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MAGNETIC AND RESISTIVE DETERMINATION OF THE OXYGEN ISOTOPE EFFECT IN $La_{1.85}Sr_{0.15}CuO_4$

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In polycrystalline samples of the superconducting oxide $La_{1.85}Sr_{0.15}CuO_4$, the substantial substitution of ^{18}O for ^{16}O causes a small downward shift in the superconducting transition temperature T_c. Although T_c(onset) measured resistively differs by as much as two Kelvin from that measured magnetically, the two measurement methods yield comparable T_c shifts upon isotope substitution. Samples with different superconducting phases (as evidenced by resistive fine structure in the transition region) show similar isotope shifts for different phases. We determine an overall oxygen isotope shift in $La_{1.85}Sr_{0.15}CuO_4$ corresponding to $\alpha = 0.140 \pm .008$, where $T_c \sim M^{-\alpha}$ and M is the oxygen mass.

INTRODUCTION

The microscopic mechanism responsible for electron pairing in the new classes of high-T_c superconducting oxides remains an unresolved and challenging question. One of the most direct tests for phonon-mediated pairing is the isotope effect, where $T_c \sim M^{-\alpha}$, with M the ionic mass. In the original BCS treatment of superconductivity[1] (one square well model), α is predicted to be 0.5. In a more general treatment[2] of α (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 ~2.2 in uranium[3].

Recently, isotope measurements were reported for the 90K superconductor $YBa_2Cu_3O_7$ and the 37K superconductor $La_{1.85}Sr_{0.15}CuO_4$. In the Y-based material, oxygen isotope substitution was originally found[4,5] to correspond approximately to $\alpha = 0.0 \pm .03$. Improvements in sample quality and refinement in experimental technique have reduced the error bars, and a small but finite shift has been established[6,7] at approximately $\alpha = 0.02 \pm .005$. 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^*.[4,7-9]

In the La-based material, one study[10] found for oxygen isotope substitution $\alpha = 0.16 \pm .02$ from magnetic susceptibility measurements, while another[11] found from combined resistivity and magnetic susceptibility measurements values of α ranging from 0.09 to 0.37. 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^*.[9,11] 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 $La_{1.85}Sr_{0.15}CuO_4$, using both magnetic susceptibility and resistivity measurements. With approximately 80% of the total oxygen content of the specimen replaced with ^{18}O, T_c is depressed by 0.4K as determined by magnetization studies. The corresponding value of α is $0.140 \pm .008$, 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 T_c determined by resistivity is on the order of 1 to 2 Kelvin higher than T_c determined by the onset of diamagnetism, isotope-induced shifts in T_c 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 T_c'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 III in table 1 of ref. 11.

EXPERIMENTS AND RESULTS

$La_{1.85}Sr_{0.15}CuO_4$ samples were prepared by mixing La_2O_3, $SrCO_3$ 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. All heat treatments for initial materials preparation were done in flowing oxygen-16. 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 $^{16}O_2$ and 92% enriched $^{18}O_2$, respectively. The sample placed in the ^{16}O environment formed the ^{16}O control sample, while the sample placed in the the ^{18}O 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, 1000°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 728 torr in the ^{16}O reservoir and 745 torr in the ^{18}O reservoir, with both pressures increasing by about 4 torr at the highest temperatures. Another set of samples ("E") was prepared with identical pressures in the two reservoirs (755 torr at 20°C, increasing to 760 torr at 1050°C), with a heat cycle of 1050°C for 32 hours, 900°C for 3 hours, 760°C for 1 hour, and 540°C for 2 hours followed by an oven cool. Although the ^{16}O and ^{18}O "arms" of the gas exchange system were constructed to be as symmetrical as possible, a check was performed to eliminate exchange asymmetries as a source of error. Isotopic exchanges were performed using identical experimental conditions to those stated above, except that the gas reservior originally containing ^{18}O was filled with ^{16}O, and vice versa. The properties of the samples were found to depend only on the oxygen isotope type.

Changes in sample weights indicated ^{18}O enrichments of 81% in sample "C" and 71% in sample "E". A more accurate determination of isotopic composition was performed using Laser-assisted Ion Mass Analysis (LIMA). In this technique, a small portion of the sample is ablated and ionized by a 4eV laser pulse. This energy exceeds all binding energies in $La_{1.85}Sr_{0.15}CuO_4$. 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 ^{18}O enrichment of 75%±2% in sample "C" and 78%±3% in sample "E". The two inequivalent O sites in $La_{1.85}Sr_{0.15}CuO_4$ each contain 50% of the total oxygen, so these measurements demonstrate that both sites are accessible to oxygen isotope diffusion. Values of α were calculated from the relation $T_c \sim M^{-\alpha}$ by assuming an average oxygen atomic mass M determined by the LIMA measurements.

The diamagnetic transitions were measured with a SHE model VTS-805 SQUID magnetometer by observing the Meissner flux expulsion. Below 50 K, the temperature of the magnetometer sample chamber was stable and accurate to within .010 K. A field of 33 Oe was used for samples "C" and "D", and a field of 23 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 T_c'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 T_c is equal to 0.41±.02 K and does not vary with temperature for at least 6K below the superconducting onset, giving α=0.140±0.009. For samples "E", in figure 2, the shift is again constant in temperature with a value 0.40±.03 K, giving α=0.139±.016. The average value of α is 0.140±0.008 for the combined susceptibility measurements. The error limits were estimated from the uncertainties in ΔT_c and in isotopic enrichments.

Meissner effect susceptibility measurements are in general a good probe of the bulk

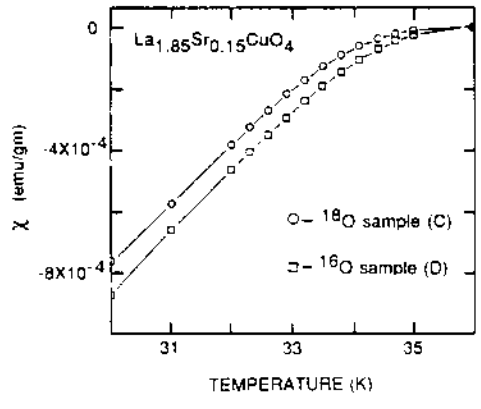

Figure 1. Magnetic susceptibility vs. temperature for $La_{1.85}Sr_{0.15}CuO_4$ samples "C" and "D".

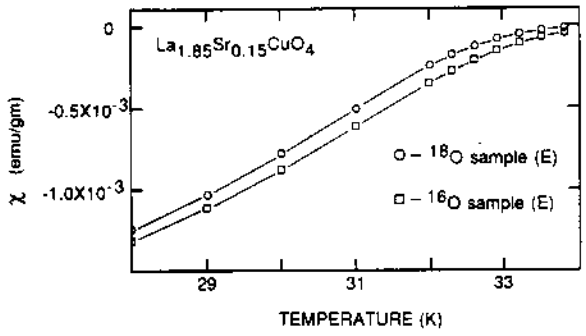

Figure 2. Magnetic susceptibility vs. temperature for $La_{1.85}Sr_{0.15}CuO_4$ samples "E".

superconducting properties of a sample. dc 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 superconducting oxides the general feature that the onset of superconductivity measured resistively is one or two degrees K higher than the onset of diamagnetism measured by flux expulsion. This sugests that percolative superonductivity 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 resistivity 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 (α=0.09) in the onset

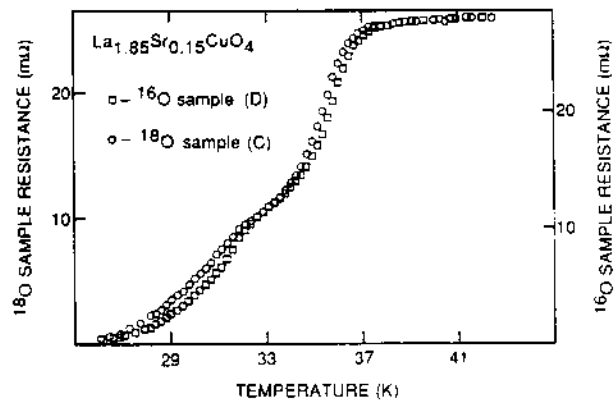

Figure 3. Resistance vs. temperature for $La_{1.85}Sr_{0.15}CuO_4$ samples "C" and "D".

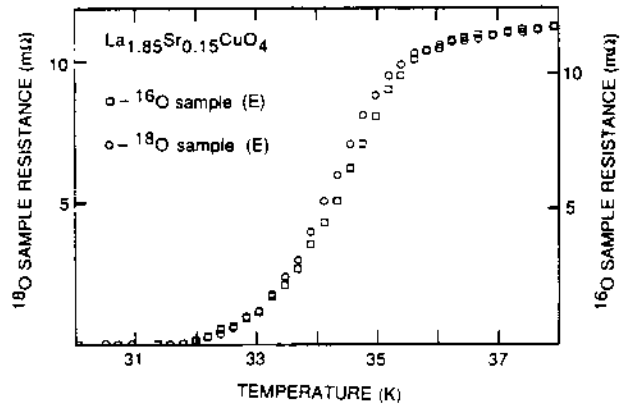

Figure 4. Resistance vs. temperature for $La_{1.85}Sr_{0.15}CuO_4$ samples "E".

region near 37 K, but the shift decreases to zero at 33 K and then increases again to near 0.78 (α=0.29) in the resistive tail at around 29 K. Samples "E" in figure 4 show a shift of about 0.2 K (α=.06) in the onset region near 35 K, with the shift decreasing to zero in the tail region near 33 K. The "bump" structure in fig. 3 is particularly interesting since it suggests two distinct phases in the C/D samples (this additional structure can be generated or removed at will depending on annealing schedule). It is apparent that both phases (those above and below 33K) show oxygen isotope shifts in the same direction and of comparable magnitude; we do not attach much importance to the fact that the shift appears somewhat larger in the lower temperature phase, since data in the tail region is subject to the greatest uncertainty.

DISCUSSION

Our magnetic susceptibility and resistivity measurements clearly identify an oxygen isotope shift in the superconducting transition region of $La_{1.85}Sr_{0.15}CuO_4$. The observed shift in the susceptibility does not vary across the transition and is essentially the same for both sets of samples. We identify the value α=0.140±0.008 from these measurements. Resistance measurements indicate a greater variablility in shifts across the resistive transition region with comparable but generally slightly smaller values of α. This is expected from percolative superconductivity near the resistive onset temperature region above the bulk superonducting transition temperature.

Barbee and Cohen[9,11] have attempted to account for measured isotope shifts and transition temperatures in $La_{1.85}Sr_{0.15}CuO_4$ within the simple two-square-well model, but find unphysical values for λ and μ^*. Calculations using the Eliashberg equations and realistic phonon spectra derived from neutron and Raman scattering show that an oxygen isotope shift of α=0.14 with a T_c of 37K can be accounted for within conventional BCS theory by using values of the coulomb interaction μ^*=0.28 and the electron-phonon interaction λ=3. This value of λ is however significantly larger than λ calculated by Weber[12] or that determined directly from resistivity measurements[13].

Batlogg et al.[10] have extended the work of Weber[12] in $La_{1.85}Sr_{0.15}CuO_4$ to show that for a T_c of 36 K due to an electron-phonon interaction, the α values should be 0.03 for the out-of-plane O site and 0.275 for the in-plane site, resulting in a net α of 0.305 for oxygen. They suggested that the discrepancy between the theoretical and experimental values of a 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 Bok[14] have considered this model and showed that variations in the Debye frequency caused by isotope substitutions should affect the transition temperature:

$$\frac{\delta T_c}{T_c} = \frac{1}{3}\frac{\delta \omega_D}{\omega_D}$$

in agreement with the Raman measurements[10] of oxygen isotope substitutions in $La_{1.85}Sr_{0.15}CuO_4$. Mattis and Mattis[15] 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 gives an isotope shift in T_c. A recent study by Fisher et al.[16] 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 $La_{1.85}Sr_{0.15}CuO_4$ ($\partial T_c/\partial P \approx 0.4$ K/kbar[17]), this effect could give a large isotope shift. One would naively expect the lattice constant to decrease as ^{18}O is exchanged for ^{16}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[18] 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 Marsiglio et al.[19] and by Cohen et al.[20] 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 α=0.140±.008. We note that this finding is in disagreement with a recent report[21] of magnetically determined isotope shifts near the transition midpoint of $La_{1.85}Sr_{0.15}CuO_4$ corresponding to α=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 seem.

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