

Locus of Pairing Interaction in $\text{YBa}_2\text{Cu}_3\text{O}_7$ by Site-Selective Oxygen Isotope Shift: ^{18}O in CuO_2 Plane Layers

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The oxygen isotope shift of T_c in $\text{YBa}_2\text{Cu}_3\text{O}_7$ has been measured for samples containing $\sim 95\%$ ^{18}O in the CuO_2 plane [O2,O3] sites and primarily ^{16}O in the apical [O4] and chain [O1] sites. The T_c of the site-selectively substituted samples is *higher* than that of the ^{16}O control samples by 0.10–0.14 K, in contrast to the *decrease* in T_c of 0.20–0.23 K for complete ^{18}O substitution at all sites. Our results indicate that the phonon-mediated contribution to the pairing mechanism in $\text{YBa}_2\text{Cu}_3\text{O}_7$ involves the apical [O4] sites, and not just the CuO_2 plane [O2,O3] sites.

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A small oxygen isotope shift (OIS) had been found in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) [1–6]. The critical temperature decreased by $\Delta T_c = 0.18 \pm 0.04$ K when ^{16}O was 85% substituted by ^{18}O [3]. Ba and Cu isotope substitutions gave $\Delta T_c = 0.0 \pm 0.1$ K [7]. In the microscopic theory of superconductivity of Bardeen, Cooper, and Schrieffer (BCS) [8], the simplest model gives $T_c \propto M^{-\alpha}$, where $\alpha = 0.5$, causing a substantial isotope shift due to phonon-mediated pairing. The very small OIS observed in 123 was taken to indicate that pairing of the charge carriers in this system is not phonon mediated. More recently, measurements in several high-temperature superconductors (HTSC) have shown that with doping the OIS increases rapidly as T_c decreases slowly when the carrier concentration is made smaller [6,9–11] or larger [10,12] than optimum. The substantial OIS obtained in these doped samples is consistent [6,10,13] with pairing by high-frequency phonons, suggesting that modes involving oxygen motion *are* important in the mechanism responsible for high-temperature superconductivity.

123 has four inequivalent oxygen sites: the CuO chain sites [O1], the edge sharing apical sites [O4], and CuO_2 plane sites [O2,O3]. In all previous OIS experiments [1–6,9–12], isotopic substitution was nearly complete and uniform among the different oxygen sites, as monitored by Raman shifts. Therefore, these studies could not distinguish the contributions of the different oxygen sites to the oxygen isotope effect.

It has been generally accepted that the superconducting pairs are located in the conducting CuO_2 planes [14,15], as evidenced by the mode softening of the 337-cm^{-1} Raman peak [16]. If the coupling which causes pairing is also located there, then one might expect the plane sites to give the OIS. It has also been suggested [17] that motion of the apical sites induces the hole pairing. In this case, one would expect that the OIS would be produced by isotopic substitution in the apical sites. Little contribution to the OIS is expected from the chain site which lies in the CuO charge reservoir layer, found only in the 123 compound. All p -type HTSC (except possibly the ACuO_2 infinite layer compound) have apical oxygen

in the (Ba,Sr) layer, as well as oxygen in the conducting CuO_2 planes. Measurement of the contributions of the apical and plane sites to the OIS will elucidate the roles of the various layers in HTSC.

We recently reported preparation of site-selective oxygen isotope substituted (SS-OIS) samples of 123 using kinetically controlled oxygen diffusion at low temperatures; we discussed the conditions under which site-selective oxygen substitution is thermodynamically possible [18]. In this Letter, we report measurement of the oxygen isotope effect in SS-OIS samples that contain ^{18}O in the plane [O2,O3] sites, and predominantly ^{16}O in the apical [O4] and chain [O1] sites.

Sample preparation is critical to the success of this experiment. Several criteria must be satisfied to accomplish and verify SS-OIS. The samples must (1) be phase pure, (2) have reasonably sharp diamagnetic transitions to enable accurate measurement of T_c , (3) have small grains to permit rapid diffusion into the grain interior via the [O1] and [O4] sites (before hopping takes place into the adjacent [O2] and [O3] sites across the relatively high intersite barriers), and (4) give Raman spectra with sharp peaks allowing accurate determination of the isotope site occupations. Standard solid-state synthesis (sintering at 930°C in 1 bar O_2) produced samples with large grains. When these samples were mechanically ground to produce $1\text{-}\mu\text{m}$ grains, the resulting strain broadened the Raman peaks and prevented accurate determination of the peak positions. Systematic preparation experiments varying starting materials, sintering temperature, and gas atmosphere were conducted and the optimum process for SS-OIS is summarized below.

“Starting samples” were prepared by dry grinding stoichiometric quantities of $\text{Y}(\text{NO}_3)_3$, BaO_2 , and $\text{Cu}(\text{NO}_3)_2$. The powder was heated to drive off nitrates, then pelletized and calcined at 800°C for 15 h in $50\text{ cm}^3/\text{min}$ $0.1\% \text{ O}_2 + 99.9\% \text{ N}_2$ flow, and furnace cooled. The above procedure was then repeated. Powder x-ray diffraction (XRD) showed single phase, tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($x > 0.5$).

The ^{18}O and ^{16}O “standard samples” were two pieces

of the same starting sample pellet which were then subjected to isotopic diffusion. Isotopic diffusion was conducted in two parallel quartz tubes (separated by ~ 2 cm) filled with ^{16}O and ^{18}O [19] to 0.994 bar at room temperature. Samples are at identical temperatures throughout the diffusion process [6]. The samples were held for 66 h at 600°C , and slow cooled over 48 h. Raman measurements [20,21] and diamagnetic onset temperatures (~ 90 K) indicated that the samples were slightly oxygen deficient, even though the orthorhombic splitting shown by XRD indicated full oxygenation [22]. The samples were returned to the diffusion apparatus, held at 600°C for 24 h, cooled over 24 h to 420°C , and held for 24 h. During the final anneal, the pressures in both sides were 1 bar and differed by $< 1\%$. Idiometric titration showed an oxygen content of 6.99 ± 0.01 , this value is confirmed by the position of the apical [O4] Raman mode at 502 cm^{-1} [20], and $T_c \approx 91$ K. The Meissner transition width was 8–10 K (10%–50%) because of the small grain size, but the onset was sharp.

“Site-selective samples” were produced by controlled diffusion of a portion of the ^{18}O standard sample in a thermogravimetric analyzer (TGA). The samples were held at 200°C for 1 h to evaporate any H_2O and volatiles, then heated to 350°C and held for 1900 min. Since 123 remains fully oxidized below 400°C in 1 bar O_2 , the observed weight loss corresponds to the isotopic exchange: $^{18}\text{O} \rightarrow ^{16}\text{O}$. The reverse site-selective substitution (^{16}O in planes; ^{18}O in apicals) is difficult to obtain in the TGA since ^{18}O gas is too expensive to use in the flow through gas system. Therefore the reverse substitution was attempted in the isotope diffusion apparatus, but in the absence of continuous weight monitoring, we were unable to obtain reproducible results.

An identical thermal treatment in the TGA was given to the ^{16}O standard sample. This is labeled the “ ^{16}O control sample.” The 1900 min anneal at 350°C sharpened the diamagnetic transition width to 5–6 K and shifted the T_c by 0.1–0.2 K. No oxygen loss was observed in the TGA for the ^{16}O control sample (see Fig. 1). Recycling the ^{16}O control sample of Expt. 1 through the TGA thermal treatment a second time (“ ^{16}O cycled sample”) gave no further change in T_c (within experimental error), indicating equilibrium had been achieved. Since the starting samples were fully oxygenated (annealed in O_2 at 420°C), and since no weight loss was observed for the control samples (annealed in O_2 at 350°C), they must also be fully oxygenated. This is confirmed by the position of the “ 502-cm^{-1} ” Raman peak of the ^{16}O cycled sample, measured at 501.4 cm^{-1} , indicating ≤ 0.02 oxygens/unit cell were lost [20] due to the TGA treatment. Thus the small shift in T_c of the control sample is not due to oxygen loss, but may reflect increased order in the CuO chains. The SS-OIS and ^{16}O control sample underwent identical thermal treatments, and the site-selective OIS was measured with respect to the ^{16}O control sample.

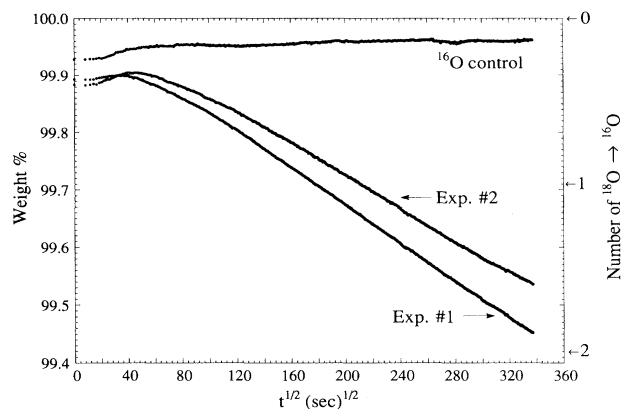


FIG. 1. Weight loss of ^{18}O samples due to isotopic exchange as a function of $t^{1/2}$. The weight of the ^{16}O control sample shows that no oxygen was lost during the soak cycle. Two experiments were conducted. The linear trend of the isotopic exchange indicates that diffusion is by random walk process [18]. Data are plotted with $t=0$ defined at the start of the 350°C thermal anneal, and “100% weight” is the intersection of the straight line behavior with $t=0$. The number of oxygens exchanged per unit cell is indicated on the right axis.

Site occupancy of the ^{16}O and ^{18}O isotopes was determined by Raman spectroscopy. Spectra were generated by the 488-nm line of an Ar^+ laser, focused to a 15-mm spot. The laser power was ≤ 30 mW to avoid possible damage. The scattered light was imaged through a holographic interference notch filter and onto the entrance slit of a 0.3-m single spectrometer. The dispersed light was detected by a microchannel plate photomultiplier. Typical collection times were 5–10 min at instrumental resolution of 2.5 cm^{-1} . Peak positions were determined by Lorentzian fits to the spectral lines after correction for instrument response.

Field-cooled (Meissner effect) magnetic susceptibility curves were measured in a quantum design superconducting quantum interference device (SQUID) magnetometer at $H \approx 10$ Oe. Temperatures were measured by a platinum resistance thermometer (Lakeshore PT-111) placed in direct contact with the sample and driven by a microprocessor controlled ac bridge. The temperature resolution is 2.5 mK and reproducibility is 10 mK at 77 K [6]. T_c 's and OIS's were determined from the method used in Ref. [6].

Two separate site selective experiments were performed on two different starting pellets, designated Expt. 1 and Expt. 2. The weight loss due to isotopic diffusion in each of the ^{18}O standard samples is shown in Fig. 1, as a function of the square root of time ($t^{1/2}$). No oxygen is lost from the ^{16}O control sample. The number of oxygens exchanged for a given weight percent has been calculated and is indicated on the right axis of the graph. In Expt. 1, nearly 2 oxygens per unit cell were exchanged; in Expt. 2, $\sim 1\frac{1}{2}$ were exchanged. The difference in the number of oxygens exchanged may result from different porosity

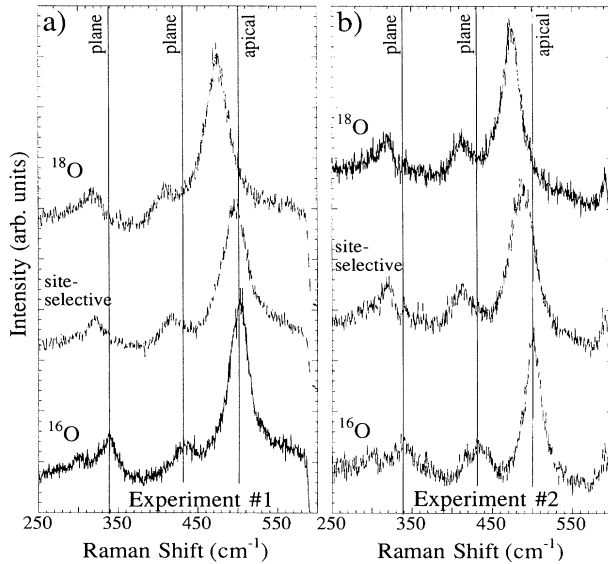


FIG. 2. Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples subjected to controlled diffusion. The peaks of ^{16}O positions are labeled according to site. Isotopic content of the samples is indicated. The position of the ^{18}O sample peaks indicates nearly complete ^{18}O substitution [24]. The “site-selective” sample has ^{18}O in the plane oxygen sites, while the apical peak is shifted toward the ^{16}O position. Peak positions are given in Table I.

or grain size of the two pellets.

Figures 2(a) and 2(b) show the Raman spectra of the ^{16}O standard, ^{18}O standard, and site-selective samples for Expts. 1 and 2. The peak assignments [20,21] are as follows: The 340 and 435 cm^{-1} peaks correspond to the [O2,O3] motion; the 502 cm^{-1} peak, to [O4] motion. Table I gives the corresponding peak positions for each of the samples. In both experiments the ^{16}O standard sample's peak positions agree well with the established values [20]. The positions of the ^{18}O substituted peaks indicate nearly 100% substitution [23], uniform over all the oxygen sites. The position of the CuO_2 plane mode peaks for the SS-OIS sample in Expt. 1 indicates that the [O2] and [O3] sites remain fully occupied by ^{18}O ; the peak corresponding to the [O4] site has shifted back to 497 cm^{-1} , indicating significant occupation by ^{16}O .

TABLE I. Raman peak positions (cm^{-1}) for isotopically substituted samples. ^{16}O peak positions for $\text{YBa}_2\text{Cu}_3\text{O}_7$ [20] are indicated.

Expt.	Sample	Plane	Plane	Apical
	^{16}O from [20]	340	435	502
No. 1	^{16}O standard	339	432	502
No. 1	^{18}O standard	318	409	474
No. 1	Site-selective	321	416	497
No. 1	^{16}O cycled	338	430	501
No. 2	^{16}O standard	341	433	501
No. 2	^{18}O standard	317	412	474
No. 2	Site-selective	318	412	488

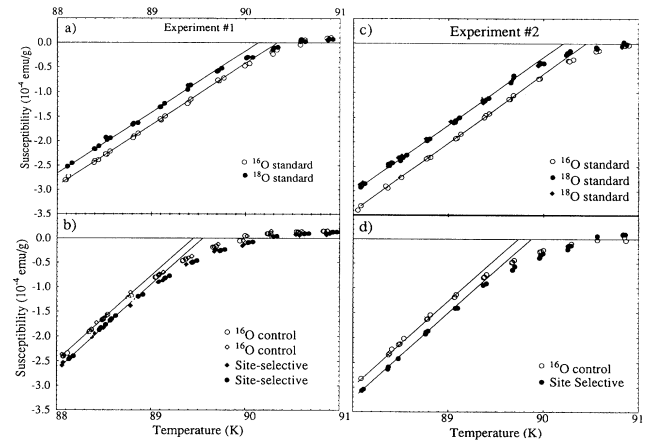


FIG. 3. Diamagnetic transitions of (a) uniform isotopic substitution for Expt. 1; (b) site selective and ^{16}O control sample for Expt. 1; (c), (d) same as (a) and (b) for Expt. 2. For uniform ^{18}O substitution, T_c is 0.20 K (Expt. 1), and 0.23 K lower (Expt. 2) than the ^{16}O sample. T_c for the site-selective samples is higher than that of the ^{16}O controls, by 0.10 and 0.14 K for Expts. 1 and 2, respectively. The transitions are parallel for at least a fourth of the full transition width. The shift in T_c was determined by measuring the temperature difference of the parallel segments near the onset of the transition.

Similarly for Expt. 2, the plane [O2,O3] oxygen peak positions are virtually unchanged with respect to the ^{18}O sample. The peak corresponding to the apical [O4] motion is at 488 cm^{-1} , indicating that less ^{16}O has diffused into this site than in Expt. 1, in agreement with the TGA data (Fig. 1). The Raman data show that these samples have site-selective oxygen isotope occupation.

Figures 3(a) and 3(c) show the diamagnetic transitions for the ^{16}O and ^{18}O standard samples for Expts. 1 and 2, respectively. The OIS for uniform and nearly complete ^{18}O substitution is -0.20 and -0.23 K (the ^{18}O samples have lower T_c 's), in good agreement with the results of [1–6]. Figure 3(b) shows the diamagnetic transitions of the ^{16}O control sample and the SS-OIS sample of Expt. 1. The transition of the SS-OIS sample, which contains ^{18}O in the planes, is 0.10 K above the transition of the ^{16}O control sample [6], while in Expt. 2 [Fig. 3(d)] the transition of the SS-OIS sample is 0.14 K above the ^{16}O control sample. Experiment 2, which has less ^{16}O exchanged in the apical sites than Expt. 1, showed a larger increase in transition temperature (40 mK) due to the SS-OIS. We take this as an indication of the size of our systematic errors.

TGA data give a bulk measurement of isotopic exchange, and Raman data give a surface measurement of site occupation ~ 2000 Å into the grain [24]. TGA data of Expt. 1 show that $\frac{2}{7}$ of the oxygens/unit cell have been exchanged, and Raman data show that the [O2,O3] sites contain only ^{18}O at the surface. Since isotopic exchange occurs first at the surface, then proceeds further into the grain, and since the [O2,O3] sites near the surface are

unexchanged and occupied by ^{18}O , the four [O2,O3] sites in the unit cell must be occupied by ^{18}O throughout the entire grain. This indicates $\frac{2}{3}$ of the one chain [O1] and two apical [O4] sites have been exchanged to ^{16}O . The isotope occupation in the chain [O1] site cannot be directly determined because it is not Raman active. The isotope occupation in the apical [O4] sites is indicated by the position of the “502-cm $^{-1}$ ” line, which shifts nonlinearly with isotopic content, and has been measured and modeled by Altendorf *et al.* [23]. Fitting the data for our SS-OIS samples to their model, we find that the ^{16}O content in the apical [O4] oxygens at the surface is $\sim 80\%$ for Expt. 1 and $\sim 65\%$ for Expt. 2. Since the diffusion is most rapid in the chains [18], exchange in the chain site should be at least as large as in the apical sites. Substitution is smaller in the interior of the grain than at the surface; i.e., the centers of the grains contain more ^{18}O than near the surface. Since uniform ^{18}O substitution decreases T_c [3], the greater ^{18}O content in the interior cannot be responsible for the higher T_c observed in the SS-OIS samples compared to the ^{16}O control samples.

In summary, we have shown that the plane sites are occupied by ^{18}O , while the apical and chain sites contain predominantly ^{16}O , and this produces a small *increase* in T_c , in contrast to the small *decrease* in T_c when ^{18}O is substituted at all sites. If all oxygen sites contributed equally to the OIS, one would expect a 0.15 K *decrease* in T_c when $\frac{2}{3}$ of the oxygens in the unit cell are occupied by ^{18}O , as in our SS-OIS samples. Our result contradicts the behavior expected if the pairing mechanism was located exclusively in the conducting CuO_2 planes. In that case one would expect that ^{18}O occupation of the plane sites would give the same *decrease* in T_c of ~ 0.2 K found when ^{18}O was substituted at all sites.

Small negative OIS's (increase T_c with ^{18}O substitution) have also been observed in the Bi based HTSC [11]. Eliashberg theory allows for small and even negative isotope shifts when the Coulomb-pseudopotential μ^* and the electron-phonon coupling constant λ are of comparable size. In this scenario, however, T_c is small. Models involving van Hove singularities in the electronic density of states [25] can explain the anomalous OIS found in HTSC in the context of phonon-mediated pairing, although the form of the electronic density of states influences the agreement with experimental results [13,26]. Theoretical models involving anharmonic potentials [27,28] can also explain the OIS seen in HTSC [1-6,8-10] within the BCS framework. It has also been shown [28] that small negative OIS's are possible in the anharmonic model. Crespi and Cohen [29] have analyzed our results and find them consistent with a dominant anharmonic planar contribution along with a moderate harmonic planar contribution and a harmonic off-plane contribution. This indicates that more than one significant phonon mode is contributing to the charge pairing mechanism.

Although the exact role of the apical oxygens is not fully understood, our results indicate that the phonon contribution to the pairing mechanism responsible for superconductivity in 123 is not located exclusively in the CuO_2 plane layers; the apical sites play a significant role in the phonon-mediated contribution to pairing in this system.

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