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OXYGEN ISOTOPE EFFECT IN THE HIGH TEMPERATURE SUPERCONDUCTORS
 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, WITH ^{18}O SUBSTITUTED BY DIFFUSION

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One of the most suggestive tests for electron-phonon coupling in conventional superconductors is the isotope effect, where T_c is sensitive to ionic mass: $T_c \propto M^{-\alpha}$. The presence of an isotope shift would demonstrate an important role played by the phonons in the superconductivity mechanism. The high- T_c superconducting oxide $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have many structural¹ and electronic² features in common. An important feature common to both the layered perovskite K_2NiF_4 structure of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Ba}$, Sr , or Ca) and the distorted oxygen-defect perovskite structure of $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($R = \text{Y}$ or some lanthanide rare-earth elements) is the existence of two-dimensional copper-oxygen planes which are most responsible for the metallic conduction.

Despite the similarities, however, there are important differences between $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, including a significantly lower T_c , ($\approx 40\text{K}$ vs. 90K), and a lack of one dimensional Cu-O "chains" in the La material. Also, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ has dramatically different elastic properties³. Band-structure calculations² on $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ demonstrate that the density of states at the Fermi level is due largely to hybridized Cu $3d$ and O $2p$ states. Calculations of the electron-phonon interactions in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ by Weber⁴ suggest that strong coupling of specific oxygen phonons to the conduction electrons can lead, within conventional (phonon mediated) BCS theory, to T_c values of 30-40K. It is therefore expected that vibration of the O ions would be involved if electron-phonon coupling is responsible for the superconductivity in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.

A non-zero oxygen isotope shift has been observed in the superconducting oxide $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, in sharp contrast to our observation^{5,6} of no oxygen isotope shift in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Substitution of ^{18}O for ^{16}O in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ results in a depression of

the superconducting transition temperature T_c . The substitution was carried out in a similar manner as in $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (see below), but was more difficult. Magnetic (Meissner effect) and resistive measurements indicated that T_c is depressed by 0.3 - 1.0 K in various samples when the isotope ^{18}O is substituted for 65% to 78% of the ^{16}O in the sample. The observed shifts in T_c were extrapolated to 100% ^{18}O . With $T_c \approx M^\alpha$, where M is the oxygen mass, we find $0.10 < \alpha < 0.35$. This non-zero isotope shift indicates that in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, phonons may play an important role in the superconductivity mechanism. We examine the consequences of this result for phonon mediated electron pairing, within the framework of BCS theory.

We previously searched for an isotope effect in $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$, by substituting the isotope ^{18}O for ^{16}O . The oxygen isotope exchange was carried out by placing a fine grained porous sample in a fused quartz tube connected to an ^{18}O reservoir and heating at 950°C for 12 hr. We were able to substitute an estimated 90% of the ^{16}O in the sample by ^{18}O (see below). No shift in T_c was observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ within 0.3 K, the experimental uncertainty. The expected isotope shift in basic BCS theory ($T_c \propto M^{-1/2}$) would correspond to a reduction in T_c of ~ 4.6 K on substitution of 90% of the ^{16}O by ^{18}O , if T_c is determined by motion of the O ions. We found^{5,6} that the oxygen isotope effect is absent in this material, $\alpha = 0 \pm 0.027$.

In order to determine the appropriate conditions for oxygen isotope substitution, a series of thermogravimetric analysis (TGA) experiments were carried out on $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (Ref 6) and on $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Samples were heated in oxygen or argon and then cooled at various rates. All experiments were carried out at ambient pressure. The change in oxygen content of the sample was measured by the change in sample weight following a change in temperature or of the partial pressure of oxygen in the surrounding space. It was found that the equilibrium oxygen content varies with temperature, and the partial pressure of oxygen in the surrounding space. At temperatures above about 450°C in $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$, or above 700°C in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, oxygen is lost, but the process is reversible up to at least 1000°C , where the weight loss in O_2 at one atmosphere pressure reaches about 1.3% in $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$. This corresponds to about 9% of the total oxygen content or a change of ~ 0.5 oxygen per formula unit. When $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ samples were cooled slowly in O_2 , the oxygen content increased until a maximum was reached at $400\text{-}450^\circ\text{C}$. The oxygen loss from $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ was much smaller.

Heating $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ in argon nearly doubled the weight loss at each temperature; the loss was only reversible by annealing and cooling in O_2 . The effects of heating and cooling in argon and in oxygen at various rates on the superconducting properties were studied.

The time constants for oxygen diffusion into or out of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were found by observing the change in sample weight following a rapid temperature step. The sample weight was found to approach the new equilibrium value by an exponential decay, rather than following a $(\text{time})^{-1/2}$ dependence as would be expected if the diffusion was slow and the interior of the grains did not reach equilibrium. The time constants for oxygen release and uptake were found to be quite short, $10^1 - 10^3$ sec., depending on temperature and sample grain size. We concluded that oxygen in this material is mobile at temperatures above 400-500°C, with very high diffusion rates. The time constants for oxygen diffusion into or out of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ at elevated temperatures were also found to be short, though the changes in oxygen content with temperature in an O_2 atmosphere were much smaller than in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

The very rapid oxygen diffusion in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ suggested that simple diffusion at elevated temperature at constant O_2 pressure would be an effective method to replace the ^{16}O in a sintered sample by ^{18}O , from $^{18}\text{O}_2$ gas placed in the surrounding space. Fine grained porous pellets were used in these experiments. The untreated pellets had sharp resistive transitions to the superconducting state. Several pieces of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ pellets were heated to 950°C in an atmosphere of $^{18}\text{O}_2$, held at that temperature for 10 hours and cooled in 6 hours. This temperature and reaction time were chosen to insure maximal ^{18}O exchange with ^{16}O at both weakly bound and tightly bound sites.

In the case of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ the porous pellets were heated to 940°C-1000°C in an $^{18}\text{O}_2$ atmosphere, held at that temperature for 20 hours or more, and then heated to 1050°C-1100°C to complete the sintering. All samples were slow cooled. The extent of isotope substitution was verified by temperature programmed reduction measurements using a quadrupole mass spectrometer. The superconducting resistive transitions remained sharp after the isotope substitution. Pieces broken from the same pellets were given almost identical diffusion treatment in ^{16}O as a control. The T_c of the ^{18}O substituted materials were compared to the controls, and to fragments of the untreated pellets.

Figure 1 shows χ vs. temperature for an ^{18}O substituted $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ sample and for the corresponding ^{16}O sample. For the ^{16}O samples the diamagnetic onset temperature is 35 K, while for the ^{18}O substituted sample (65% ^{18}O , 35% ^{16}O) the onset temperature is 34.4 K. The shift in diamagnetic onset temperature is 0.6 K. At lower temperatures the offset between the two curves increases for reasons not completely understood.

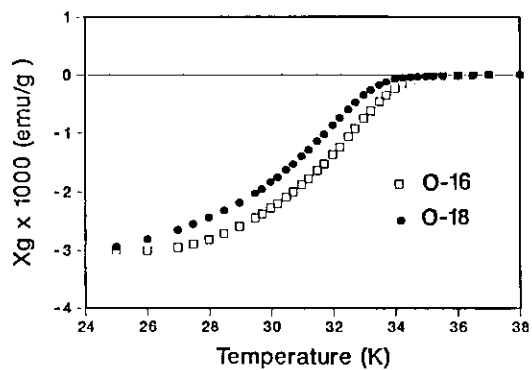


Figure 1: Magnetic susceptibility per gram $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ versus temperature for an ^{18}O isotope substituted portion (65% ^{18}O , 35% ^{16}O) and the ^{16}O portion of the same pellet.

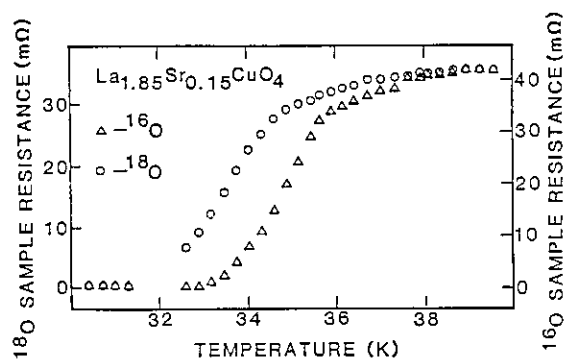


Figure 2: Resistance of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ vs. temperature for the ^{18}O substituted and ^{16}O portions of the same pellet as Figure 1. The sample dimensions and lead spacing vary, so the normal state resistances differ.

Figure 2 shows resistance data near T_c for the same specimen used for the susceptibility measurements of Fig. 1. A well defined break in the R vs. temperature curve occurs at $T_c = 35.5\text{K}$ for the ^{16}O sample and at $T_c = 34.5\text{K}$ for the ^{18}O sample.

Both our magnetic and resistance experiments demonstrate a consistent and finite isotope effect in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. With $\alpha = 0.5$ as predicted from phonon BCS theory, one would expect an $^{18}\text{O} - ^{16}\text{O}$ shift of T_c of about 2.1 K, much larger than we observed. We find $0.1 < \alpha < 0.3$ for this material, significantly less than the BCS prediction $\alpha = 0.5$, but in sharp contrast to the null isotope effect observed for $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$, where $\alpha = 0.0 \pm 0.027$ (Refs 5 and 6).

The implications of the observed oxygen isotope shift in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ may be examined within the context of conventional phonon-mediated electron pairing within the BCS theory as we have done previously for $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Ref 5). We have considered the possibility of obtaining an isotope shift in the observed range both within the two square-well model and from numerical solutions of the Eliashberg equations using a model phonon spectrum. Within these models, we have considered the limits on the parameters of the electron-electron interaction that arise from the constraints of the observed T_c and give isotope shifts in the range $0.10 < \alpha < 0.35$. We use a model phonon spectrum derived from the inelastic neutron-scattering data of Renker *et al.*⁷ assuming a constant electron-phonon interaction. Within this model, we find solutions with $T_c = 37\text{K}$ for all $\lambda > 1.1$. The separate conditions $\alpha = 0.1, 0.15, 0.20, 0.25, 0.30,$ and 0.35 can also be satisfied for $\lambda > 3$. An isotope effect of $\alpha = 0.15$ with $T_c = 37\text{K}$ is found for $\lambda \approx 5.25$ and $\mu^* \approx 0.43$.

Experimentally, values of $\alpha > 0.3$ are possible and further studies are needed to obtain a firm upper limit. If we take an upper limit of $\alpha = 0.35$, then the resulting $\lambda \approx 2.9$ and $\mu^* \approx 0.28$ are consistent with values obtained by Weber⁴, when account is taken of the different phonon spectra used. Phillips⁸ has predicted an isotope shift $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ of $\alpha \approx 0.2$, which agrees well with the results presented here. Phillips' analysis is based on the role of oxygen vacancies in determining lattice stability and a phonon-induced electron-electron pairing.

We conclude therefore that if we do not consider material properties as Phillips has done but used conventional Eliashberg theory, then $\alpha \approx 0.15$ gives very large values for λ and μ^* . However, $\alpha \approx 0.35$ leads to μ^* 's near the range observed previously for other superconductors.⁹ We also note that if parts of the phonon spectrum are shifted independently, then the $\alpha = 0.15$ value can be obtained for smaller λ and μ^* .

In conclusion, a non-zero oxygen isotope shift has been found in the superconducting oxide $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, in sharp contrast to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in which we found that the oxygen isotope effect is absent.

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