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# Site-selective oxygen-isotope substitution in $YBa_2Cu_3O_{7-\delta}$

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We report selective substitution of oxygen-18 and oxygen-16 isotopes into the inequivalent oxygen lattice sites in $YBa_2Cu_3O_{7-\delta}$. The technique involves gas-phase diffusion and exploits the site dependence of diffusion rates. The $CuO_2$-plane [O(2),O(3)] sites of $YBa_2Cu_3O_{7-\delta}$ can be filled with $^{18}O$ while the apical [O(4)] and CuO-chain sites [O(1)] contain $^{16}O$ (the opposite distribution can also be made). The site-selective isotope occupation has been confirmed by Raman spectroscopy. Our method will permit experiments to determine the contributions of the different oxygen sites to the isotope effect, in order to locate the pairing interaction within the unit cell.

## I. INTRODUCTION

Oxygen-isotope substitution by gas-phase diffusion has been useful for measurement of the oxygen-isotope effect in high-$T_c$ oxide superconductors. For $YBa_2Cu_3O_{7-\delta}$, this technique has led to a consensus on its small oxygen-isotope shift[1-4] ($\Delta T_c \approx 0.19$ K for ~85% substitution of $^{18}O$, giving $\alpha \approx 0.019$). In these isotope-shift experiments, isotope substitution (monitored by Raman shifts) has been nearly uniform among the different oxygen sites, and so none of these studies could distinguish the contributions of the different sites to the oxygen-isotope effect. In $YBa_2Cu_3O_{7-\delta}$ the distinguishable inequivalent oxygen sites are the CuO-chain sites [O(1)], the edge-sharing apical sites [O(4)], and the $CuO_2$-plane sites [O(2),O(3)], shown in Fig. 1. The $CuO_2$ planes in $YBa_2Cu_3O_{7-\delta}$ are conducting, and the electron-pairing mechanism may be located there. If so, we might expect the oxygen-isotope shift to be dominated by the contribution of the O(2) and O(3) oxygen sites. On the other hand, some authors[5] have suggested that motion of the apical oxygen [O(1)] induces pairing. To determine experimentally the contributions to the isotope shift from oxygen at the different sites, we wish to selectively substitute one oxygen isotope into the apical (and chain) sites, while a different isotope occupies the plane sites. Because site-selective isotope occupation involves reduced entropy, it is not a thermodynamic equilibrium state, but can be achieved as a metastable state by exploiting the site-dependent kinetics of oxygen diffusion. In this paper we discuss this problem and demonstrate that, under suitable conditions, it is possible to accomplish site-selective isotope substitution by controlled diffusion.

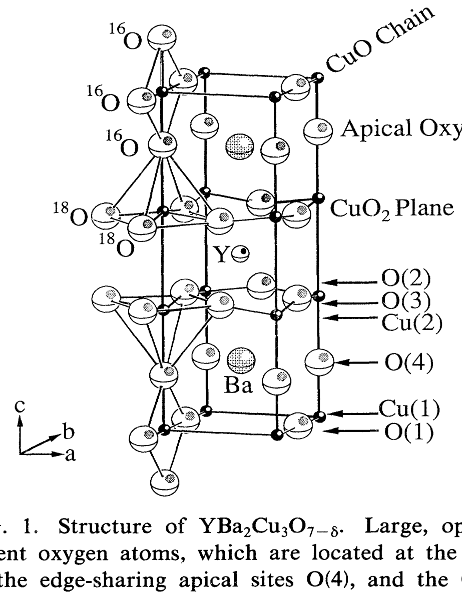

FIG. 1. Structure of $YBa_2Cu_3O_{7-\delta}$. Large, open spheres represent oxygen atoms, which are located at the chain sites O(1), the edge-sharing apical sites O(4), and the $CuO_2$-plane sites O(2) and O(3). Small solid spheres represent copper atoms. Yttrium and barium atoms as labeled. Labels at the left indicate oxygen-isotope locations after site-selective substitution.

## II. MODEL OF DIFFUSION IN $YBa_2Cu_3O_{7-\delta}$

The relative binding energies of the different oxygen sites in $YBa_2\ Cu_3O_{7-\delta}$ can be estimated from the results of neutron-diffraction studies (Jorgensen *et al.*[6]) which give site occupancies. For example, at $T = 490\,°C$ and $P[O_2] = 10^{-2}$ bar, over 40% of the chain sites [O(1)] are vacant, while <5% of the apical and nearly none of the plane sites are vacant (Fig. 2 of Ref. 7). This indicates that oxygen in the chain sites [O(1)] has the lowest binding energy, with larger binding energy in the apical [O(4)] and still stronger binding in the $CuO_2$ plane [O(2),O(3)] sites.

Since oxygen diffuses through the lattice by hopping from one site to the next (an activated process governed by the intersite saddle-point energy barriers), oxygen diffusion in $YBa_2Cu_3O_{7-\delta}$ is path dependent. This is illustrated schematically in Fig. 2, where the diffusion paths are represented by a grid of pipes whose width varies inversely with barrier height (the narrowness of the pipes represents difficulty of diffusion), and in Fig. 3, which represents the sequence of barrier energies encountered during diffusion. We neglect differences in diffusion between the **a** and **b** directions, and group together the two plane sites [O(2),O(3)] because of their similarity in location and chemical environment. In this structure there are six paths between sites, which have different saddle-point barrier heights (see Fig. 2). We denote them by $E_{15}$, $E_{51}$, $E_{14}$,$E_{42}$, $E_{44}$, $E_{23}$, $E_{22}$, etc., where the first index is the initial oxygen site and the second index is the destination site. The barrier height is measured from the initial-site energy (see Fig. 3). Since an ion in a deep energy well must surmount a high barrier to hop to an adjacent site, the activation energies for diffusion should correlate with the binding energy of the site from which the hopping takes place. Because oxygen in the chain site [O(1)] has much lower binding energy than the other sites, $E_{15}$ should be much smaller than both $E_{44}$ and $E_{23}$. Therefore, diffusion along the CuO-chain sites [O(1)] will be most rapid, and $E_{15}$ will be the rate-determining activation energy for diffusion in the **a**-**b** plane. Thus hopping along paths marked $E_{44}$ and $E_{23}$ in Fig. 2 can be neglected. Also, $E_{22}$ need not be considered since a plane site can be more easily accessed from the adjacent apical sites via the path $E_{42}$ than from sites in the adjacent plane layer. Thus we focus on $E_{15}$, $E_{14}$, and $E_{42}$ (in boldface in Fig. 2). As discussed above, their magnitudes should rank in order of the site binding energies, i.e., $E_{15} < E_{14} < E_{42}$. This means that hopping between chains sites is easier than from chain to apical sites, which is in turn easier than from apical to plane sites. Then, given the substantial difference in the activation energies, diffusion should proceed in the order of accessibility, i.e., first along the **a**-**b** plane between chain sites [O(1)], then across to the adjacent apical site [O(4)], and last from [O(4)] into the adjacent plane sites [O(2),O(3)]. Because the structure is layered, with the weak binding chain sites [O(1)] in the **a**-**b** plane, diffusion is extremely anisotropic,[7] proceeding much more readily along the chains layers in the **a**-**b** plane than along the $c$ axis. This anisotropy can be exploited by judicious choice of diffusion temperature and time to control the diffusion of oxygen isotopes into specific sites.

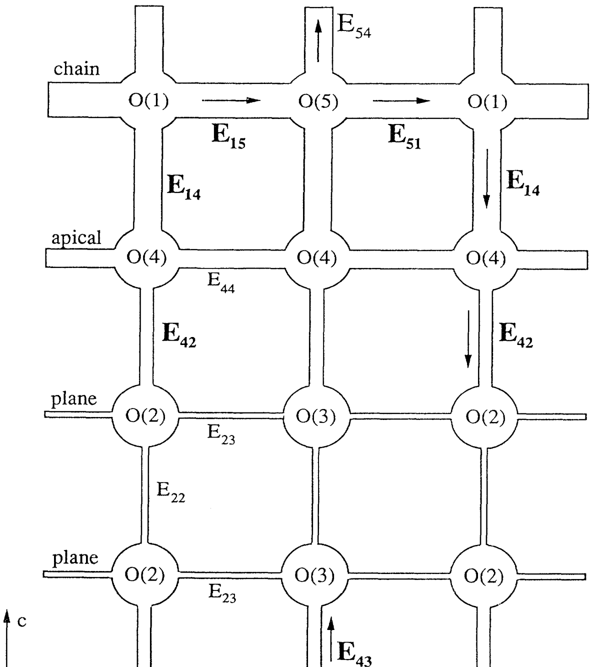

FIG. 2. Schematic representation of oxygen diffusion in $YBa_2Cu_3O_{7-\delta}$. The grid of pipes represents hopping paths, with the circular junctures denoting oxygen sites. The layers (chain, apical, and plane; cf. Fig. 1) run horizontally, and the **c** axis is vertical. Narrowness of each pipe represents barrier height and, therefore, difficulty of diffusion. The paths are labeled $E_{15}$, $E_{51}$, $E_{14}$, $E_{42}$, $E_{44}$, $E_{23}$, $E_{22}$, etc., where the first index is the initial oxygen site and the second index is the destination site. Paths which are significant for site-selective diffusion ($E_{15}$, $E_{14}$, and $E_{42}$) are in bold script. Since $E_{15}$ is very small, diffusion is very anisotropic, proceeding more readily along the chain layer than between the layers along the **c** axis. An oxygen diffusion path is indicated by arrows.

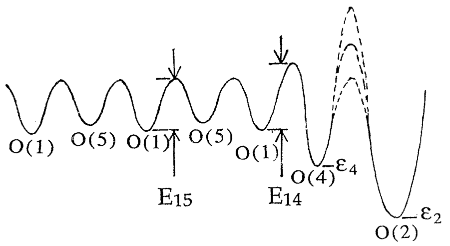

FIG. 3. Schematic representation of oxygen site energies and relevant saddle-point barrier heights between sites (see Fig. 2). The barrier heights are identified as $E_{15}$ [between O(1) and O(5) sites], $E_{14}$ [between O(1) and adjacent O(4) sites], $E_{42}$ is the (uncertain) barrier height between O(4) and O(2),O(3) sites, indicated by the dashed lines. $\varepsilon_2$ is the energy for the creation of a vacancy in the O(2),O(3) sites, and $\varepsilon_4$ is the same for the O(4) sites. An oxygen ion diffuses in from the surface of the grain along the chain layers between successive O(1) and O(5) sites, finally crosses to an O(4) site, and for there it can hop to the O(2) or O(3) site.

## III. THERMODYNAMICS OF OXYGEN DIFFUSION

To treat this heuristic model more quantitatively,we consider the thermodynamics of diffusion. First, we note that oxygen content is nearly constant ($\sim 7$) at low diffusion temperatures ($< 400\,^\circ C$). In this case, since no concentration gradient is present, there is no need to consider the thermodynamic factor $\partial(\ln P[O_2])/\partial x$, which enters in case of diffusion in a concentration gradient.[8] Isotopic exchange proceeds by self-diffusion, following random-walk statistics. From the Einstein equation, the effective (rms) diffusion distance in time $\tau$ is given by

$$\langle x^2 \rangle^{1/2} = (2D\tau)^{1/2} . \tag{1}$$

Following Bakker *et al.* (Ref. 8), the diffusivity $D$ is given by

$$D = \tfrac{1}{2} d^2 p f \omega , \tag{2}$$

where $d$ is the distance of a single hop, which is the intersite distance ($d \approx 3$ Å); $p$ is the probability of finding the adjacent site vacant; $f$ is the correlation factor between successive hops, which accounts for the likelihood of returning to the previous site; and $\omega$ is the vacancy-atom exchange frequency. For diffusion in the Cu-O layer, these quantities are averages over the sublattices consisting of the O(1) and O(5) oxygen sites, and over all atomic configurations (see Ref. 8).

The vacancy-atom exchange frequency $\omega$ can be approximated by $\omega \approx \omega_D \exp(-E/kT)$, where $E$ is the intersite barrier height, $k$ is Boltzmann constant, $T$ is the absolute temperature, and $\omega_D$ is the attempt frequency, which is the same order of magnitude as the Debye frequency.[9] Substituting , Eq. (1) becomes

$$\langle x^2 \rangle / d^2 = \omega_D \exp(-E/kT) p f \tau . \tag{3}$$

Solving for $\tau$, the characteristic diffusion time, we have

$$\tau = (1/p f \omega_D)(\langle x^2 \rangle / d^2) \exp(E/kT) . \tag{4}$$

## IV. DEPENDENCE OF DIFFUSION TIME ON PATHS BETWEEN DIFFERENT SITES

We wish to substitute a particular oxygen isotope in the chain [O(1)] and apical [O(4)] sites, while the $CuO_2$-plane sites [O(2),O(3)] remain occupied by a different isotope. This will permit us to distinguish the contributions to the isotope effect of the plane and apical/chain sites. Under suitable circumstances (discussed in the following section), the diffusion will take place in three stages, with differing characteristic diffusion time scales.

The first stage is diffusion along the chains into the center of each grain. To calculate the time constant needed to fully substitute the chain sites in the grain, the effective diffusion distance is taken as the grain size $R$. Equation (4) then gives the expression for the characteristic diffusion time,

$$\tau_1 \approx (R/d)^2 (1/f_1 p_1 \omega_D) \exp(E_{15}/kT) , \tag{5}$$

where $E_{15}$ is the energy barrier height between chain sites. In the orthorhombic phase, the oxygen atoms are ordered in linear Cu-O-Cu-O chains, so that nearly all nearest-neighbor sites of the oxygen site in the CuO-chain layers are empty (constitutional vacancies) and are accessible for temporary occupation during the diffusion process; therefore, following Bakker *et al.*,[8] we take $p_1 \approx 1$. The value of $f_1$ has been calculated in Ref. 8 with values ranging from ~0.25 at 350 °C to ~0.83 at 500 °C and ~0.93 at 600 °C.

The second state is diffusion from a chain site to the nearest apical site. Here the effective diffusion distance is equal to the intersite distance (i.e., $x = d$). Only a single hop is required, but a reverse hop has high probability since the fraction of vacant chain sites, $\exp(-\varepsilon_1/kT)$, is much higher than that of vacant apical sites, $\exp(-\varepsilon_4/kT)$, where $\varepsilon_4$ is the energy required to create a vacancy in the apical [O(4)] site. Therefore, $f_4$ will be small, and $\tau_4$ will become large [the indices correspond to the oxygen site O(4)]. The characteristic time for transfer from chain sites to adjacent O(4) apical sites is

$$\tau_4 \approx (1/p_4 f_4 \omega_D) \exp(E_{14}/kT) , \tag{6}$$

where $E_{14}$ is the barrier height between chain [O(1)] and apical [O(4)] sites.

The third stage is diffusion from the apical [O(4)] site to the adjacent $CuO_2$-plane site. Here, again, only a single hop is needed, and the probability of a reverse hop is large since the vacancy concentration is greater in apical sites than in plane sites, because of the greater binding energy in plane [O(2),O(3)] sites. This indicates that $f_2$ is small, again leading to a large time constant. The characteristic time is

$$\tau_2 \approx (1/p_2 f_2 \omega_D) \exp(E_{42}/kT) , \tag{7}$$

where $E_{42}$ is the barrier height between apical and plane sites. We can approximate $p_2$ by the fraction of vacant plane [O(2),O(3)] sites, which is determined by the Boltzmann factor $\exp(-\varepsilon_2/kT)$. Here $\varepsilon_2$ is the energy required to create a vacancy in the O(2) or O(3) plane site. The binding energy of the apical [O(4)] site is lower than that of the plane [O(2),O(3)] sites, as shown by the partial depopulation of O(4) sites at high temperature.[5] This suggests that the activation energy $|E_{14}| < |E_{42}|$ (see Fig. 3). Since the hop from O(1) to O(4) and the hop from O(4) to O(2) [or O(3)] are consecutive, the larger activation energy will be rate limiting; i.e., the hop from O(4) to O(2) [or O(3)] is the "bottleneck" which controls diffusion from O(1)→O(4)→O(2) [O(3)] sites. Therefore, we expect $\tau_4 < \tau_2$, and $\tau_4$ is neglected in the following.

## V. ESTIMATION OF THE REQUIRED DIFFERENCE IN BARRIER HEIGHT

In order to substitute a particular oxygen isotope in the chain and apical sites but not in the plane sites, diffusion must take place along the chain sites throughout the entire grain before diffusion from the apical to the adjacent plane site takes place; i.e., the site-selective criterion is $\tau_2 > \tau_1$. Using eqs. (4) and (7), we have the inequality

$$(1/f_2 p_2) \exp(E_{42}/kT) > (R/d)^2 (1/f_1 p_1) \exp(E_{15}/kT) , \tag{8}$$

and solving for the required difference in activation energy,

$$E_{42} - E_{15} > kT[2\ln(R/d) - \ln(f_1 p_1) + \ln(f_2 p_2)] . \tag{9}$$

The term $2\ln(R/d)$ is easily evaluated: The grain size in a porous ceramic is typically $\sim 3$ $\mu$m, so that $R/d \approx 3$ $\mu$m/3 Å$\approx 10^4$ and $2\ln(R/d) \approx 18$. Equation (9) shows that site-selective isotope substitution is favored at low temperatures. At temperatures $T \le 375\,^\circ$C and $P[O_2] = 1$ atm, the material will be nearly fully oxygenated.[5] The correlation factor for diffusion in the chain layer, $f_1$, has been calculated by Bakkar *et al.*,[8] and at 375 °C, $f_1 \approx 0.37$. Also, $p_1 \approx 1$ as discussed above. Thus $\ln(f_1 p_1) \approx -1$. The correlation factor $f_2$ for returning to an apical oxygen site from a $CuO_2$-plane site is small since there are more vacancies in the O(4) site than in the O(2) and O(3) sites. In the absence of a better estimate, we take $f_2 = 0.1$; this value is not critical, as it enters only logarithmically. The value of $p_2$ is taken as the Boltzmann factor $[\exp(-\varepsilon_2/kT)]$, as discussed previously. The inequality (9) becomes

$$E_{42} - E_{15} + \varepsilon_2 > 17kT \ . \tag{10}$$

Thus there are three factors in $YBa_2Cu_3O_{7-\delta}$ which favor site-selective oxygen substitution: (1) small intersite saddle-point barriers between the O(1) and O(5) sites, permitting rapid diffusion into the grain; (2) a relatively high saddle-point barrier energy between apical [O(4)] and plane [O(2),O(3)] sites, because of the stronger binding in the O(4) site relative to the O(1) site; and (3) strong binding of oxygen in the O(2) and O(3) plane sites, leaving an extremely small concentration of vacancies in those sites and slowing diffusion into them.

Site-selective substitution is favored at low temperatures, but since the diffusion rate varies exponentially with temperature, the temperature must be sufficiently high to accomplish the diffusion in a reasonable time (limited by the lifetime of the experimenter). A thermogravimetric study of self-diffusion in $YBa_2Cu_3O_{7-\delta}$, which is planned to be published elsewhere,[10] has shown 650 K ($\approx 375\,^\circ$C) to be a suitable temperature, since the diffusion time at this temperature is on the order of a few hours. At this temperature the condition for site-selective oxygen-isotope substitution in $YBa_2Cu_3O_{7-\delta}$ given by Eq. (10) is

$$E_{42} - E_{15} + \varepsilon_2 > 1 \text{ eV} \ . \tag{11}$$

## VI. DEMONSTRATION OF SITE-SELECTIVE SUBSTITUTION IN $YBa_2Cu_3O_{7-\delta}$ BY CONTROLLED DIFFUSION

### A. Diffusion procedure

To demonstrate the feasibility of our method, we carried out a series of controlled oxygen-isotope diffusion experiments on polycrystalline $YBa_2Cu_3O_{7-\delta}$ samples and then measured the site occupation of isotopes by Raman spectroscopy. First, the samples were prepared by solid-state reaction according to the recipe and procedure given in Ref. 1. A pellet of the sample then underwent $^{18}O$ substitution according to the gas-phase diffusion procedure given in Ref. 1. The diffusion was carried out at 930 °C for 48 h and resulted in > 85% substitution (as estimated by the increase in sample weight). A portion of the same pellet was diffused simultaneously in $^{16}O$ in an adjacent quartz tube as a control. The pellet containing $^{18}O$ was broken into several pieces, each of which was reduced in flowing $N_2$ at 800 °C for 3 h and then subjected to controlled diffusion in flowing $^{16}O$ for a different time. This $^{16}O$ diffusion was carried out in a thermogravimetric analyzer (TGA), in order to monitor sample weight change as isotopic exchange took place. The samples were rapidly heated (< 2 min) to 375 °C ($\sim$650 K) in flowing $^{16}O$ (30 cc/min), held for various durations (short time, $\frac{1}{4}$, 1, 4, 16, and 167 h), then quickly cooled (< 2 min). All diffusion experiments in the TGA were carried out at a pressure of 1 atm.

### B. Determination of site occupation of oxygen isotopes by Raman analysis

The samples were examined by Raman spectroscopy to determine the extent of oxygen-isotope substitution in the various lattice sites as a function of diffusion time. Raman spectroscopy probes the vibrational energies of various lattice phonon modes. Isotope substitution will alter the vibrational energies by changing the masses of the atoms involved in the phonon modes. Calculations of the phonon modes for $YBa_2Cu_3O_{7-\delta}$ and measurements of mode symmetries by polarized Raman studies have provided definitive assignments of the various Raman-scattering peaks observed for this material.[11] The major modes involving oxygen vibrations which are observed in $YBa_2Cu_3O_{7-\delta}$ samples prepared with $^{16}O$ are at 338, 433, and 502 cm$^{-1}$, respectively. The 338-cm$^{-1}$ mode ($A_g$ symmetry in the orthorhombic lattice) is dominated by out-of-phase motion of the Cu-$O_2$-plane oxygens [O(2),O(3)] along the *c* axis. The 433-cm$^{-1}$ mode ($A_g$) involves *c*-axis bending of the O(2)—Cu and O(3)—Cu bonds in the Cu-$O_2$ planes. The 502-cm$^{-1}$ mode ($A_g$) involves a symmetric stretch of the apical oxygen O(4)—Cu(1) bonds along the *c* axis.

Raman spectra were obtained using a conventional backscattering geometry with a spot size of approximately 100 $\mu$m and a beam power of 50 mW. A commercial spectrograph with a subtractive-dispersive filter stage was used along with a two-dimensional photon-counting detector. The sample was continually flushed with flowing argon gas in order to reduce the background at low scattering energies resulting from atmospheric gases. The spectra reported here were obtained in 10 min using 488-nm laser excitation. The apical and plane sites gave well-resolved scattering peaks. Because of mode symmetry, the chain sites are not Raman active. In our experiments the isotopic occupation of the chain sites [O(1)] was inferred from that of the apical sites.

Figure 4 shows the sequence of Raman spectra. The bottom spectrum, for an untreated $^{16}O$ sample, has the expected 338-, 433-, and 502-cm$^{-1}$ peaks corresponding to the plane [O(2),O(3)] and apical [O(4)] sites containing $^{16}O$ (the peak at $\sim$630 cm$^{-1}$, which is seen in some of the spectra, is due to a small amount of $BaCuO_2$ impurity within the 100-$\mu$m spot size probed by the exciting laser; since the Raman cross section of $BaCuO_2$ is much greater than that of $YBa_2Cu_3O_7$, a large peak results from trace amounts of $BaCuO_2$). The next spectrum, for an $^{18}O$-substituted sample, has the same peaks shifted to 323, 418, and 479 $cm^{-1}$ (compared with 317, 408, and 473 $cm^{-1}$ expected for 100% $^{18}O$ substitution), indicating that all the sites contain predominantly $^{18}O$. The following spectra are essentially stop-sequence snapshots of controlled diffusion, tracking the progress of isotopic substitution. In the spectrum labeled "short time," both peaks involving plane oxygens remain at positions characteristic of $^{18}O$, while the peak involving apical oxygens has shifted back slightly towards the $^{16}O$ position as well as broadened, indicating the presence of some $^{16}O$ in the apical site. In the $\frac{1}{4}$-h spectrum, the apical [O(4)] peak has shifted nearly to the $^{16}O$ position, while the O(2),O(3) peaks remain close to their $^{18}O$ positions. In the 1-h spectrum, the O(2),O(3) peaks broaden and begin to shift back to their $^{16}O$ positions. The subsequent spectra continue in this trend, with all the peaks restored to their $^{16}O$ positions in the 167-h case. A spectrum (not shown) was also taken from a control sample, which underwent the same diffusion schedule as the 16-h sample, but with $^{16}O$ in both the initial diffusion (390 °C) and the subsequent diffusion (375 °C). This spectrum is virtually identical to that of the untreated $^{16}O$ sample, thus demonstrating that the heat treatment has not introduced any spurious shifts in the Raman peak frequencies. This is particularly significant for the apical peak (at 502 $cm^{-1}$), whose position is sensitive to small variations in oxygen content.[12] Our result is consistent with the expectation that after the initial diffusion the temperature used for the $^{16}O$ diffusion, 375 °C, was enough to achieve full oxygenation.

Spectra taken from different spots on each sample using the 100-$\mu$m beam showed some scatter in peak positions. Each of the spectra shown in Fig. 4 is representative of the spectra taken from each sample. The peak positions an their scatter are plotted as a function of diffusion time in Fig. 5. The scatter for each peak position is represented by additional data points plotted at $\pm 1$ standard deviation from the mean of measurements taken at five different spots on the sample. In general, the scatter is most pronounced for the plane-oxygen peaks, particularly at intermediate diffusion times. This reflects nonuniformity of isotope occupation throughout the sample and is attributable to either inhomogeneities in the surfaces exposed to diffusion (i.e., fractured grains), varia-

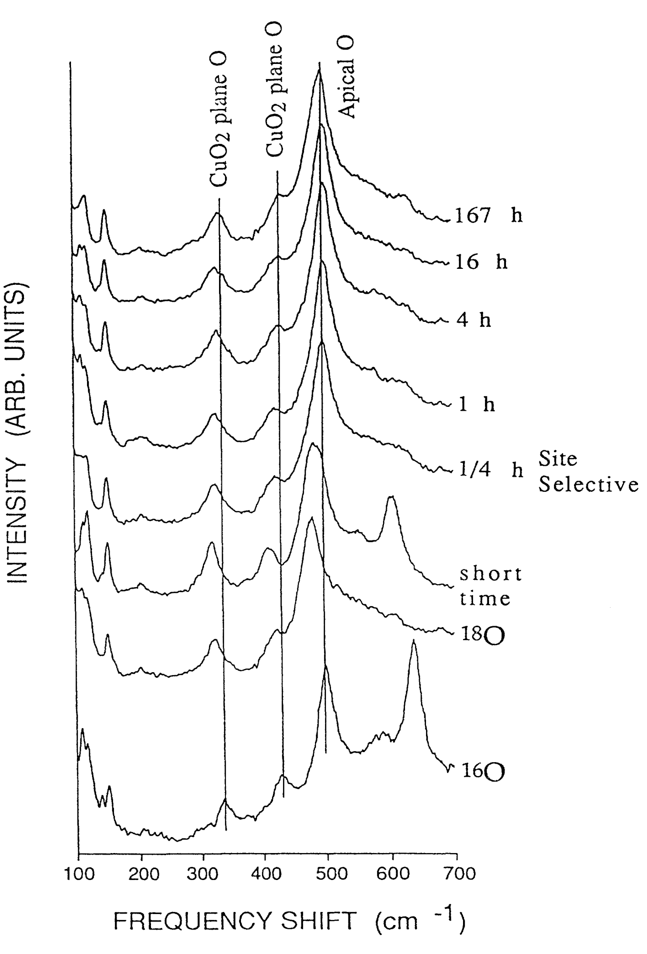

FIG. 4. Raman spectra of $YBa_2Cu_3O_{7-\delta}$ samples subjected to controlled diffusion. The intensities are plotted vs frequency shift and are stacked in time sequence to illustrate the process of site-selective diffusion. The peaks of interest are labeled according to site. Vertical lines are drawn through the respective $^{16}O$ positions as a visual aid. Peak positions and their standard deviations are plotted in Fig. 5.

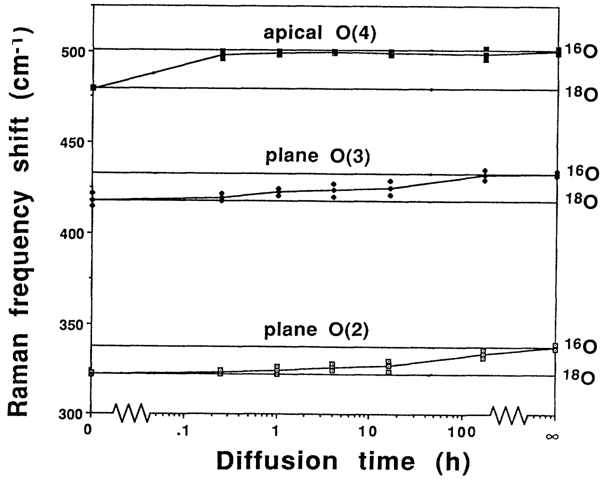

FIG. 5. Raman peak positions (and standard deviations) plotted vs diffusion time (logarithmic time scale) to trace the progress of controlled diffusion. Lines are drawn through the respective $^{16}O$ and $^{18}O$ positions to aid comparison. Site-selectivity between the apical and plane sites is clearly achieved at $t \approx \frac{1}{4}$ h. Points at $t = \infty$ are for the control sample, treated with $^{16}O$ throughout.

tions in the grain size, or crystal defects which vary the pathways for diffusion into the plane sites.

## VII. DISCUSSION AND CONCLUSIONS

Site-selective oxygen-isotope substitution in $YBa_2Cu_3O_{7-\delta}$ has been accomplished as indicated by the $\frac{1}{4}$-h diffused sample (see Fig. 4). However, since Raman spectroscopy probes a surface layer only ~200 Å deep, corroborating data is needed to confirm uniformity of site-selective occupation throughout the sample. The fraction of isotopic substitution can be monitored by weight change in the TGA. Since isotopic exchange in the interiors of the grains inevitably lags behind that at the surfaces, exchange into the O(2) and O(3) plane sites occurs first near the surfaces of the grains. So long as the surface remains selectively exchanged [i.e., there is no shift seen in the 317- and 408-$cm^{-1}$ ($^{18}O$) Raman lines, although the 473-$cm^{-1}$ line is shifted back to 502 $cm^{-1}$, the $^{16}O$ position], no substitution can yet have occurred into the O(2) and O(3) sites in the interiors. If the 317- and 408-$cm^{-1}$ Raman lines are still not shifted back to the $^{16}O$ position when the weight change indicates that ~40% of all the oxygens (corresponding to three of the seven in the unit cell) have been substituted, then we can be sure that uniform site-selective occupation throughout the sample grains must have been achieved.

In our experiment site selectivity on the surface persisted up to ~1 h, by which time over 30% ( > $\frac{2}{7}$) of the oxygens have been substituted according to the weight change. This confirms that the site-selective substitution has indeed pervaded the bulk of each grain. Naturally, the completeness of substitution in the O(1) and O(4) sites without filling the [O(2),O(3)] sites can be improved by (1) lowering the diffusion temperature, although this would lengthen the time scale for the isotopic substitution; and/or by (2) using ultrafine-grain samples, which would shorten the diffusion time. This would ensure better uniformity of site-selective occupation throughout each grain—a condition crucial for an isotope-shift experiment.

Our technique for site-selective controlled diffusion relies only on the basic thermodynamics of diffusion in a complex oxide and may be applied to any complex oxide having the following properties: (1) A layered structure with weak binding sites separated by small barriers which form a continuous network so that diffusion throughout the grains can take place rapidly. We note that constitutionally vacant sites [such as the O(5) site in $YBa_2Cu_3O_{7-\delta}$] between the weakly bound sites [O(1) sites] are advantageous as they result in large $p$ factor,[8] even at low temperatures where the concentration of thermal vacancies is small. This provides rapid diffusion at low temperatures. (2) Other strongly bound sites with at least 1 eV greater binding energy than the weakly bound sites.

Our results show that site-selective oxygen-isotope substitution is possible, but only when substitution is carried out at low temperature and for short times. This settles earlier disputes[13] about whether the $^{18}O$ isotope substituted in $YBa_2Cu_3O_7$ at 600 °C (Ref. 1) and over 900 °C (Refs. 2 and 3) was complete on all sites.

In our experiment, $^{18}O$ was selectively substituted into the plane sites and $^{16}O$ into both the apical and chain sites, but the opposite isotope arrangement can easily be achieved, simply by switching the isotopes in the diffusion procedure. Our technique should therefore permit experiments to measure the contribution of the apical [O(4)] and chain [O(1)] oxygens to the oxygen-isotope effect, separately from the contributions of the plane oxygens [O(2),O(3)], and thereby help locate the pairing mechanism.

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