temperature dependences of the oxygen diffusion coefficients should also be quite valuable in elucidating the detailed defect structure of this unique oxide system.

Some preliminary work on oxygen diffusion in Ba$_2$YCu$_3$O$_{7-\delta}$ has already been reported, using various chemical relaxation techniques such as electromotive force (3), conductivity (4), and thermogravimetry (5–7). A gravimetric isotopic exchange study using O^{18} gas under chemically equilibrated condition (8) was also reported. However, the published data show significant scatter. The reason for this may be attributed to the fact that, in addition to the difference in experimental ranges and techniques applied by various authors, specimens having various qualities in terms of sintered density, grain size, and pore distribution were utilized. Thus, questions seem to remain regarding the effective diffusion length which was utilized for the calculation of the diffusion coefficient. There also seems to exist some confusion in the interpretation of the experimentally determined values as chemical or self-diffusion coefficients.

The purpose of the present investigation is to determine systematically the compositional and temperature dependences of chemical diffusion coefficients in Ba$_2$YCu$_3$O$_{7-\delta}$ by a thermogravimetric relaxation technique. It is particularly emphasized that we have utilized sintered polycrystalline pellets with well-defined geometry which contain virtually no interconnected pores.

Although a use of single crystals is extremely desirable in order to clarify structural anisotropy of the diffusion coefficient expected in the present oxide system, large crystals usable in gravimetric measurements such as in this study are not available at the present time. Because of this, the diffusion coefficient determined here

should be considered as average values with respect to crystal orientations. In addition, a possible contribution of grain boundary diffusion is not totally excluded. Nevertheless, the compositional dependence of the diffusion coefficient is interpreted in this study by assuming a bulk diffusion model where the two-dimensional motion of oxygen atoms is the decisive factor. Some conclusions made here are accordingly tentative. However, the present study still seems to clearly demonstrate remarkable features in the defect structure and atomic motions in the unique crystal structure of 90 K-class superconductors.

II. Experimental

2.1 Sample Preparation

Specimens utilized in this study were prepared by two methods both being so-called solution routes in order to ensure the homogeneity of specimens.

Powder specimens used for the nonstoichiometry measurement were prepared by a spray-drying technique. Acetate solutions of Ba, Y, and Cu were first prepared separately by dissolving BaCO$_3$ (99.99% purity), Y$_2$O$_3$ (99.99%), and Cu(C$_2$H$_3$O$_2$)$_2$ (99.9%) in acetic acid at a concentration of typically 0.3 mole/liter. After determining their accurate concentrations through an EDTA titration technique, appropriate amounts of each solution were mixed together and dried in air at 150°C in a commercial spray-drying apparatus. The obtained fine powder was first calcined at 400°C for 10 hr and further fired at 900°C for 6 hr and finally at 950°C for 10 hr. All the heat treatments were performed under air and between each procedure specimens were ground into powder using mortar and pestle.

For the preparation of disk-shape pellets for the diffusion study, very homogeneous submicron-size powders of Ba$_2$YCu$_3$O$_{7-\delta}$

were first prepared through an ethanol-aided coprecipitation technique and fired in air at 800°C. Details of this procedure can be found elsewhere (9). Calcined powders were then cold-pressed into various thickness disk-shape pellets at a pressure of 8 MPa and sintered in oxygen stream (~ 10 cm^3/min) at 1020°C for 8 hr.

Powder and pellet specimens of Ba_2YCu_3 $O_{7-\delta}$ prepared as above were subjected to powder X-ray diffraction analysis. As for the pellet specimens, evaluation of micro-structure was further made by examining the polished cross sections of the specimens by SEM and EPMA. From X-ray and EPMA analyses, the specimens used in the present study were found to consist of a pure single phase of $Ba_2YCu_3O_{7-\delta}$. Crystal grains of the pellets exhibited rather elongated cross-sectional structures, indicating that the grains were actually platelets in three dimensions. A typical grain size along longer edges was 50 μm with an aspect ratio of approximately 4 to 6. The density of the pellets was found by the conventional Archimedes technique to be about 98% in agreement with the SEM observation that the present specimens contained only a small number of unconnected pores.

2.2 Thermogravimetric Measurements

Measurements of the oxygen nonstoi-chiometry and chemical relaxation rate were performed using a thermogravimetric microbalance (Shimadzu TG-31H) appa-ratus connected to a gas mixture system previously described (10, 11). Although our gas system was capable of circulating a controlled gas mixture of O_2/Ar, only pure O_2 gas was employed at various pressures throughout the present investigation. The buoyancy correction of the weight was ap-propriately made for all the experimental points.

For the nonstoichiometry measurement, 1.05 g of fully oxidized powders of Ba_2YCu_3 $O_{7-\delta}$ was accurately weighed and placed in a Pt basket. The nonstoichiometry was de-termined in a temperature range of 300 to 900°C under an oxygen pressure of 1 to 10^{-2} atm. The equilibrium after weight relax-ation for each data point was cross-checked by stepwise change of both increasing and decreasing temperatures and sometimes by changing the oxygen pressure at a constant temperature. Although the stability range of $Ba_2YCu_3O_{7-\delta}$ is much wider according to our earlier study (11), the experimental temperature range was restricted as above in order to avoid accidental decomposition of the specimen at high temperatures. Oxy-gen partial pressure dependence was inves-tigated only above 10^{-2} atm, because at lower pressures than this, hysteresis of weight change was recognized and reliable data could not be obtained especially at low temperatures.

The chemical diffusion was studied in a temperature range from 550 to 850°C in an oxygen pressure range of 1 to 10^{-2} atm us-ing pure O_2 gas. Two pieces of similar ge-ometry of the specimens were selected from the same batch of the disk-shape pel-lets prepared. Both pieces were 8 mm in average diameter and 0.89 mm in average thickness with uncertainty of 0.04 mm de-pending on the position of the pellets. They were placed in a Pt basket so that they did not stand too close to each other. In order to check the thickness dependence of the relaxation rate, specimen pellets, three pieces in this case, with average thickness of 0.43 mm were also examined in the relax-ation measurements. The results for the 0.43 mm, however, were not perfectly re-producible probably reflecting some micro-cracks contained in such thin specimens. Therefore, in this paper, we present mainly the results obtained with the 0.89-mm pel-lets.

The chemical relaxation was studied as follows. After equilibrating the specimen at the desired temperature and oxygen pres-sure, the pressure was changed stepwise,

and the succeeding weight relaxation was recorded until the specimen reached a new equilibrium weight. Since the relaxation rate was found to be strongly dependent on oxygen pressure at given temperatures, it was desirable to minimize the change of oxygen pressure for each run to as small a value as possible but large enough for the weight change over which reliable relaxation curves could be obtained. Based on the nonstoichiometry data, the degree of the pressure change was actually adjusted so that each pressure change corresponded to the change in the oxygen deficiency, $\Delta\delta$ = 0.05 in all runs. Most of the measurements were made in a direction of oxygen pressure decrease, a reducing direction, because an abrupt pressure increase in our apparatus tended to cause more disturbance to the thermobalance system and spoiled the relaxation data in the initial period. However, the relaxation rates for reducing and oxidizing directions were confirmed to be essentially the same except for the final period approaching the new equilibrium.

III. Results

The result of the nonstoichiometry measurement in the present study is illustrated in Fig. 1. The reference point to place the absolute value of the oxygen deficiency δ was selected at P_{O_2} = 1 atm and 300°C where δ = 0.07 was assumed. The reason for this assignment and evaluation of the nonstoichiometry data obtained here will be described in the next section. The chemical relaxation measurement in the present study was made on the basis of this result.

Figure 2 shows typical results of the relaxation measurements made at a selected temperature of 650°C around various oxygen deficiency δ values. Each curve illustrates normalized weight change of the specimen with time. The normalization was made as $[w(t) - w(\infty)]/[w(0) - w(\infty)]$, where
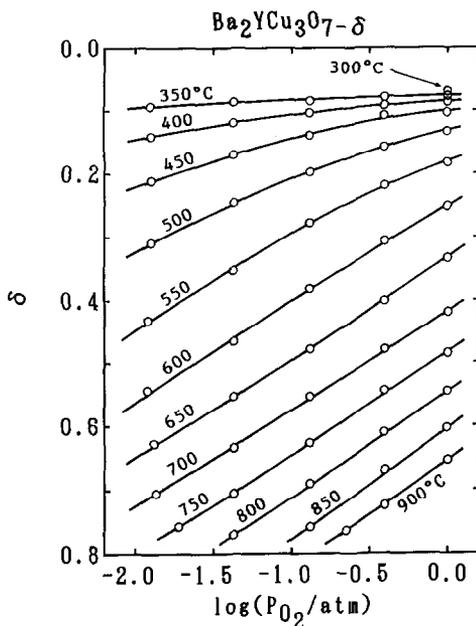
FIG. 1. Reexamined result of oxygen nonstoichiometry of Ba₂YCu₃O₇₋δ as a function of oxygen partial pressure and temperature.

$w(t)$, $w(0)$, and $w(\infty)$ are the weight of the specimen at time t, time zero, and the time when the specimen reached a new equilibrium, respectively. The specified δ for each curve stands for the oxygen deficiency as the relaxation was performed from δ − 0.025 to δ + 0.025.

It was found that the relaxation behavior shown in Fig. 2 was an exponential type which possibly suggests diffusion-controlled kinetics. When the specimens of 0.43 mm thickness were used, the relaxation rate increased about four times. These observations clearly suggest that the principal rate-determining process is the chemical diffusion of oxygen in Ba₂Y Cu₃O₇₋δ. The chemical diffusion coefficient, $\bar{D}$, is a diffusion coefficient which is associated with the mobility of a chemical species under chemical potential gradient and defined as

$$\frac{\partial c}{\partial t} = \text{div}(\bar{D} \text{ grad } c), \qquad (1)$$
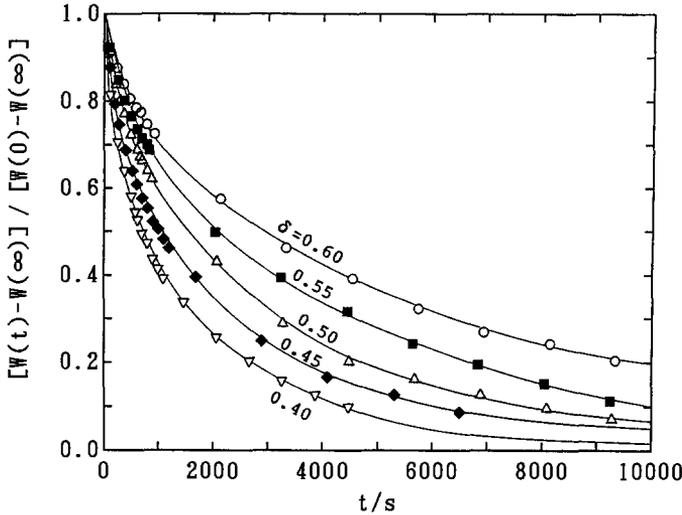
FIG. 2. Gravimetrical relaxation curves of $Ba_2YCu_3O_{7-\delta}$ at 650°C around various δ values. The vertical scale represents the normalized specimen weight as defined in the text. Smoothed lines are drawn as a guide for eyes.

where c and t are the concentration of the chemical species and time, respectively. Since the specimens used in the present study were thin pellets, the diffusion can be approximated to occur in one dimension perpendicular to the flat plate of an infinite size. Then Eq. (1) can be rewritten as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(\bar{D}\,\frac{\partial c}{\partial x}\right) = \frac{\partial \bar{D}}{\partial c}\left(\frac{\partial c}{\partial x}\right)^2 + \bar{D}\,\frac{\partial^2 c}{\partial x^2}. \quad (2)$$

The first term on the right-hand side of Eq. (2) contains concentration dependence of $\bar{D}$. When this term is neglected, Eq. (2) becomes the well-known formula for Fick's second law of diffusion. It may be argued whether this common assumption can be applied to the present experiment, since the diffusion coefficient in the $Ba_2YCu_3O_{7-\delta}$ strongly depends on the composition and the first term may not be small enough. However, considering that the present experiment was performed on the polycrystalline specimens with rather anisotropic grain structures, a detailed analysis of the diffusion profile may not be particularly mean-

ingful. Thus we have neglected the first term.

Using the initial and boundary conditions

$$c(x, 0) = c_0 \qquad \text{for } 0 \leq x \leq h$$

$$c(0, t) = c(h, t) = c_1 \qquad \text{for } 0 \leq t,$$

where h is the thickness of the specimen, and defining

$$\bar{c}(t) = \frac{1}{h} \int_0^h c(x, t)dx \qquad (3)$$

the diffusion equation can be solved as

$$\frac{\bar{c}(t) - c_1}{c_0 - c_1} = \frac{w(t) - w(\infty)}{w(0) - w(\infty)} = \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j + 1)^2}$$

$$\exp\left(-\frac{(2j + 1)^2 \pi^2}{h^2}\bar{D}t\right). \quad (4)$$

In order to analyze the actual data, the following procedure was adopted. Since the right-hand side of Eq. (4) is a function of $(\bar{D}t)$ for a fixed value of h, this was first numerically calculated by taking the first eight terms for the summation. Thus a nu-

merical table compiling the normalized weight change, $[w(t) - w(\infty)]/[w(0) - w(\infty)]$ as a function of $(\tilde{D}t)$ was constructed.

Then, from the experimentally obtained $[w(t) - w(\infty)]/[w(0) - w(\infty)]$, $(\tilde{D}t)$ for each point was calculated. All the data points in Fig. 2 are thus converted to $(\tilde{D}t)$ vs t and plotted in Fig. 3. It should be understood that the slope of the curve at each point corresponds to the chemical diffusion coefficient $\tilde{D}$. It is seen in Fig. 3 that the $\tilde{D}t$ vs t curve passes through the origin and is almost perfectly linear in the initial period of the relaxation. This suggests that the present analysis is successful in terms of the time dependence of the relaxation rate.

The most notable feature observed in Figs. 2 and 3 is the dependence of $\tilde{D}$ on oxygen deficiency δ. For example, $\tilde{D}$ for $\delta = 0.4$ is found to be about three times larger than that for $\delta = 0.6$. Such a strong compositional dependence of $\tilde{D}$ is considered to be the reason why all the relaxation curves in Fig. 3 deviate from linear behavior for the final period approaching the new equilibrium. Because of this, the least-squares fitting of the data points for the calculation

of $\tilde{D}$ was limited only to the regions shown in solid lines in Fig. 3.

All the relaxation data were analyzed with this procedure and the determined chemical diffusion coefficients are plotted in Fig. 4. Figure 4 is shown in terms of a plot of log $\tilde{D}$ vs δ for convenience of presentation.

IV. Discussion

4.1 Nonstoichiometry

Oxygen nonstoichiometry of Ba$_2$YCu$_3$ O$_{7-\delta}$ has been reported by a number of laboratories and an extensive review on this subject has been recently presented by Lindemer and Sutton (12). In their review article, several sets (11, 13–17) of nonstoichiometry data were compared and appreciable divergence between data sets were pointed out. Although it is not possible to assess the qualities of the specimens utilized by independent workers, phase purity could be one of the reasons for the disagreement. In our data in the previous study (11), the specimen was possibly pushed out of the stability range when
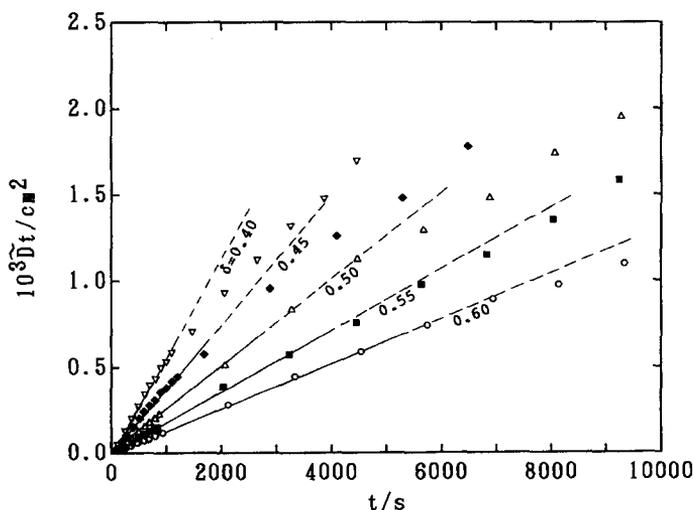
FIG. 3. Relation between t and $\tilde{D}t$ calculated from the data points in Fig. 2 using Eq. (4). Linear least-squares fitting was made using the data points of the initial period where solid lines are indicated.
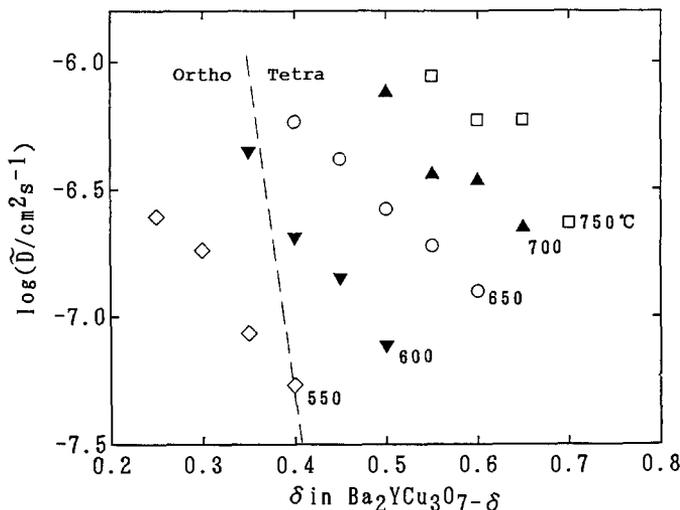
FIG. 4. Determined chemical diffusion coefficient $\tilde{D}$ of oxygen in $Ba_2YCu_3O_{7-\delta}$ as a function of δ. Approximate phase boundary between orthorhombic and tetragonal phases (15) is indicated by a dashed line.

1000°C data were measured at $\log(P_{O_2}/atm)$ = −0.7, causing partial decomposition. In the present study, we have carefully checked the specimen by a powder X-ray analysis before and after the nonstoichiometry measurement. The fully oxidized specimen after all the measurement was confirmed to be a single phase with lattice parameters, a_0 = 3.820(4), b_0 = 3.887(4), and c_0 = 11.684(10).

The determination of the absolute values of oxygen contents at some reference points is also worth discussion. For this, various techniques such as hydrogen reduction, carbon reduction, and iodometric titration have been performed, and oxygen deficiency δ of $Ba_2YCu_3O_{7-\delta}$ has been reported to be approximately in the range 0.08 to 0.02 in the fully oxidized specimens. However, close comparison of the analyzed values seems to reveal slightly but consistently larger δ determined by the iodometry technique (11, 18) than the result obtained by the reduction methods (13–15, 17). Such a tendency can also be found in a study by Harris et al. (19) who applied the two independent techniques on a single batch of specimens. This difference may arise from inherent problems in these analytical methods; however, the details are not known.

The present authors have made iodometric titration analyses on a large number of $Ba_2YCu_3O_{7-\delta}$ specimens as well as those with rare-earth substitution. According to these experiences, δ = 0.07 ± 2 has been the most frequently observed value for the oxygen deficiency of fully oxidized specimens. This is why we have placed our reference composition as described in Fig. 1.

Finally, it is added that in all of the reported studies, the cationic compositions of the specimens have always been assumed to be perfectly stoichiometric in Ba_2YCu_3 $O_{7-\delta}$, but in none of them does this assumption seem to be based on detailed chemical analysis. Therefore, this might cause the difference in the oxygen content among various specimens.

4.2 Chemical Diffusion Coefficient and Diffusion Mechanism

Discussion is now turned to the chemical diffusion coefficient obtained, and interpre-

tation is focused on how a strong dependence of $\tilde{D}$ on δ can arise in $Ba_2YCu_3O_{7-\delta}$.

Among the various known mechanisms of diffusion in crystalline systems, the simplest ones are the vacancy and the interstitial mechanisms.

In perovskite oxides such as $La_{1-x}Sr_x$ $CoO_{3-\delta}$ and $LaFeO_{3-\delta}$, Fueki *et al.* (20) found that the chemical diffusion coefficient $\tilde{D}$ was independent of the vacancy concentration, c_V, and demonstrated that the diffusion was operative via a simple vacancy mechanism. In this case, the diffusion coefficient of the oxygen vacancy D_V was also independent of δ, which is the behavior expected in a dilute limit where there are no interactions among defects. However, the observed strong dependence of $\tilde{D}$ on δ in $Ba_2YCu_3O_{7-\delta}$ clearly contradicts such a simple mechanism.

Although the nonstoichiometry of Ba_2 $YCu_3O_{7-\delta}$ has been frequently described in terms of the "oxygen deficiency," δ, this nomenclature is rather confusing from a structural point of view. As is well known, the oxygen composition of $Ba_2YCu_3O_{7-\delta}$ can be varied by removing or inserting oxygen on the horizontal Cu(1) plane between the Ba sites (21), where the average occupancy of the oxygen sites in this plane never exceeds 0.5 even under the fully oxidized condition. When δ increases to 1.0, the occupancy approaches zero. From this structural aspect, therefore, it would not be appropriate to regard the unoccupied oxygen sites as oxygen vacancies. Alternatively, it would be better to consider the oxygen on these sites as intercalated species. The oxygen diffusion then should be viewed to proceed via an interstitial-like mechanism. Under this picture, the oxygen composition of the present system is described as $Ba_2YCu_3O_{6+y}$, where y represents the amount of excess oxygen.

4.3 Self-Diffusion Coefficient of Oxygen

Following the treatment by Steele (22), the chemical diffusion in a multicomponent system with predominantly electronic conduction is expressed as

$$\tilde{D} = D_i^* \left(\frac{\partial \ln a_i}{\partial \ln c_i}\right), \qquad (5)$$

where D_i^*, a_i, and c_i are self-diffusion coefficient, activity, and concentration of the species i, respectively. In the present case, we assume the diffusing species is only oxygen and it predominantly takes place through the oxygen sites in the Cu(1) plane. Furthermore, the atomic jump is assumed to be isotropic within this plane, neglecting the orthorhombic site distribution of the oxygen atoms. Then Eq. (5) becomes

$$\tilde{D} = \tfrac{1}{2} D_O^* \left(\frac{\partial \ln P_{O_2}}{\partial \ln c_O}\right) = \tfrac{1}{2} D_O^* \left(\frac{\partial \log P_{O_2}}{\partial \log y}\right), \qquad (6)$$

where c_O is the concentration of oxygen atoms in the Cu(1) plane being equal to $y/2$ and P_{O_2} is the oxygen pressure.

One may conjecture that the y dependence of $\tilde{D}$ shown in Fig. 4 comes from the so-called thermodynamic factor, $\partial \log P_{O_2}/\partial \log y$. However, this is not the case. As shown in Fig. 5, the thermodynamic factor corresponding to the slopes in Fig. 5 does not appreciably change with y under a given temperature. The calculated oxygen self-diffusion coefficient, D_O^*, as shown in Fig. 6, is found to be also strongly y dependent, suggesting that strong correlation among the oxygen atoms on the Cu(1) plane might be sought.

According to a standard textbook (23), the self-diffusion coefficient operated via an interstitial mechanism is expressed, using microscopic parameters, as

$$D_O^* = \left(\alpha \, a_0^2 \, \nu \, \exp \frac{\Delta S_m}{k}\right) \exp\left(-\frac{\Delta H_m}{kT}\right), \quad (7)$$

where α, a_0, and ν are geometrical constant, jump distance, and attempt frequency of mobile species, respectively, and ΔS_m and ΔH_m stand for the entropy and enthalpy of the motion.

The question is then whether the strong
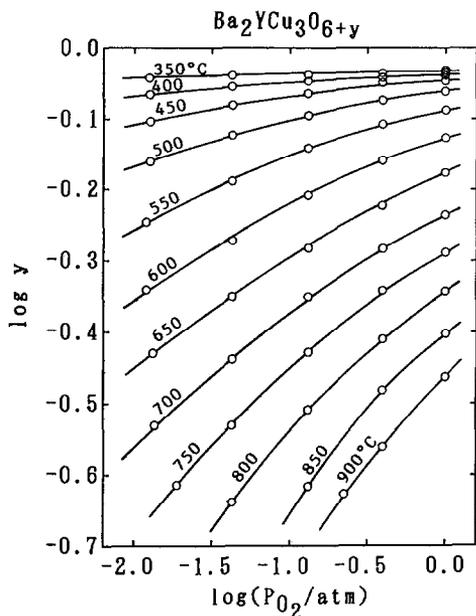
FIG. 5. Relation between $\log y$ vs $\log P_{O_2}$. The slope corresponds to the thermodynamic enhancement factor of chemical diffusion.

only weakly composition dependent. Second, it is tempting to consider y dependence of ν which may arise from highly correlated and anisotropic motion of oxygen. In such a case, however, more clear difference of D_O^* in the orthorhombic and tetragonal crystal structures should be expected. In Fig. 6, the approximate phase boundary given by Specht *et al.* (15) is indicated, across which no discontinuity in D_O^* is found. The compositional dependence of ΔS_m may also be appreciable; however, this does not explain the observed behavior either, because ΔS_m is expected to be smaller for larger y, which should lead to smaller D.

The compositional dependence must therefore be attributed to ΔH_m, and it was decided to obtain the empirically fitted equation of D_O^* under this model. Since the semilogarithmic plot of Fig. 6 gives nearly linear behavior, the fitting was made according to

compositional dependence of D_O^* can be explained in terms of these microscopic parameters. First of all, α and a_0 are readily excluded since these are either constant or

$$D_O^* = A(2 - y)\exp\left(-\frac{1}{kT}[H_0 - 2y\,H']\right),$$

$$(8)$$
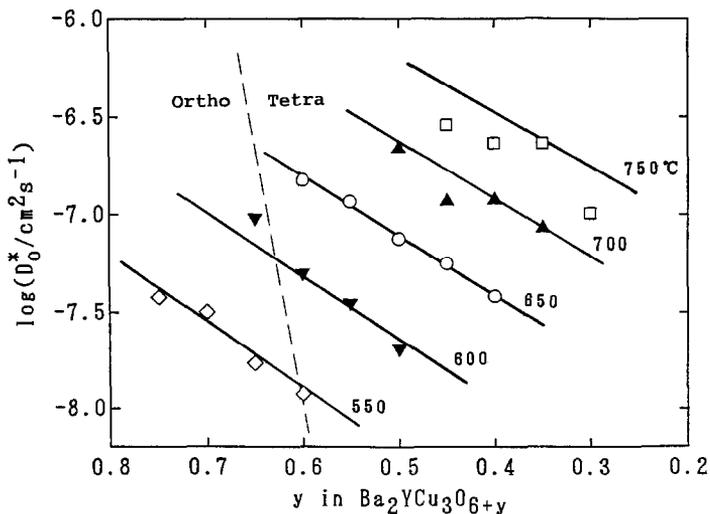
FIG. 6. Calculated oxygen self-diffusion coefficient D_O^* as a function of y. The fitted lines to Eq. (8) with parameter values described in the text are also shown.

where a correction factor $(2 - y)$ is included since the oxygen atom cannot jump into the sites already occupied.

The parameters A, H_0, and H' were obtained by least-squares fitting of the data points in Fig. 6 as 9.55×10^1 cm^2 sec^{-1}, 2.0 eV, and 0.31 eV, respectively. The fitted lines with these parameters are indicated in Fig. 6 by solid lines, and it is found that Eq. (8) fits the data points fairly well. The self-diffusion coefficients are plotted in an Arrhenius form in Fig. 7, where $y = 0.3, 0.4, 0.5$, and 0.6 were fitted by linear functions. The activation enthalpy for these lines ranges from 1.81 to 1.63 and extrapolates to 1.38 eV at $y = 1.0$.

The strong compositional dependence of chemical diffusion coefficient $\bar{D}$ in Ba$_2$YCu$_3$O$_{7-\delta}$ can thus be explained through a similar dependence of oxygen self-diffusion coefficient D_O^* which results from the variation in enthalpy of oxygen motion with y. Larger oxygen content y (or smaller deficiency δ) is associated with smaller ΔH_m and results in larger D_O^*. The reason for this could be related to the interaction energy between neighboring or next-nearest-neighbor oxygens on the Cu(1) sites, but is only speculative and remains an open question.

Finally it is desirable to compare the self-diffusion coefficient obtained here with those determined by other investigators. However, as stated under Introduction, no literature can be found which reports D_O^* in the present system in an unambiguous manner, except for the study made by Ikuma and Akiyoshi through isotopic exchange measurement (8). Their result of D_O^* determined in the temperature range 250–400°C for the composition of $y = 0.93$ was

$$D_O^*/\text{cm}^2 \text{ sec}^{-1} = 2.87 \\ \times 10^{-1} \exp(-1.79 \text{ eV}/kT) \quad (9)$$

and we consider the agreement with the present study to be fair. Although the pre-exponential factor is more than two orders different, this may arise from the inappropriate estimation for average particle size of their powder specimens and may also reflect the difference of the experimental temperature range.

Acknowledgments

FIG. 7. Replotting of data shown in Fig. 6 in the Arrhenius form.

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