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Isotope effect in $YBa_{2-x}La_xCu_3O_z$: Evidence for phonon-mediated high-temperature superconductivity

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We report the dependence of the oxygen isotope shift on transition temperature T_c in the system $YBa_{2-x}La_xCu_3O_z$ with $0 \leq x \leq 0.5$. We find a significant oxygen isotope shift at low temperatures ($\alpha_0 = 0.38$ at $T_c = 38.3$ K), which decreases gradually with increasing T_c and finally falls rapidly above 73 K to $\alpha_0 = 0.025$ for $T_c = 92.3$ K. Our data are well fitted by the expression $\alpha_0(T_c) = 0.5(1 - T_c/T_{c0})^{0.59}$, with $T_{c0} = 92.8$ K. Our results suggest a dominant role for conventional electron-phonon coupling in the high-temperature cuprate superconductors, with strong suppression of the isotope effect as T_c approaches its maximum value in this system.

High-temperature superconductivity is more than four years old, but the underlying pairing mechanism is still not certain. In low-temperature superconductors, the isotope shift provided strong support for phonon-mediated electron pairing.[1-3] In the original BCS theory, $T_c \simeq M^{-\alpha}$, with $\alpha = 0.5$. A nearly zero oxygen isotope effect α_0 was found in the high-temperature superconductor $YBa_2Cu_3O_7$ ($\alpha_0 \approx 0.02$),[4-6] and many exotic mechanisms (phonon and nonphonon) were proposed,[7-9] in addition to the conventional electron-phonon coupling interaction.[10,11] Central to the conventional model are high-frequency oxygen vibrations in the Cu-O sublattice and their strong coupling to the electronic states at the Fermi level. Recently, Cohen, Pickett, and Krakauer[12] and Phillips[12] have proposed models that are capable of explaining the small oxygen isotope effect in $YBa_2Cu_3O_7$ within the framework of phonon-mediated electron pairing. If two mechanisms, a phonon-mediated and an exotic interaction, contribute to high-temperature superconductivity, then the isotope effect α would be expected to vary with T_c, as the relative importance of the two mechanisms changes. We find a strong correlation between the isotope effect and T_c in La-doped $YBa_2Cu_3O_7$. The oxygen isotope shift is actually quite a large fraction of the BCS value up to ~ 73 K and then falls to nearly zero at the highest $T_c \simeq 92$ K of this system. The analysis in Ref. 13 gives a trend to lower α with increasing T_c, which is similar to our data.

Crawford *et al.*[14] reported measurements of the oxygen isotope shift as a function of x and T_c for $La_{2-x}Sr_xCuO_4$. They found values as large as $\alpha_0 = 0.77$, and the isotope effect did not seem to be correlated in any simple way with T_c. Franck *et al.*[15] have measured α_0 as a function of T_c in $Y_{1-x}Pr_xBa_2Cu_3O_z$. α_0 was reported to increase more than linearly with decreasing transition temperature, exceeding $\alpha_0 = 0.5$ for $T_c \approx 30$ K. As it is not quite clear what mechanism suppresses T_c in the $Y_{1-x}Pr_xBa_2Cu_3O_z$ system,[16,17] the dependence of α_0 upon T_c could be peculiar to that system. Also, the diffusion was performed at 935 °C where structural changes can take place.

We have undertaken a careful measurement of the oxygen isotope shift as a function of T_c in $YBa_{2-x}La_xCu_3O_z$ ($z \approx 7$). This system was chosen for several reasons. (1) T_c can be reduced substantially by substituting La^{3+} for Ba^{2+}. (2) For a given La content, maximum T_c values are obtained by slow cooling after oxygen substitution. (3) Because of the high mobility of oxygen in the Y-Ba-Cu-O system,[18] all oxygen in the sample can be exchanged at 600 °C, well below the temperature where cation diffusion is expected, so that the structure is unaffected by the oxygen substitution.

Samples of $YBa_{2-x}La_xCu_3O_z$ ($z \approx 7$) with $x = 0.0$, 0.1, 0.2, 0.3, 0.4, and 0.5 were prepared by solid-state reaction of Y_2O_3, $BaCO_3$, La_2O_3, and CuO powders (all 99.999% pure except La_2O_3, which was 99.99%) at 950 °C in flowing oxygen. The procedure was similar to Ref. 4 with additional annealing. By repeating the heat treatment several times, sharp superconducting transitions with well-defined, steep diamagnetic onsets were obtained for all samples except for $x = 0.3$. This composition showed a somewhat broadened transition, which started with a moderate slope; then the transition became steep for M below -2 emu/mol. All samples were single phase by x-ray diffraction (XRD) (Cu K, Ni filter), and unreacted ingredients were absent. Lattice parameters were in good agreement with previously published work.[19,20] Our samples were porous ($\rho = 4.5$ g/cm^3) to facilitate isotope exchange. A series of careful thermogravimetric analysis (TGA) experiments were performed on ^{18}O-substituted $YBa_2Cu_3O_7$ samples. These showed that oxygen in the samples freely exchanged with oxygen in the surrounding atmosphere on a reasonable time scale at 600 °C. Details are planned to be published elsewhere.[18] Further TGA experiments showed that the time constant for oxygen diffusion in La-doped $YBa_2Cu_3O_7$ was somewhat longer. Therefore, the time for the isotope diffusion treatment was increased to ensure nearly complete isotope replacement in all samples.

For each sample with x in the range $0 \leq x \leq 0.5$, four pieces were broken off from the same pellet, cut into bars of $2 \times 2 \times 5$ mm^3 with ≈ 80 mg mass, and subjected to simultaneous thermal treatment during the diffusion process carried out in a tube furnace. All samples were

TABLE I. Dependence of oxygen isotope shift and α_0 on T_c in $YBa_{2-x}La_xCu_3O_z$ ($z \approx 7$).

x	Percent (%) ^{18}O [a] exchange	T_c (K)	ΔT_c [b] (K)	α_0 [c]
0.0	97	92.3	0.28	0.025±0.002
0.1	97	91.9	0.41	0.039±0.003
0.2	97	77.3	1.29	0.140±0.003
0.3	97	73	1.86	0.213±0.015
	97	60	1.93	0.269±0.004
0.4	95	49.3	1.92	0.324±0.013
0.5	94	38.3	1.75	0.380±0.013

[a] From weight changes, error limits are ±2%.

[b] Averaged from 12 individual measurements as described in the text.

[c] Limits are statistical, calculated from errors of T_c and ΔT_c.

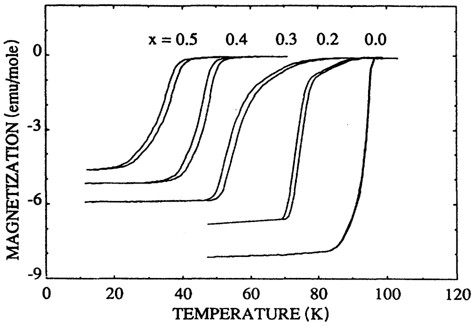

FIG. 1. Meissner curves for several ^{16}O- and ^{18}O-substituted samples of $YBa_{2-x}La_xCu_3O_z$ ($z \approx 7$) measured in a field of 3.16 Oe; in each case the ^{18}O curves are lower.

weighed on a microbalance, wrapped loosely in gold foil, and placed in parallel 10.5-mm-i.d. quartz tubes, connected to 1256-cm^3 borosilicate reservoirs. The outlet of each reservoir was connected via electropolished stainless-steel tubes with an i.d. of 5 mm to the other end of the quartz tubes on the opposite side of the furnace. Convection-driven, continuous flow of the gas around the system was established by heating a vertical section of the parallel stainless-steel tubes with an ir lamp. The layout of the diffusion apparatus was completely symmetric with the ^{18}O circulation loop being an exact duplicate of the ^{16}O loop. Except for the circulation loops, the diffusion apparatus was identical to the one used in previous experiments.[4,5] Two pieces of each sample were heated in an $^{18}O_2$ (96.9% ^{18}O, 2.6% ^{16}O, 0.5% ^{17}O, $CO < 18$ ppm, $CO_2 < 18$ ppm, $CH_4 < 7$ ppm, $N < 21$ ppm, $H < 18$ ppm, and $HE < 15$ ppm). Two other pieces of each sample were heated in an identical, adjacent tube containing $^{16}O_2$ (99.993% ^{16}O, 0.005% ^{17}O, 0.002% ^{18}O, $CO < 14$ ppm, $CO_2 < 7$ ppm, $CH_4 < 5$ ppm, $H < 39$ ppm, $He < 13$ ppm, and $N < 18$ ppm). During the heat treatment, all samples were within 2 cm of each other, well inside the isothermal heating zone of 6 cm length at the center of the furnace.

Both loops of the system were outgassed, evacuated to <0.04 mbar, and then filled to 993 mbar with their respective oxygen isotopes. The pressures were identical within 1 mbar. The samples were heated at 20 °C/min to 600 °C, held for 144 h, cooled at 12.5 °C/h to 300 °C, and furnace cooled to room temperature. During the thermal treatment, the pressure increased to 1012±1 mbar in both loops and returned to 990±1 mbar after cooling to room temperature. In all cases the ^{16}O samples showed small weight losses (≈0.10%±0.5%) due to the annealing schedule, while the ^{18}O samples showed significant weight increases (≈2%). The incorporated ^{18}O was calculated from the difference in ^{18}O-versus-^{16}O sample weight changes (Table I). The oxygen isotopic mixture from the reservoir replaced almost 100% of the oxygen originally present in the samples, indicating almost complete exchange at all oxygen sites.

Field-cooled (Meissner-effect) magnetic susceptibility curves were measured in a Quantum Design superconducting quantum interference device (SQUID) susceptometer at 3.16 Oe. Temperature measurements were performed with a platinum resistance thermometer (Lakeshore PT-111) placed in direct contact with the sample and driven by a microprocessor controlled ac bridge. The resolution is 2.5 mK and reproducibility 10 mK at 77 K after cycling to room temperature. The power dissipated in the resistor was less than 10^{-9} W. The paramagnetic moment of the platinum resistor ($m \approx 2.5 \times 10^{-7}$ emu in the 3.16-Oe field over the range $20 < T < 100$ K) was subtracted from the measured curves. The bar-shaped samples were oriented with their longest axis parallel to the magnetic field to minimize demagnetization effects. For each sample piece, a run was made over a larger temperature range to determine the shape of the curve (Fig. 1). The two curves for each ^{18}O,^{16}O pair are parallel over a wide temperature range. Next, for each sample piece, a selected section (usually from −3 to 0 emu/mol) of the susceptibility curve was measured in steps of 100–300 mK, depending on the sharpness of the transition. Thus, for each T_c, four curves were obtained: two sample pieces for each isotope, except for $x=0.0$, which had one sample for each isotope. The difference between the curves of the two pieces with the same x and containing the same isotope was found to be < 50 mK for all samples investigated (see Fig. 2). ΔT_c values were measured horizontally across the steepest portions of the paired curves at three values of M, as indicated in the figure. The samples showed Meissner effects of ~20%, and so the curves at the measured values of M indicate properties representative of the whole sample. The curves are nearly parallel in all cases. For $x=0.0$, 0.4, and 0.5, T_c values were measured at $M=-1.5$, −1.0, and −0.5 emu/mol. For $x=0.1$, measurements were at $M=-2.5$, −2.0, and −1.5 emu/mol, while for $x=0.2$ at $M=-3.5$, −3.0, and −2.5 emu/mol. Since the curves for $x=0.3$ samples had broadened transitions consisting of two different slopes, T_c values were measured at $M=-3.5$, −3.0, and −2.5 emu/mol and at −0.75, −0.5, and −0.25 emu/mol. Thus, for each T_c, 12 ΔT_c values were obtained and averaged. The oxygen-isotope-effect parameter α_0 was calculated according to the formula $\alpha_0 = \log_{10}(1 - \Delta T_c / T_c) / \log_{10}(m_{16}/m_{18})$, where T_c is the transition temperature of the ^{16}O sample and $m_{16}/m_{18} = \frac{16}{18}$, the oxygen isotope masses. The T_c for

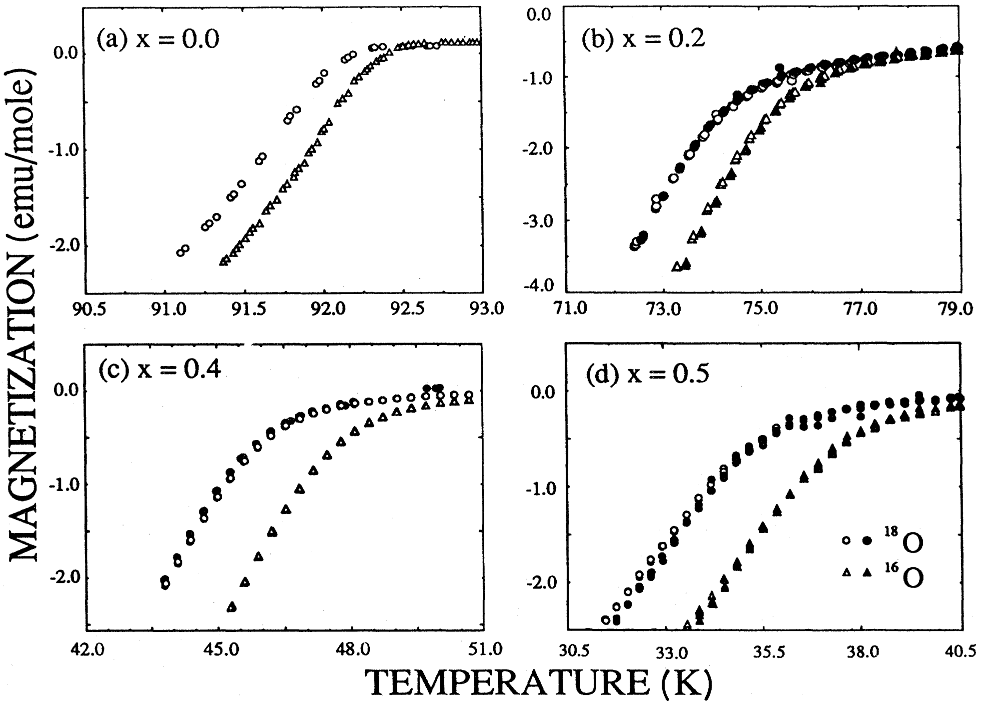

FIG. 2. Sections near T_c of the Meissner curves of several samples of $YBa_{2-x}La_xCu_3O_z$. Measurement intervals 100–300 mK. Data displayed on expanded temperature scales.

each ^{16}O sample was taken at the extrapolation to $M=0$ of a straight line through the three points where values were measured. Averaged values for T_c and ΔT_c values adjusted for 100% ^{18}O substitution are given in Table I. To separate the real isotope shift from any intrinsic difference in transition temperatures caused by sample nonuniformity, the samples were again diffused, half the pieces in the same isotope as before, the rest in the other isotope. Conditions were the same as before. Whereas samples diffused in the same isotope showed no measurable change in weight, the others exhibited significant weight increases or decreases, which indicated that the respective oxygen isotope had been almost completely reexchanged. Samples that were rediffused with the opposite isotope had T_c shifted, consistent with the oxygen isotope used (with 60 mK of the original samples of the same isotope), while T_c values of samples rediffused with the same isotope remained unchanged within error limits. This confirms that the observed shifts are really due to the oxygen isotope effect.

We find a substantial increase in ΔT_c as T_c drops from 92 to 73 K and only small changes in ΔT_c as T_c is further reduced [see Fig. 3(b)]. The variation of α_0 calculated from these data is shown in Fig. 3(c). At low T_c, α_0 is quite large, approaching the BCS value $\alpha_0=0.5$. α_0 decreases gradually with increasing T_c, for $T_c=60$ K, $\alpha_0=0.27$, still more than 50% of the BCS value. As T_c approaches its maximum value, α_0 falls rapidly. The value we obtain for α_0 at $x=0.0$ is consistent with previous measurements.[4] Our results are well fit by the expression $\alpha_0(T_c)=0.5(1-T_c/T_{c0})^{0.59}$, with $T_{c0}=92.8$ K. As an alternative, we have calculated α_0 using for T_c the temperature at which the sample magnetization reaches the specified value. Representative values for α_0 calculated by this method are included in Fig. 3(c). The quite substantial slope (≈ 0.02/K) of the curve for T_c in the range 88–92 K may account for the discrepancies among the α_0 values reported in the literature for undoped $YBa_2Cu_3O_7$,[4–6,21] since small differences in T_c appear to cause substantial differences in the value of α_0.

The oxygen content z of our samples, determined by titration and the corresponding formal average copper valence (FCV) versus T_c of the ^{16}O samples, is plotted in Fig. 3(a). The values agree well with those reported in the literature.[19,22,23] ^{18}O and ^{16}O samples were found to be the same within experimental resolution. With decreasing T_c the hole concentration, as given by the FCV, is found to decrease. However, since the variation of mobile hole concentration with La content x is not known, the dependence of T_c upon doping level, especially in the highly doped compound ($x \geq 0.4$), may include various other contributions, such as structural changes induced by the La substitution. It is not clear at the moment what variable α_0 can be related to other than T_c. Additional experiments, such as Hall-effect measurements up to high La concentrations and measurements of bond-length changes, will be required to reveal the causes(s) for the dependence of T_c upon La content x in

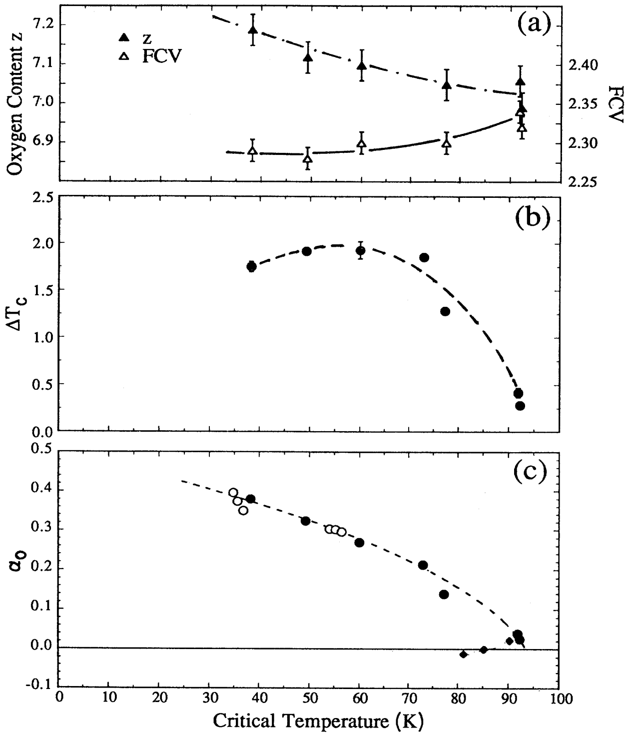

FIG. 3. (a) Oxygen content z as determined from titration and corresponding formal average copper valence (FCV) vs T_c. The values of z and FCV for ^{18}O and ^{16}O samples are the same within experimental resolution. (b) Shifts in transition temperatures ΔT_c as a function of T_c for $YBa_{2-x}La_xCu_3O_z$ samples corrected to 100% isotope content. (c) Oxygen isotope effect α_0 vs transition temperature T_c. The dashed curve follows the expression $\alpha_0(T_c)=0.5(1-T_c/T_{c0})^{0.59}$, with $T_{c0}=92.8$ K. The exponent and T_{c0} were fit to the experimental data (solid symbols). Open symbols show values of α_0 obtained using the alternative method for evaluation of T_c (see text). Solid diamonds: data for Sr substitution at the Ba site; α_0 decreases with T_c as the Sr content increases.

this system.

Experiments in which Sr instead of La was substituted on the Ba site showed quite different results, as shown in Fig. 3(c). T_c gradually decreased with Sr doping, as is known from the literature,[24,25] but the oxygen isotope shift decreased systematically with T_c and became slightly negative for Sr content $x=1.0$, which gave $T_c=81.2$ K. Details are planned to be published elsewhere.[26] The experimental technique was exactly the same as for La substitution. The oxygen content determined by titration did not vary with Sr content within experimental resolution. Since Sr has the same valence as Ba, the changes in T_c and α_0 are apparently unrelated to total hole concentration, although the fraction of mobile holes might change. Thus the effect on the oxygen isotope shift of substitution of different ions at the same site is quite different. Clearly, systematic changes in oxygen isotope shift with doping of various ions at different sites in high-temperature superconductors are a rich source of information and may help to sort out theories.

Two possible causes of systematic errors, which we cannot entirely exclude, could possibly mimic an isotope shift since they would be correlated with oxygen isotope: (1) change in T_c caused by a difference in trace gas content of the ^{18}O and ^{16}O gases and (2) slight differences in total oxygen content after slow cooling of the samples because of slightly different diffusion rates of ^{18}O and ^{16}O. Since T_c decreases quite rapidly with increasing δ in $YBa_2Cu_3O_{7-\delta}$ ($d\Delta T_c/d\delta \approx 100$ K for $6.7 \leq \delta \leq 7$), a different oxygen deficiency δ as small as 0.02 would change T_c by ~2 K. We do not believe that such effects are significant in the experiments presented in this Brief Report.

In summary, we find a strong correlation between the isotope effect and T_c. The oxygen isotope effect α_0 is quite large at low T_c, decreases gradually with increasing T_c, and finally falls to nearly zero at the highest T_c. Our results suggest a dominant role for phonon-mediated electron pairing in the high-temperature superconductors with progressive suppression of the oxygen isotope effect α_0 as T_c approaches ~93 K, its maximum value for this system.

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