

Oxygen Diffusion in High- T_c Superconductors

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OXYGEN DIFFUSION IN HIGH- T_c SUPERCONDUCTORS

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Topics: High- T_c Superconductors, Diffusion, Oxygen, Anisotropy

ABSTRACT

The cuprate superconductors are fascinating not only because of their technical promise, but also because of their structures, especially the anisotropy of the crystal lattice. There are some structural similarities among these compounds, but also significant differences. Measurements of the oxygen tracer diffusion coefficients have been carried out as a function of temperature, oxygen partial pressure, crystal orientation, and doping in the La-Sr-Cu-O, Y-Ba-Cu-O, and Bi-Sr-Ca-Cu-O systems. These measurements have revealed a variety of defect mechanisms operating in these compounds; the exact nature of the mechanism depends on the details of the structure.

INTRODUCTION

At the time of the discovery of the cuprate high- T_c superconductors [1,2], we were engaged in measuring the tracer diffusion of oxygen in CoO [3]. We were fortunate enough to obtain good samples of the high- T_c materials from our colleagues in the Ceramics Section of Argonne's Materials and Components Technology Division, and embarked on a program of measuring the tracer diffusion coefficient of oxygen in these materials. The measurements were motivated by the obvious influence of the oxygen ion vacancies on the superconducting properties both for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [4] and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [5], as well as by the desire to elucidate the point defect behavior in these materials and in the newer Bi-based superconductors. This paper summarizes the results of these investigations and describes the wide variety of defect structures and diffusion mechanisms in the high- T_c superconductors.

EXPERIMENTAL TECHNIQUES

In principle, we tried to measure the tracer diffusion coefficient of oxygen (D), i.e., the diffusion coefficient of oxygen in the absence of a gradient of oxygen potential, because we believed that this type of measurement was more likely to throw light on the basics of atomic motion than measurements of chemical diffusion. To do this, the samples were subjected to a pre-diffusion anneal under the same oxygen partial pressure (P_{O_2}) of natural oxygen (0.2 at.% ^{18}O) and at the same temperature (T) as was later used for the diffusion anneal in ^{18}O , but for a much longer time, so that no oxygen concentration gradient existed over the diffusion zone.

The depth profiles were determined by secondary ion mass spectrometry (SIMS), and the diffusion coefficients were calculated from fits of these depth profiles to the appropriate solutions of the diffusion equation [6]. The solutions used, as well as the experimental details, are given in the papers referenced below. It should be noted that selecting the appropriate solution for diffusion in polycrystalline samples was complicated by the anisotropy of the diffusion in these materials, and by the fact that the analyzed area covered several grains of different orientation, but not enough grains to allow the use of an average D over the entire hemisphere of orientations [7]. These effects increased the scatter in the data; the reproducibility of the measured values of D was a factor of 2, but occasionally worse scatter was observed.

The anisotropy follows from the fact that D is a second-rank tensor [8]. In an orthorhombic material, the diffusion coefficient in a direction that makes angles Θ_a , Θ_b , and Θ_c with the principal axes is given by:

$$D(\Theta) = D_a \cos^2\Theta_a + D_b \cos^2\Theta_b + D_c \cos^2\Theta_c, \quad (1)$$

where the D 's are the diffusion coefficients along the principal crystallographic axes. If the material is tetragonal, $D_a = D_b = D_{ab}$. (Of the materials considered in this paper, $La_{2-x}Sr_xCuO_4$ is tetragonal for $x > 0.08$, $YBa_2Cu_3O_{7-x}$ is orthorhombic (at temperatures below the phase transformation, see below), but behaves as a tetragonal material because of twinning in the ab -plane, and the $BiSrCaCuO$ compounds are (nearly) tetragonal.) In a tetragonal crystal,

$$D(\Theta) = D_{ab} \sin^2\Theta + D_c \cos^2\Theta, \quad (1a)$$

where Θ is the angle between the diffusion direction and the c -axis. In a polycrystalline aggregate of randomly oriented tetragonal grains,

$$D = \frac{2}{3} D_{ab} + \frac{1}{3} D_c. \quad (2)$$

Most of our experiments were carried out on polycrystals. Single crystals were used when available; these were usually thin plates with the large face parallel to the ab -plane, so diffusion in the c -direction was measured. In all of these materials $D_c \ll D_{poly}$, so $D_{poly} \approx D_{ab}$.

DIFFUSION IN $La_{2-x}Sr_xCuO_4$

Quite early in studies of this compound, a peak was observed in the plot of T_c vs. x (critical temperature vs. Sr concentration) at $x \approx 0.15$ (figure 1). The peak suggested a connection between the superconducting properties and the concentration of

oxygen vacancies, since the vacancies could compensate for the charge difference between the Sr^{2+} ions and the La^{3+} ions they replaced. We measured the diffusion of oxygen in polycrystals with $x = 0.10, 0.15,$ or 0.20 [9] (figure 2) and positron annihilation [10] in similar samples. Figure 2 also contains oxygen diffusion data measured on c -axis single crystals [11]; we show only the lines for $x = 0$ and 0.07 . For the polycrystals, D decreased with increasing x ; the fact that the c -direction diffusion for $x = 0.07$ is approximately equal to diffusion in a polycrystal with $x = 0.2$ indicates that $D_c < D_{ab}$. If the same inequality holds for $x = 0$, it is easy to see that diffusion in the polycrystals with $x = 0$ would be very fast indeed; we were unsuccessful in measuring diffusion in compounds with $x = 0$ for this reason.

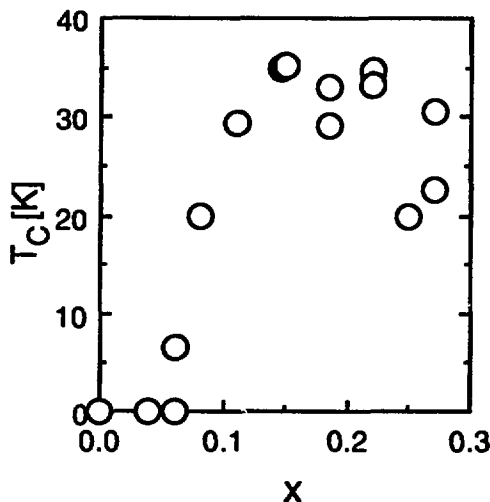


Fig. 1. Plot of T_c for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ vs. x . Data from ref. 4.

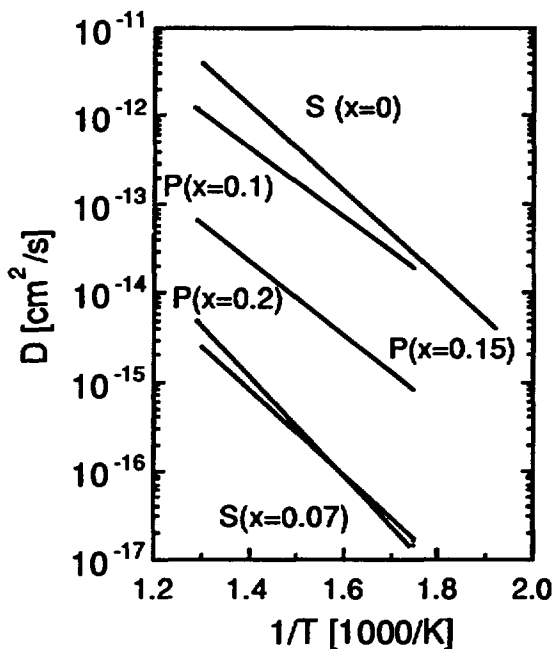


Fig. 2. Arrhenius plots for the diffusion of oxygen in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. S indicates diffusion in the c -direction in single crystals [11], P indicates diffusion in polycrystals [9].

The apparently contradictory behavior in the polycrystals between the increase in vacancy concentration, but a decrease in D as x increases, was explained by a model [10] that suggested that at low Sr concentrations, when most of the Sr ions were likely to be isolated, their excess negative charge *vis à vis* the La ions was compensated by electron holes (charge = +1), and that these holes were responsible for the superconductivity. Near $x = 0.15$, however, the Sr atoms started to occur as pairs on nearest-neighbor La sites, and the charges of these pairs were compensated by oxygen ion vacancies (charge = +2). Thus the hole concentration and hence T_c peaked and the vacancy concentration started to increase at $x \approx 0.15$. The activation energy for diffusion increased because these Sr_2 -vacancy complexes not only were immobile, but also impeded the diffusion of oxygen. This phenomenon is similar to the decrease of oxygen ion conductivity with doping at high

concentrations of di- or trivalent dopants observed in the CeO_2 and stabilized ZrO_2 systems [12]. Calculations based on this model [10] qualitatively reproduced the experimental peaks, and the experimentally observed [13, 14] vacancy concentrations (figure 3).

Opila et al. [15] extended not only the diffusion measurements, but also the defect model to low x . They showed that the rapid diffusion of oxygen at low x is due to diffusion via interstitials. With the addition of Sr, vacancies become the dominant diffusion mechanism, with a consequent slowing down of diffusion. At still higher values of x , the above-mentioned complex formation takes place, resulting in still slower diffusion. The defect structure can be described in a classical Kröger-Vink diagram.

DIFFUSION IN $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

The influence of oxygen stoichiometry on T_c in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (figure 4) is even more spectacular than in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, but the defect structure is different. Oxygen vacancies are introduced not by doping with aliovalent cations, but by changing the temperature or oxygen partial pressure, and their charge is compensated by changes in the hole concentration [16]. The oxygen ion vacancies occur (mostly) on the O1 sites (see figure 5 for the five different kinds of oxygen sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [17]). As the temperature is increased (or the P_{O_2} is decreased), an increasing

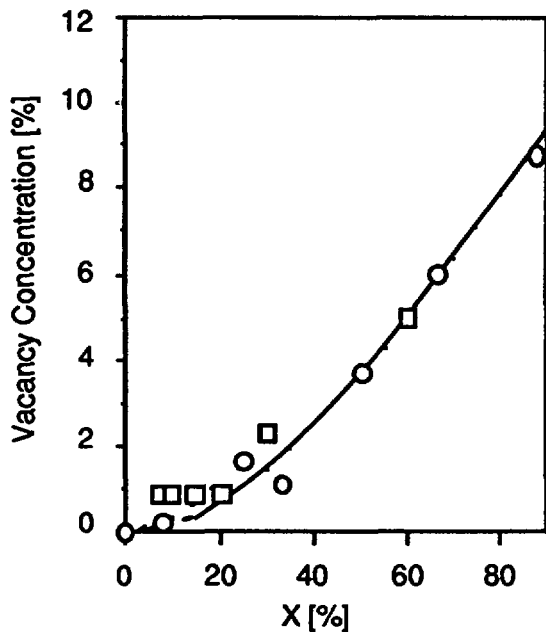


Fig. 3. Plot of oxygen vacancy concentration in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ vs. x . Line: calculated from the model of Smedskjær et al. [10]. Squares: neutron diffraction data [13]. Circles: from thermogravimetric analysis [14].

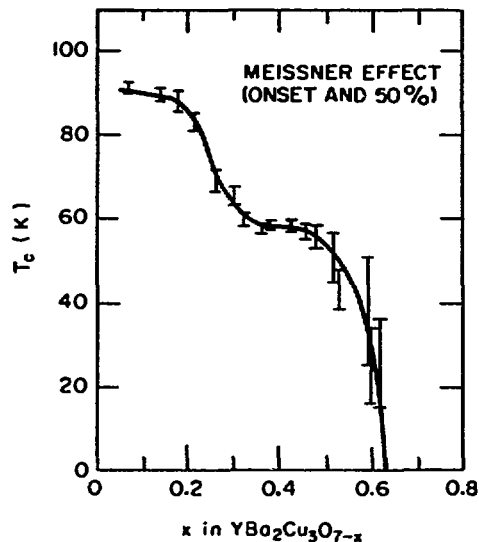


Fig. 4. Plot of T_c in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ vs. x [5].

number of O1 sites becomes vacant, and x increases. The vacancies, however, do not occur at random; there is a tendency for the remaining oxygen ions to be ordered in row segments [18]. The filled rows themselves tend to order; e.g., at $x = 0.5$, alternate rows of O1 sites are full or empty. (This configuration is responsible for the plateau in T_c at 60K.) At temperatures not far below the orthorhombic-tetragonal (O-T) transformation, some oxygen ions occur on O5 sites, again in rows. At the (O-T) transformation, which occurs at $\approx 685^\circ\text{C}$ under 1 atm PO_2 , the same number of O5 and O1 sites are occupied, but the occupied sites still tend to be in rows. Phase diagrams corresponding to these configurations have been calculated by several groups, see e.g. [18].

We carried out measurements of the tracer diffusion of oxygen in polycrystals under one atmosphere of oxygen [7] (a constant pressure, not constant x experiment), as a function of PO_2 at 400°C and 600°C , on single crystals in the c -direction and in the ab -plane, and on detwinned single crystals [19] in the a - and b -directions. The salient points of the results were:

1. Diffusion was highly anisotropic, with $D_c \ll D_{ab}$ (figure 6).
2. $D_a \ll D_b$ in the one experiment where both of these were measured [19] (figure 7), the triangle in figure 6 was obtained for D_b and a value at least 100 times smaller for D_a .

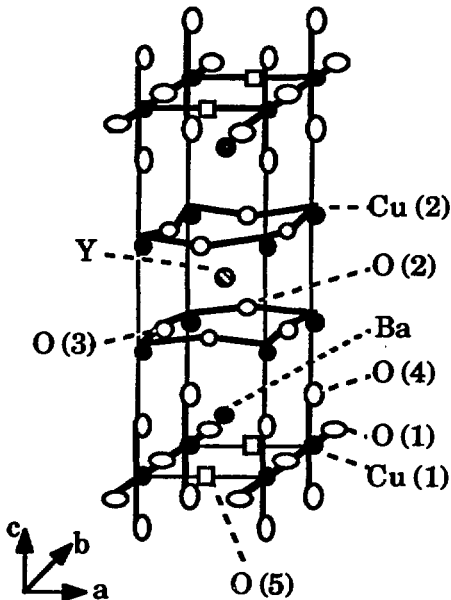


Fig. 5. Structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [17].

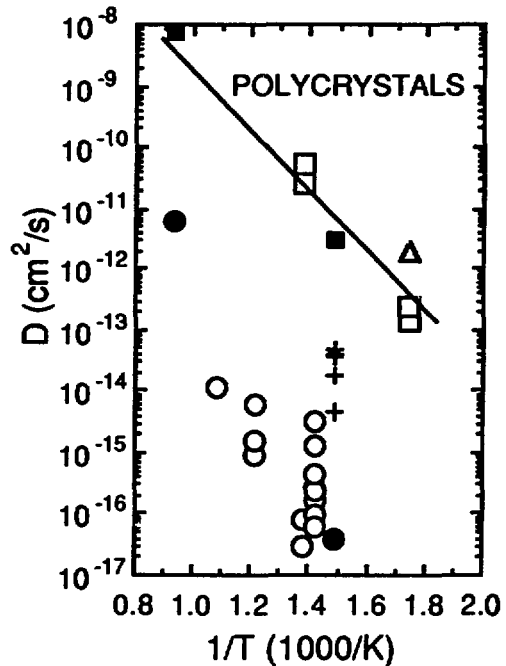


Fig. 6. Arrhenius plot for the diffusion of oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Line: polycrystals [7]. Hollow squares: D_{ab} in twinned crystals, triangle: D_b , crosses: see text, open circles: D_c [19]. Filled circles: D_c , filled squares: D_{ab} [20].

3. $D_{ab} \approx D_{poly}$, $D_b \approx 10 \times D_{poly}$ (figure 6).
4. The values of D_c were scattered over several orders of magnitude (figure 6).
5. The Arrhenius plot for diffusion in polycrystals was straight, showing no break or bend at the O-T transformation, within the above-mentioned factor of 2 uncertainty (figure 8).
6. The diffusion coefficient in polycrystals was independent of P_{O_2} , within the above-mentioned factor of 2 uncertainty (figure 9).

The data of refs. 20 and 21 were in good agreement with ours, but not the data of Ikuma and Akiyoshi [22]. Possible reasons for this discrepancy were given in [7]. The diffusion coefficients calculated from internal friction data (see ref. [19]) are also in agreement with our results.

The above six points can be explained as follows. The observed anisotropy of diffusion is a fact of nature, stemming from the crystal and defect structures of the material. $D_c \ll D_{ab}$ was expected because of the high concentration of vacancies on the O1 sites relative to the other sites. The anisotropy $D_a \ll D_b$ can be explained by diffusion via lattice vacancies [23,24] or by interstitial diffusion along the Cu-O chains, as first suggested in a theoretical paper by Ronay and Nordlander [25].

The near equality of D_{ab} and D_{poly} follows directly from eq. 2 and the anisotropy. The fact that $D_b \approx 10 D_{ab}$ can be understood from figure 10, which shows that for diffusion in the b -direction in an untwinned crystal, all the jumps are in the diffusion direction, whereas in a twinned crystal, only the jumps in the twins oriented so that the b -direction is parallel to the diffusion direction (i.e., the analyzing beam) are effective in giving rise to observable diffusion. (Jumps in the

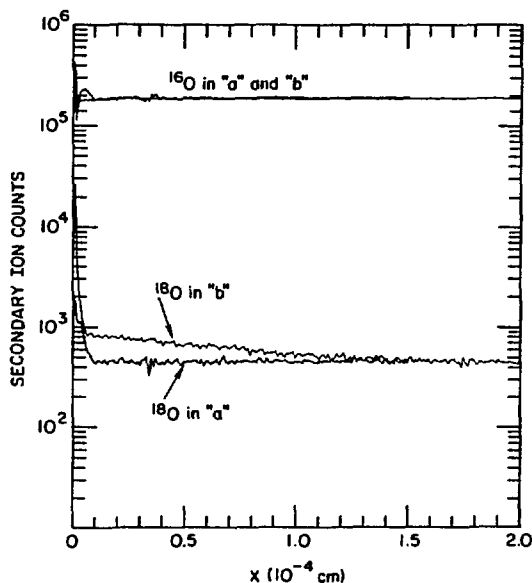


Fig. 7. Counts for ^{16}O and ^{18}O for both a - and b -directions in untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ single crystals. [19]

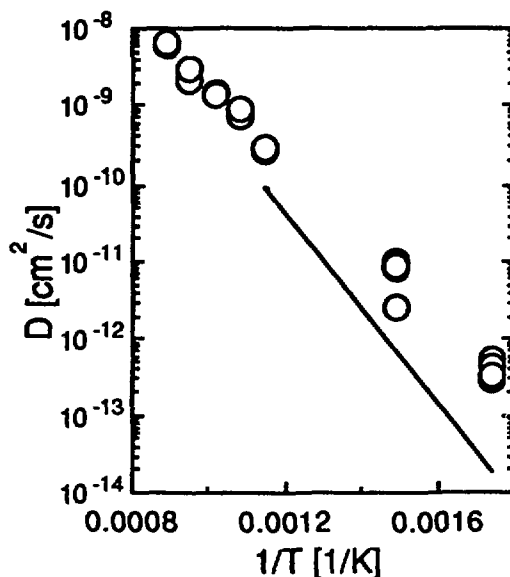


Fig. 8. Arrhenius plot for the diffusion of oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ polycrystals. Circles: [7], line: [21].

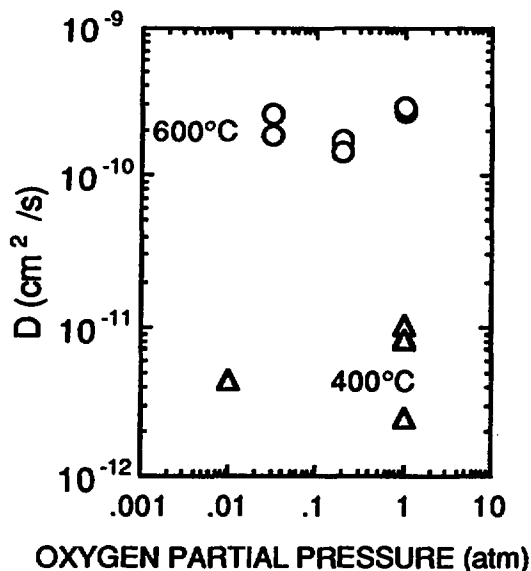


Fig. 9. Effect of P_{O_2} on diffusion in $YBa_2Cu_3O_{7-x}$ polycrystals [7,19].

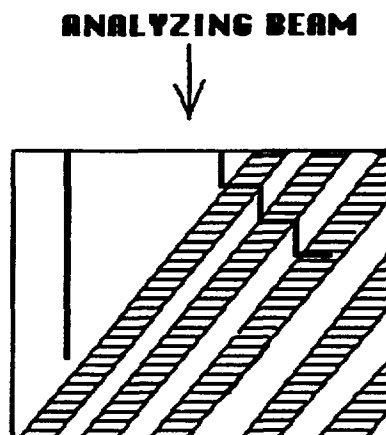


Fig. 10. Diffusion in untwinned and twinned areas. White: b vertical, shaded: b horizontal.

twins that are oriented so that the b -direction is perpendicular to the analyzing beam take place with the same frequency, but do not move the atoms in a measurable way.) If the atom diffusing in a twinned crystal encountered a large number of twins with the same total thickness in both orientations, D_b would equal $4 D_{ab}$. The scatter in the values of the crosses in figure 6 is another manifestation of this phenomenon. These values were obtained from selected area measurement on one crater in a detwinned crystal; the original diffusion direction had been b , but the crystal retwinned to a . The scatter is caused by the different amount of twins with diffusion direction parallel to b in each analyzed area; thus $D_a \leq$ the lowest cross at this temperature.

The huge scatter in the measured values of D_c derives from equation 1a and the mosaic structure of the single crystals; if $D_c \ll D_{ab}$, even a small misorientation can lead to an ab -contribution that completely overwhelms the contribution from D_c , even though Θ is very close to 0° .

Results 5 and 6 above, the straight Arrhenius plot for diffusion in $YBa_2Cu_3O_{7-x}$ polycrystals and the P_{O_2} -independence of D , cannot be explained on the basis of purely geometric arguments, but can be used to shed some light on the atomistics of the diffusion mechanism. From the simple defect reaction:



the vacancy concentration would vary as $(P_{O_2})^{-1/2}$; the fact that the P_{O_2} dependence of D is much weaker than this indicates that the diffusion does not take place by a simple vacancy mechanism, such as proposed by Bakker [23] or Tu [24].

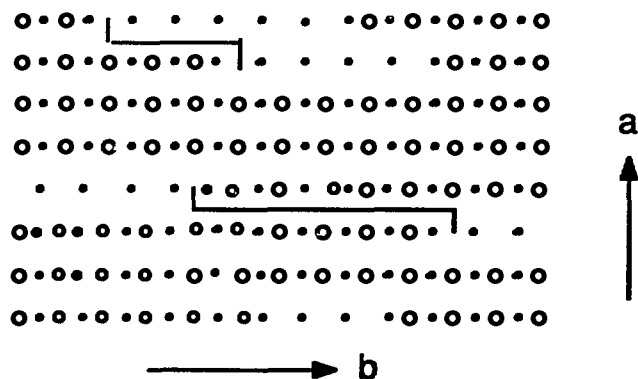


Fig. 11. Schematic sketch of proposed diffusion mechanism for oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$. Open circles – oxygen, Closed circles – copper.

The defect model that fits all of our experimental observations is the one of Hong et al. [26], in which the mobile oxygen ions are the ones at the ends of a row (figure 11). Diffusion takes place by one of these ions moving to an O5 site, running along O5 sites until it comes to another row end and dropping into the O1 site there. (This mechanism may not apply for near-perfect stoichiometry, but no diffusion measurements were performed for $x \approx 0$.) The model fits the low P_{O_2} dependence of D because the number of row ends only changes slightly with P_{O_2} . (The length of the rows changes as oxygen ions are added or removed; the number of rows changes with the phase changes described above. Oxygen ions are not removed from the middle of a row because this would increase the number of three-coordinated Cu ions, and this is not an energetically favored configuration [26].) The Arrhenius plot is straight because the rows still exist in the tetragonal phase. The a - b anisotropy at low temperature can also be explained by this mechanism.

Measurements of oxygen tracer diffusion in the related compound $\text{YBa}_2\text{Cu}_4\text{O}_8$ (124) have been begun. The structure of the 124 compound is similar to that of 123 except that 124 contains two Cu-O chains along the b -direction [27], and there are no oxygen vacancies due to non-stoichiometry in 124 [28]. Preliminary (at this writing) oxygen diffusion measurements on a polycrystalline sample furnished by Robert Williams (Oak Ridge National Laboratory) and U. Balachandran (Argonne) displayed non-Fickian behavior (poor fits of the depth profiles to the sum of two complimentary error functions), as well as a diffusion coefficient that decreased with time at the beginning of the diffusion anneal. The values of D were, however, clearly several orders of magnitude lower than in 123, indicating that the oxygen ion vacancies present in 123 are in some way essential to the rapid diffusion of oxygen ions.

Since we do not yet know the extent of the anisotropy, nor the activation energy for diffusion, we can speculate on the mechanism of diffusion in 124 unhampered by too much data. Perhaps the Ronay-Nordlander mechanism [25] is not dominant in 124 because the "rows" are very long, being broken only by thermal vacancies, so an O1-O5 jump will in most cases be followed by an immediate return jump, or in other words, the correlation factor (and therefore D_0) are very low. Or the difference in D could be in the activation energy because of the need to form a vacancy for the

diffusing atom to fall into. On the other hand, the mechanism could be completely different: since there is now a two-dimensional network of O1 sites in the *b*-direction, diffusion via vacancies should be possible along this network. If diffusion in the *ab*-plane takes place via vacancies, the anisotropy between D_c and D_b can be predicted to be smaller in 124 than in 123. Further measurements, including ones on 124 *c*-direction single crystals furnished by Bogdan Dabrowski, are under way, and with luck, will have indicated the operative mechanism by the time of the conference.

DIFFUSION IN THE BiSrCaCuO SUPERCONDUCTORS

The BiSrCaCuO system contains three superconducting compounds: $\text{Bi}_2\text{Sr}_2\text{CuO}_x$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$. They are often referred to by the cation subscripts as 2201, 2212, and 2223. All of these compounds are layered perovskites [29] consisting of Bi-O, Sr-O, Ca, and Cu-O layers (figure 12). The structures undergo an incommensurate modulation [30] thought by some to be due to interstitial oxygen atoms located in the Bi-O plane. We have measured D_c and D_{poly} on the 2212 [31] and D_c and D_{ab} on 2201 single crystals [32]; as this is written, the phase purity of the available 2223 is not yet sufficient to allow interpretation of a diffusion measurement.

The diffusion of oxygen in the 2212 (figure 13) is anisotropic, with $D_{\text{poly}} \gg D_c$, i.e., $D_{ab} \gg D_c$ and:

$$D_{\text{poly}} = (1.7_{-0.8}^{+1.5}) \times 10^{-5} \exp[-(0.93 \pm 0.04)\text{eV}/kT] \text{ cm}^2\text{s}^{-1}, \quad (4)$$

$$D_c = (0.6_{-0.2}^{+0.3}) \exp[-(2.2 \pm 0.03)\text{eV}/kT] \text{ cm}^2\text{s}^{-1}. \quad (5)$$

The anisotropy of the D_0 's is especially striking: the value of D_{0c} near unity suggests that diffusion in the *c*-direction takes place via vacancies [33], whereas the much lower value of D_{0ab} suggests that diffusion in the *ab* -plane takes place via the motion of interstitials. The ideas that oxygen interstitials in the Bi-O planes cause the incommensurate modulations and that diffusion takes place via interstitials in the *ab*-plane thus reinforce each other, even though neither one is conclusively proven.

Since the structures of the *ab*-planes in 2201 are the same as in 2212, the diffusion coefficient in these planes can be expected to be the same, and this is indeed found experimentally (figure 13). Why the values of D_c for the two compounds differ by only a factor of ≈ 4 , even though the 2212 contains a Ca plane and a Cu-O plane not found in the 2201, is less obvious. The data are too scattered to allow us to decide whether the difference is in the D_0 or the activation energy. Our qualitative analysis is the following: The activation barrier is nearly the same for the *c*-direction jump in the two compounds, indicating that the activation barrier occurs between similar pairs of planes in the two compounds. It seems reasonable to assume that there is one activation barrier, i.e., one interplanar jump, that is rate-controlling. The jump distance is therefore equal to the *c* parameter, so the square of the jump distance, which is a factor in D_0 , is 1.6 times greater for 2212 than for 2201. However, we have no quantitative explanation for the remaining factor of 2.5.

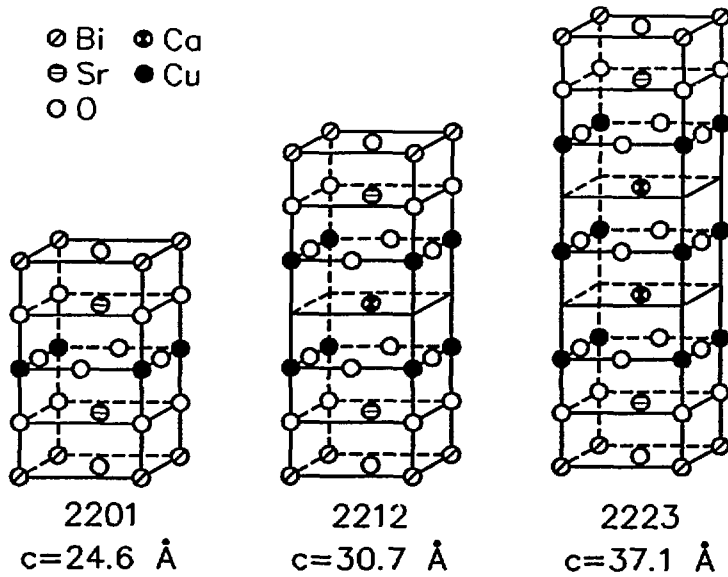


Fig. 12. Structure of BiSrCaCuO super-conductors. [29]

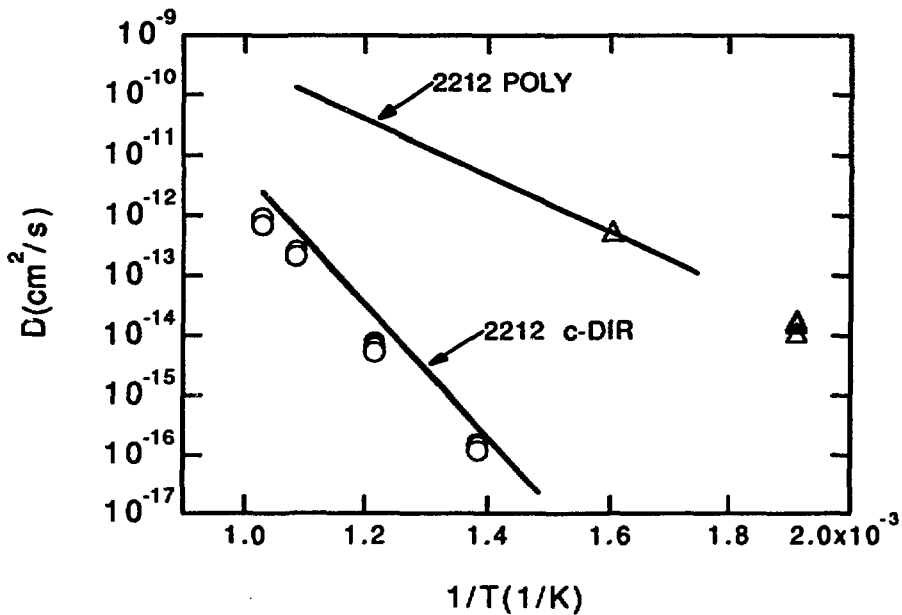


Fig. 13. Arrhenius plot for the diffusion of oxygen in BiSrCaCuO.
 Lines: diffusion in 2212 [31]. Triangles: D_{ab} in 2201. Circles: D_c in 2201 [34].

SUMMARY

The object of this paper has been to sketch the variety of mechanisms responsible for diffusion in the cuprate superconductors. These are:

La_{2-x}Sr_xCuO₄: oxygen interstitials at low Sr concentration, oxygen vacancies at high Sr, but D decreases with increasing vacancy concentration due to the formation of Sr₂-V_O complexes.

YBa₂Cu₃O_{7-x}: an interstitial-type mechanism for diffusion along rows in the *ab*-plane; probably vacancies along the *c*-direction.

YBa₂Cu₄O₈: diffusion much slower than in YBa₂Cu₃O_{7-x}, but mechanism has not been determined.

Bi₂Sr₂CuO_x, Bi₂Sr₂CaCu₂O_y: interstitials in the *ab*-plane, vacancies in the *c*-direction.

It is to be noted that the high-T_c oxide superconductors offer rich possibilities for further studies of diffusion. Data and models for oxygen diffusion in 123 YBCO and the 2201 and 2212 BSCCO compounds are well established, and it would be interesting to see how 124 YBCO, 2223 BSCCO, and the Ti-Ba-Ca-Cu-O superconductors fit these patterns; the processing of the last two of these materials is very sensitive to P_{O₂}. Furthermore, cation diffusion has only been investigated in 123 [34,35] and for Ag in 2212 [36]. Cation diffusion experiments in more of these systems are also underway in our laboratory and we anticipate that the results will be as interesting and varied as the results from the oxygen diffusion experiments.

Acknowledgments

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