MAGNETIC AND RESISTIVE DETERMINATION OF THE OXYGEN ISOTOPE EFFECT IN La₁,₄Sr₁,₅CuO₄

L.C. Bourne, S. Hoen, M.F. Crommie, W.N. Creager, A. Bettl, and Marvin L. Cohen
Department of Physics, University of California at Berkeley, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratories, Berkeley, California 94720
Louis Hernandez and John Kinney
Lawrence Livermore National Laboratory
Livermore, California 94550
Donald E. Morris
Physics Department
Lawrence Berkeley Laboratory
Berkeley, California 94720

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In polycrystalline samples of the superconducting oxide La₁,₄Sr₁,₅CuO₄, the substantial substitution of ¹⁸O for ¹⁶O causes a small downward shift in the superconducting transition temperature Tc. Although Tc (onset) measured resistively differs by as much as two Kelvin from that measured magnetically, the two measurement methods yield comparable Tc shifts upon isotope substitution. Samples with different superconducting phases (as evidenced by resistive line structure in the transition region) show similar isotope shifts for different phases. We determine an overall oxygen isotope shift in La₁,₄Sr₁,₅CuO₄, corresponding to α = 0.142 ± 0.086, where Tc = Mα and M is the oxygen mass.

INTRODUCTION

The microscopic mechanism responsible for electron pairing in the new classes of high-Tc superconducting oxides remains an unresolved and challenging question. One of the most direct tests for phonon-mediated pairing is the isotope effect, where Tc = Mα, with M the ionic mass. In the original BCS treatment of superconductivity (one square well model), α is predicted to be 0.5. In a more general treatment ofα (two square well model) the value of α is reduced from 0.5 and can even assume negative values. Indeed, experimentally determined values of α for conventional (phonon-mediated electron pairing) superconductors, range from 0.5 in mercury to 0.2 in uranium.

Recently, isotope measurements were reported for the 90K superconductor YBa₂Cu₃O₇ and the 37K superconductor La₁,₄Sr₁,₅CuO₄. In the Bi-based material, oxygen isotope substitution was originally found to correspond approximately to α = 0.5 ± 0.3. Improvements in sample quality and refinement in experimental technique have reduced the error bars, and a small but finite shift has been established at approximately α = 0.6 ± 0.5. In the framework of three-dimensional phonon-mediated electron pairing, this small value of α is inconsistent with a 90K transition temperature and physically reasonable values of the electron-phonon coupling constant λ and the effective Coulomb interaction μ*.

In the La-based material, one study found for oxygen isotope substitution α = 0.16 ± 0.02 from magnetic susceptibility measurements, while another found from combined resistivity and magnetic susceptibility measurements values of α ranging from 0.0 to 3.7. Values of α within these limits are compatible with phonon-mediated electron pairing but they place severe constraints on the allowed magnitudes of λ and μ. Since λ and μ are sensitive functions of α and they can be independently determined, it is important to measure α as accurately as possible in this material.

We here report on a detailed study of the oxygen isotope effect in La₁,₄Sr₁,₅CuO₄, using both magnetic susceptibility and resistivity measurements. With approximately 80% of the total oxygen content of the specimen replaced with ¹⁸O, Tc is depressed by 0.4K as determined by magnetization studies. The corresponding value of α is 0.142 ± 0.086, which is within the range of α's reported in refs. 10 and 11. Our new measurements substantially improve the error limits for α.

We find that although Tc determined by resistivity is on the order of 1 to 2 Kelvin higher than Tc determined by the onset of diamagnetism, isotope-induced shifts in Tc measured resistively are comparable to those determined magnetically. The resistive shifts vary slightly across the width of the transition, as expected for percolative superconductivity just above the bulk transition.
temperature. Samples with different superconducting phases, as evidenced by fine structure in the resistivity in the transition region, show similar oxygen isotope shifts for different phases whose intrinsic Tc's lie within several degrees K of one another. Results of some of our resistivity measurements have been previously published; sample sets C/D and E are respectively samples IV and I in table I of ref. 11.

EXPERIMENTS AND RESULTS

La0.85Sr0.15CuO4 samples were prepared by mixing La2O3, SrCO3 and CuO in a ball mill with acetone, then drying and calcining on a platinum sheet at 900°C for 6 hours. The material was then ground in an agate mortar, pressed into pellets, heated to 1050°C for 20 hours and then slowly cooled, and heat treatments for initial materials preparation were done in flowing oxygen-18. The resulting dense sintered pellets were ground again in an agate mortar and re-pressed, thus increasing the porosity and the oxygen diffusivity.

Oxygen isotope exchange was achieved with a high-temperature gas diffusion technique.4,11 The samples were placed on platinum boats in two quartz tubes that were placed side-by-side in the same oven and connected to identical static gas reservoirs containing 18O2 and 92% enriched 16O2, respectively. The sample placed in the 18O environment formed the 18O control sample, while the sample placed in the 16O environment formed the isotopically exchanged sample. Isotopic substitution was induced by a series of heat treatments for the sample pair. One set of samples ("C" and "D") was heated at a series of increasing temperatures to maximize the oxygen diffusion through the pellet before densification occurred, followed by a slow cool to maximize oxygen content: the heat cycle was 940°C for 10 hours, 1050°C for 3 hours, 1080°C for 2 hours, and 870°C for 5 hours followed by an oven cool. The oxygen pressures at room temperature were 726 atm in the 16O reservoir and 745 atm in the 18O reservoir, with both pressures increasing by about 4 atm at the highest temperatures. Another set of samples ("E") was prepared with identical pressures in the two reservoirs (755 atm at 20°C, increasing to 760 atm at 1050°C), with a heat cycle of 1050°C for 15 hours, 900°C for 3 hours, 760°C for 1 hour, and 540°C for 2 hours followed by an oven cool. Although the 16O and 18O "arms" of the gas exchange system were constructed to be as symmetrical as possible, a check was performed to eliminate any asymmetric source of error. Isotopic exchanges were performed using identical experimental conditions to those stated above, except that the gas reservoir originally containing 18O was filled with 16O, and vice versa. The properties of the samples were found to depend only on the oxygen isotope type.

Changes in sample weights indicated 18O enrichments of 81% in sample "C" and 74% in sample "E". A more accurate determination of isotopic composition was performed with Laser-assisted Ion Mass Analysis (LIMA). In this technique, a small portion of the sample is ablated and ionized by a 4E laser pulse. This energy exceeds all binding energies in La0.85Sr0.15CuO4. The ions from the resulting plasma are accelerated through a time-of-flight mass spectrometer, and relative abundance of a certain isotopic species is thus determined within 2 or 3% accuracy. The LIMA technique is capable of probing the surface of a sample, as well as isotopic content as a function of depth into the specimen. Our LIMA results indicate uniform 18O enrichment of 75±2% in sample "C" and 78±3% in sample "E". The two inequivalent O sites in La0.85Sr0.15CuO4 each contain 50% of the total oxygen, so these measurements demonstrate that both sites are accessible to oxygen isotope diffusion. Values of δ were calculated from the relation Tc=1/2 by assuming an average oxygen atomic mass K determined by the LIMA measurements.

The diamagnetic transitions were measured with a SQUID model VTS-505 SQUID magnetometer by observing the Meissner flux expulsion. Below 50 K, the temperature of the magnetometer sample chamber was stable and accurate to within 0.01 K. A field of 33 Oe was used for samples "C" and "D", and a field of 20 Oe was used for samples "E". dc resistance measurements were performed with four-point silver paint contacts, with the samples placed side by side on a copper bar next to a calibrated diode, surrounded by a copper heat shield. The samples were cooled with a helium gas flow system. The resistively determined Tc's were observed to vary by no more than 0.05 K when the sample positions were exchanged, indicating negligible thermal gradient across the resistance measurement probe.

Figure 1 shows the magnetic susceptibility data for samples "C" and "D". The shift in Tc is equal to 0.41±0.02 K and does not vary with temperature for at least 5 K below the superconducting onset, giving p=0.140±0.009. For samples "E", in figure 2, the shift is again constant in temperature with a value 0.40±0.03 K, giving p=0.139±0.016. The average value of p is 0.140±0.008 for the combined susceptibility measurements. The error limits were estimated from the uncertainties in δ and in isotopic enrichments. Meissner effect susceptibility measurements are in general a good probe of the bulk

![Graph](image-url)
The superconducting properties of a sample, as indicated by resistance measurements, on the other hand, probe those portions of the sample with the least resistance, i.e., those (potentially small) portions with the highest superconducting transition temperature. Filamentary superconductivity can give sharp transitions and zero resistance. We have observed for different classes of high-$T_c$ superconductors the general feature that the onset of superconductivity measured resistively is one or two degrees Kelvin higher than the onset of diamagnetism measured by flux expulsion. This suggests that percolative superconductivity exists above the bulk superconducting transition temperature. We find, however, that isotope shifts measured near the resistive onset of superconductivity are comparable to those measured by flux expulsion.

Figures 3 and 4 show respectively the resistance measured near the superconducting transition region in sample sets C/D and E. In fig. 3, the onset of superconductivity for sample set C/D occurs near 37K; the same sample set displays an onset of diamagnetism near 35K (fig. 1). A similar difference is observed for sample set E, where resistively the transition onset occurs near 36K (fig. 4) and magnetically near 35K (fig. 2). The resistive measurements give an isotope shift that is comparable to that determined magnetically, but with greater variability. In figure 3, samples "C" and "D" show a shift of 0.31 K (the uncertainty).
Batlogg et al. have extended the work of Weber in La$_{1.85}$Sr$_{0.15}$CuO$_4$ to show that for a $T_c$ of 38 K due to an electron-phonon interaction, the $\alpha$ values should be 0.03 for the out-of-plane $\alpha$ site and 0.275 for the in-plane site, resulting in a net $\alpha$ of 0.303 for oxygen. They suggested that the discrepancy between the theoretical and experimental values of $\alpha$ could be due to anharmonic effects or to additional unconventional coupling mechanisms.

The existence of Cu-O planes suggests that a reduced dimensionality of the Fermi surface may play a role in the superconducting mechanism. In two dimensions, the electron density of states diverges logarithmically at a van Hove singularity. If the Fermi surface is pinned at this singularity, the resulting high density of states could give high $T_c$'s. Labbe and Box have considered this model and showed that variations in the Debye frequency caused by isotope substitutions should affect the transition temperature, $T_c$:

$$ T_c = \frac{1}{\alpha} $$

in agreement with the Raman measurements of oxygen isotope substitutions in La$_{1.85}$Sr$_{0.15}$CuO$_4$. Mattis and Mattis have also proposed a two-dimensional model, with a bond asymmetry term that introduces a gap in the oxygen band and gives logarithmic singularities at the band edges.

The change of the electron-electron attraction caused by changes in phonon frequencies from isotope substitutions is only one of the mechanisms that give an isotope shift in $T_c$. A recent study by Fisher et al. examines the effects of isotope substitutions on lattice constants and hopping parameters, which can produce indirect isotope shifts in $T_c$. The change in the zero point atomic vibrational modes with isotope substitutions will change the lattice constants, producing in effect pressure changes on the lattice. Since $T_c$ is very sensitive to pressure in La$_{1.85}$Sr$_{0.15}$CuO$_4$ ($\Delta T_c/dP = 0.4 K/kbar$), this effect could give a large isotope shift. One would naively expect the lattice constant to decrease as $T_c$ is exchanged for $^{18}$O, increasing $T_c$, but it is possible for the crystal anisotropy to give the correct shift if the contraction occurs along an axis that shows a negative pressure dependence of $T_c$.

Phillips has given a qualitative argument that shows how the structural chemistry of oxygen vacancies could give a reduced isotope effect that is dependent on sample composition. Phillips assumes that superconductivity is due to the conventional electron-phonon mechanism, but that the number and positions of the oxygen vacancies adjust to maximize $T_c$ in the presence of parameter changes in quantities such as pressure or isotope species. It is possible that sample inhomogeneities are affecting the current paths in such a way as to cause the resistive measurements to sample different stoichiometries as the temperature is varied, thus producing the observed variation of isotope shift with temperature.

Finally, combined phonon-electronic excitation mechanisms have been proposed by Marzilio et al. and by Cohen et al. for the La$_{1.85}$Sr$_{0.15}$CuO$_4$ system. This seems to be one of the most promising approaches for explaining both high-$T_c$'s and the presence of small but finite isotope shifts.

In conclusion, we have shown the existence of an oxygen isotope effect in La$_{1.85}$Sr$_{0.15}$CuO$_4$ with a value $\Delta T_c = 0.140$. We note that this finding is in disagreement with a recent report of magnetically determined isotope shifts near the transition midpoint of La$_{1.85}$Sr$_{0.15}$CuO$_4$ corresponding to $\Delta T_c = 0.31$. Our observed shifts are smaller than expected from conventional BCS calculations for an isotropic medium. Whether the electron pairing is mediated by the conventional phonon mechanism with large anisotropy playing an important role, or whether a novel pairing mechanism is involved, remains to be seen.

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