Observation of an Oxygen Isotope Shift in the Superconducting Transition Temperature of La$_{1.85}$Sr$_{0.15}$CuO$_4$

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An oxygen isotope shift is observed in superconducting La$_{1.85}$Sr$_{0.15}$CuO$_4$ when ^{18}O is substituted partially for ^{16}O; the superconducting transition temperature T_c is lowered by 0.3 to 1.0 K in different samples. We examine these results using conventional phonon-mediated BCS theory and conclude that for La$_{1.85}$Sr$_{0.15}$CuO$_4$, phonons play an important role in the pairing mechanism.

The discovery of superconductivity near 37 K, in La$_{1.85}$Sr$_{0.15}$CuO$_4$[1] and near 92 K in YBa$_2$Cu$_3$O$_7$[2,3] has generated great interest in the mechanism of superconductivity in these materials. Although the conventional phonon-mediated electron-pairing mechanism[4] may be consistent with superconductivity above 30 K, novel mechanisms are under consideration. One experiment that investigates whether a phonon mechanism is involved is to measure the superconducting transition temperature T_c for samples containing different isotopes.[5,6] In YBa$_2$Cu$_3$O$_7$, the mass of the ion at the yttrium site can be varied by rare-earth (R) substitutions; although T_c differs for various RBa$_2$Cu$_3$O$_7$ compounds, there is no obvious correlation with mass.[7,8] Experiments in which ^{18}O was substituted for ^{16}O in YBa$_2$Cu$_3$O$_7$ have suggested the absence of an isotope shift.[9-11] In addition, for this system, Cu and Ba isotope substitution produces no measurable shift in T_c.[12] In contrast to the 92-K superconductor, we report here[13] that we have detected an oxygen isotope effect in the 37-K superconductor La$_{1.85}$Sr$_{0.15}$CuO$_4$.

Our Meissner-effect and resistance measurements indicate that T_c is shifted to lower temperatures when ^{18}O is substituted partially for ^{16}O in La$_{1.85}$Sr$_{0.15}$CuO$_4$. The magnitude of the shift is between 0.3 and 1.0 K, depending on the sample. If we use the original BCS treatment[4] of $T_c \propto M^{-\alpha}$, where M is the oxygen mass and $\alpha = 0.5$, the shift predicted for a 37-K superconductor is approximately 2.1 K. This is an upper limit since it assumes that the frequency of the phonon mode depends only on the mass of oxygen.

In order to provide convincing evidence that the shift in T_c is due to ^{18}O substitution, rather than sample inhomogeneity or other sample-to-sample variations, five samples of La$_{1.85}$Sr$_{0.15}$CuO$_4$ were isotopically exchanged. These samples were synthesized independently with starting materials obtained from different sources. Isotopic exchange was accomplished by the annealing of each sample in ^{18}O$_2$. The resistance and magnetic susceptibility of these samples were compared with control samples annealed in ^{16}O$_2$ under nearly identical conditions.

The two best characterized samples of La$_{1.85}$Sr$_{0.15}$CuO$_4$, referred to below as samples I and II, were prepared by our dissolving stoichiometric ratios of La$_2$O$_3$, SrCO$_3$, and CuO in concentrated nitric acid, adding oxalic acid, and evaporating to dryness. Sample I was fired in a platinum crucible in air for 14 h at 800 °C with one intermediate grinding. The powder was then reground, pressed into a pellet, and fired for 12 h at 900 °C, 2 h at 1100 °C, 6 h at 900 °C, and finally slow cooled to room temperature in 8 h. The processing of sample II was similar. Both products were ground and pressed into $\frac{1}{4}$-in. pellets for further annealing in ^{18}O$_2$ and ^{16}O$_2$ atmospheres. Powder x-ray diffraction showed that both samples consisted of single-phase La$_{1.85}$Sr$_{0.15}$CuO$_4$.

To exchange ^{18}O for ^{16}O, a portion of sample I was placed in a static ^{18}O$_2$ atmosphere at 650 Torr. The sample temperature was raised to 1000 °C, held for 20 h, raised linearly in 1 h to 1100 °C, held at 1100 °C for 1 h, and then cooled to room temperature in 24 h. A second portion of sample I was annealed in the same manner in 20 cm^3 (STP)/min of flowing ^{16}O$_2$ (Matheson, 99.999%) at 760 Torr. Isotope exchange in sample II was accomplished by annealing in a static ^{18}O$_2$ atmosphere at 530 Torr for 20 h at 950 °C, followed by cooling to 500 °C in 4 h and quenching to room temperature. A second por-
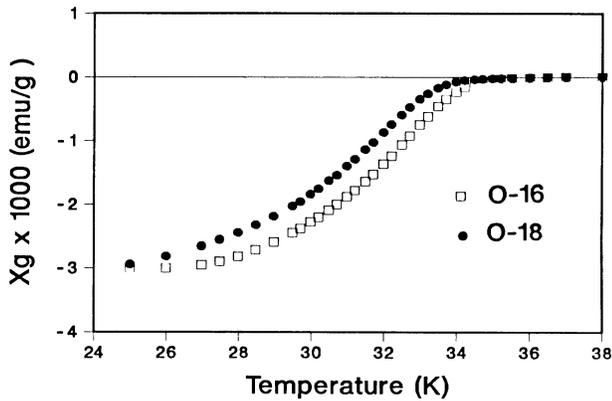
FIG. 1. Magnetic susceptibility of $La_{1.85}Sr_{0.15}CuO_4$ vs temperature for ^{18}O and ^{16}O portions of sample I.

FIG. 2. Resistance of $La_{1.85}Sr_{0.15}CuO_4$ vs temperature for the ^{18}O and ^{16}O portions of sample I.

tion of sample II was annealed in the same manner in 20 cm^3 (STP)/min of flowing $^{16}O_2$ at 760 Torr. In addition, a third portion of this sample was annealed in a static pressure of 530 Torr.

Isotope substitution in these compounds was verified by temperature-programmed reduction (TPR) measurements employing a quadrupole mass spectrometer, as described elsewhere.[14] During heating in flowing hydrogen, the samples were reduced to La_2O_3, SrO, and Cu metal, thus removing approximately 1 of the 4 mol of oxygen initially present in the sample. We assume that the isotope ratio of ^{18}O to ^{16}O in the H_2O which desorbs is the same as the isotope ratio of the oxygen remaining in the decomposed sample. Sample I was found to contain 68% ^{18}O and sample II contained 75% ^{18}O.

Measurements of the Meissner effect of our samples were performed on a SHE Corp. SQUID magnetometer in a field of 12.0 G. In Fig. 1, the magnetic susceptibilities for the ^{18}O and ^{16}O portions of sample I are shown by the circles and squares, respectively. For the ^{16}O portion the onset temperature is 35 K, while for the ^{18}O-exchanged sample the onset temperature is 34.4 K, indicating a shift to lower T_c. However, the magnitude of the shift is a function of temperature and reaches a maximum of 1.5 K near 28 K.

Figure 2 shows resistance data near T_c for sample I. A well-defined break in the resistance versus temperature curve occurs at T_c(onset) = 35.5 K for the ^{16}O sample and at T_c(onset) = 34.5 K for the ^{18}O sample. The transition midpoint of the two samples differs by approximately 1.2 K.

The results of the magnetic measurements of the exchanged and unexchanged portion of sample II are shown in Fig. 3 by the circles and squares, respectively. For this sample, the onset temperature is approximately 37 K for the ^{16}O portion, ∼2 K higher than that of the ^{16}O portion of sample I. This difference is most likely due to small differences in the amount of Sr in the sample. In addition, the transition width is larger for sample II. Nevertheless, the data for the ^{18}O-exchanged portion
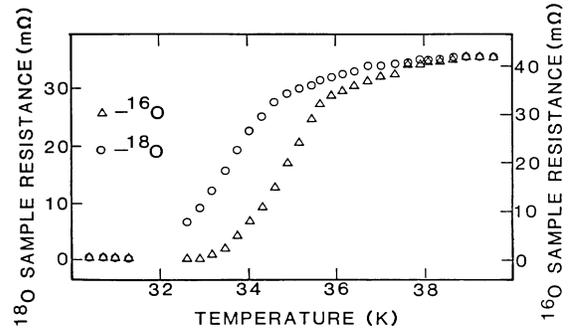
of sample II are shifted 0.45 to 0.8 K to lower temperatures, depending on the temperature at which the shift is measured. Although sample II contains more ^{18}O than sample I, its observed shift is smaller; this may be related to the broader transition for sample II.

Despite the differences in the transition temperatures and widths, all our samples clearly demonstrate that isotopic exchange of oxygen produces significant shifts in T_c. Two additional experiments were conducted to demonstrate unambiguously that these shifts are not artifacts produced by the isotopic-exchange process. In the first, the portion of sample II which was annealed in $^{18}O_2$ was subsequently annealed in flowing $^{16}O_2$ to resubstitute ^{16}O for ^{18}O; the magnetic measurements of this sample are shown by the triangles in Fig. 3. The results are essentially identical to those obtained on the sample which was never isotopically exchanged. The residual ^{18}O in this sample was 2%, as measured by temperature-programmed reduction. In the second experiment, another portion of the original sample II was annealed in static $^{16}O_2$ at 530 Torr. The magnetic sus-

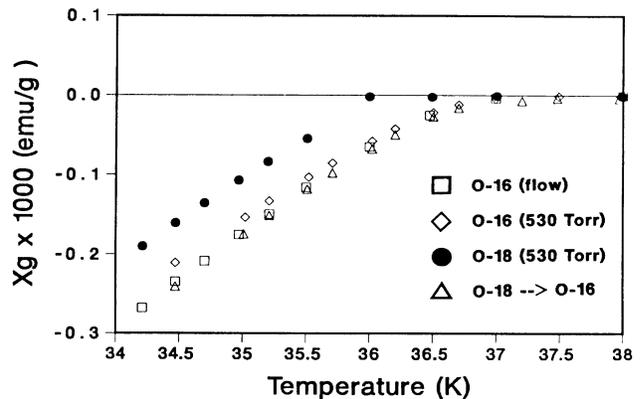FIG. 3. Magnetic susceptibility of $La_{1.85}Sr_{0.15}CuO_4$ vs temperature for sample II prepared as follows: in flowing $^{16}O_2$ (squares), in 530 Torr of $^{16}O_2$ (lozenges), and in 530 Torr of $^{18}O_2$ (circles). Also shown are the data for the ^{18}O reexchanged with $^{16}O_2$ (triangles).

TABLE I. Summary of oxygen-isotope-shift data for La$_{1.85}$Sr$_{0.15}$CuO$_4$.

Sample	T_c(onset) (K)	T_c^{mag} shift (K)[c]	T_c^{res} shift (K)[d]	^{18}O (%)	α[e]	α[f]
I	35 [a]	0.60	1.0	68	0.22	0.37
II	37 [a]	0.45	· · ·	75	0.13	· · ·
III	34.5 [b]	0.25	0.25	· · ·	· · ·	0.09 [g]
IV	37 [b]	· · ·	0.33	· · ·	· · ·	0.11 [g]
V	37 [b]	· · ·	0.30	· · ·	· · ·	0.10 [g]

[a]Onset of the superconducting transition as measured by magnetization.

[b]Onset of the superconducting transition as measured by resistance.

[c]The shift in T_c due to ^{18}O substitution as measured from the magnetization at approximately 1 K below the diamagnetic onset.

[d]The shift in T_c due to ^{18}O substitution as measured where the resistance is 80% of the value just above the transition.

[e]The parameter α calculated from the magnetization data by the extrapolation of the observed shifts in T_c to 100% ^{18}O substitution.

[f]The parameter α calculated from the resistance data by the extrapolation of the observed shifts in T_c to 100% ^{18}O substitution.

[g]The parameter α is calculated for these samples on the assumption that the ^{18}O substitution is 65%.

ceptibility of this material is shown by the lozenges in Fig. 3. While these data are not identical with those for samples annealed in flowing ^{16}O$_2$, the difference is small compared with the shift observed when ^{18}O is substituted. Further details on the magnetic data will be given in a subsequent publication.[15]

Three additional sets of La$_{1.85}$Sr$_{0.15}$CuO$_4$ samples (labeled III–V) were prepared and their resistive transitions were measured. These samples were prepared by direct reaction of La$_2$O$_3$, SrCO$_3$, and CuO; ^{18}O substitution was accomplished by annealing in ^{18}O$_2$ at 940 °C to 1000 °C for at least 20 h. Careful resistance measurements indicate that the change in T_c for the three samples is consistently on the order of 0.3 K, as summarized in Table I. In the one case (sample III) where both resistance and magnetization measurements were made the observed isotope shift was equal.

The main conclusion which can be drawn from the data presented in Table I is that although sample dependence is evident, there is indeed an isotope shift of at least 0.3 K for partial ^{18}O substitution. Extrapolating to 100% ^{18}O substitution indicates that the isotope shift is about 0.5 K. However, it appears from sample-I data that the shift may be as large as 1.5 K. We conclude that α is no smaller than 0.10, but may be as large as 0.37.

The implications of the observed oxygen isotope shift in La$_{1.85}$Sr$_{0.15}$CuO$_4$ may be examined within the context of conventional phonon-mediated electron pairing with the BCS theory, as we have done previously for YBa$_2$Cu$_3$O$_7$.[12,16] We consider the possibility of obtaining this shift both within the two–square-well model and from numerical solutions of the Eliashberg equations using a model phonon spectrum. Within these models, we consider the limits on the parameters of the electron-electron interaction that arise from the constraints of the observed T_c and find isotope shifts which give 0.15

$< \alpha < 0.35$.

In the weak-coupling limit, two–square-well solutions for T_c and α can be obtained analytically. The McMillan[17] equation is representative of these solutions and has the form

$$T_c = 0.69 \omega_D \exp[-1/(\lambda^* - \mu^*)],$$
$$\alpha = \frac{1}{2}\{1 - [\mu^*/(\lambda^* - \mu^*)]^2\}, \tag{1}$$

where $\lambda^* = \lambda/(1+\lambda)$, μ^* is the renormalized Coulomb interaction, and T_D is an "average" phonon temperature. Within this model, for a value of $T_D = 400$ K, the lower limit of $\alpha = 0.15$ yields values of $\lambda \approx 21$ and $\mu^* = 0.43$ which are physically unreasonable. As shown in Fig. 4,
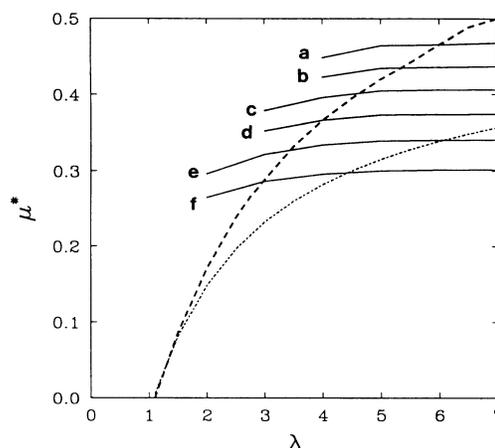

FIG. 4. Values of λ and μ^* for which $T_c = 37$ K computed from a two-square-well model (short-dashed line) and from numerical solutions of the Eliashberg equation (long-dashed line). The solid curves labeled a to f correspond to values of the isotope parameter $\alpha = 0.10$, 0.15, 0.20, 0.25, 0.30, and 0.35, respectively.

the two-square-well solution does not give accurate values of T_c in this region. Therefore, we solved the Eliashberg equations in the Matsubara representation using a model phonon spectrum derived from the inelastic-neutron-scattering data of Renker et al.,[18] and assume a constant electron-phonon interaction. Within this model, we find solutions with $T_c = 37$ K for all $\lambda > 1.1$. The separate conditions $\alpha = 0.1$, 0.15, 0.20, 0.25, 0.30, and 0.35 and can also be satisfied for $\lambda > 3$. The simultaneous solutions are shown in Fig. 4. An isotope effect of $\alpha = 0.15$ with $T_c = 37$ K is found for $\lambda \approx 5.25$ and $\mu^* \approx 0.43$.

Experimentally, we have evidence for values of $\alpha > 0.3$ and further studies are needed to obtain a firm upper limit. If we take an upper limit of $\alpha = 0.35$, then the resulting values of $\lambda \approx 2.9$ and $\mu^* \approx 0.28$ are consistent with those obtained by Weber[19] when differences in the phonon spectra are taken into account. Phillips[20] has predicted an isotope shift in $La_{1.85}Sr_{0.15}CuO_4$, with a value of $\alpha \approx 0.2$, which is in reasonable agreement with the results presented here. Phillip's analysis is based on the role of oxygen vacancies in determining lattice stability and a phonon-induced electron-electron pairing. Therefore, we conclude that if we do not consider material properties as Phillips has done, but use conventional Eliashberg theory, then $\alpha \approx 0.15$ gives very large values for λ and μ^*. However, $\alpha \approx 0.35$ leads to λ's near the range observed previously for other superconductors.[21] We also note that if parts of the phonon spectrum are shifted independently then the value of $\alpha = 0.15$ can be obtained for smaller λ and μ^*.

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