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Oxygen isotope effect on critical temperature and phonon modes in $YBa_2Cu_3O_7$

E. L. Benitez, J. J. Lin, and S. J. Poon
Department of Physics, University of Virginia, Charlottesville, Virginia 22901

W. E. Farneth, M. K. Crawford, and E. M. McCarron
Central Research and Development Department, E. I. duPont de Nemours and Company, Inc.,
Experimental Station, Wilmington, Delaware 19898

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The effect of oxygen isotope substitution on $YBa_2Cu_3O_7$ has been studied. Powder samples in which ~90% of the ^{16}O has been replaced by ^{18}O have been prepared by gas exchange and compared to ^{16}O-^{16}O exchanged samples. The phonon frequencies, measured by far-infrared spectroscopy, are reduced after ^{18}O exchange. Magnetic measurements of the superconducting transition temperature find a shift of 0.16 ± 0.06 K, corresponding to $\alpha = 0.017 \pm 0.006$ in the Bardeen-Cooper-Schrieffer relation $T_c \propto M^{-\alpha}$.

Since the discovery of superconductivity at high temperatures in $La_{1.85}Sr_{0.15}CuO_4$ (Ref. 1) and in $YBa_2Cu_3O_7$ (Ref. 2), the question of whether or not the electron pairing mechanism is phonon mediated has been debated. Bardeen-Cooper-Schrieffer (BCS) theory[3] based on a weak-coupling electron-phonon mechanism successfully explains superconductivity in conventional superconductors. If high-temperature superconductivity were to obey BCS predictions, one would expect to see a dependence of the critical temperature on the mass of the ions in the mediating phonon modes, expressed as $T_c \propto M^{-\alpha}$. For the La-Sr-Cu-O superconductors it has been proposed that the high-frequency modes dominated by the motion of oxygen ions may be the cause of high T_c (Ref. 4), suggesting the possibility of a substantial oxygen isotope shift. Applying a similar prediction to the Y-Ba-Cu-O superconductors would suggest a downward shift in T_c by as much as 5 K (corresponding to $\alpha = 0.5$, Ref. 5) if all of the ^{16}O were replaced by ^{18}O.

The first oxygen substitution experiments in $YBa_2Cu_3O_7$, performed by Bourne *et al.*[6] and Batlogg *et al.*[7] found that the change in the superconducting onset temperature, ΔT_c, was within the range ± 0.3 and ± 0.2 K, respectively, much smaller than predicted. Leary *et al.*[8] later reported ΔT_c was 0.3–0.5 K, while Morris *et al.*[9] found $\Delta T_c = 0.18 \pm 0.04$ K. Recently, Ott *et al.*[10] prepared isotopically enriched $YBa_2Cu_3O_7$ samples using enriched nitric acid instead of gas exchange, and reported a depression in T_c of 33 K for ^{18}O enriched samples; this effect may be the result of factors other than the mass of the oxygen ion.

Since transition temperature and width are highly dependent on sample synthesis conditions, high sample quality and consistency is imperative for these measurements. The powder samples used in our experiments were prepared from BaO_2, Y_2O_3, and CuO as follows. Well-ground mixtures were heated in air to 850 °C for 3 h, after which the temperature was raised to 950 °C in flowing oxygen for 12 h. These samples were furnace cooled and reground, then fired a second time at 950 °C in flowing oxygen for 12 h. The furnace was cooled to 350 °C and held at that temperature in flowing oxygen for 48 h. The resulting single-phase powders were carefully stored and transported over drying agents. These methods avoid complications that have been reported with the use of carbonate and nitrate salts.

Paired ^{18}O and ^{16}O samples from the batch of powder underwent oxygen exchange and annealing side by side in identical reaction vessels. In a typical exchange procedure, approximately 250 mg of powder was heated to 700 °C in vacuum ($<10^{-3}$ Torr) and held under those conditions for 30 min. 96% $^{18}O_2$ was then admitted at a pressure of approximately 500 Torr. The progress of the exchange reaction was monitored by removing aliquots from the vapor above the pellet and analyzing the $^{18}O/^{16}O$ ratio by mass spectroscopy. This ratio changed rapidly over the first few minutes, but reached a constant value after 30 min. Neither continued heating at 700 °C nor increasing the temperature to 800 °C led to any further change in this ratio. The value of the limiting $^{18}O/^{16}O$ ratio was very close to the expected value for an equilibrium mixture of all of the $^{18}O_2$ initially in the gas phase and all the $^{16}O_2$ initially in the solid. To achieve ^{18}O enrichments in excess of 90%, the exchange procedure was repeated three times. ^{16}O samples were prepared simultaneously but with ^{16}O added as the gas-phase reactant.

Following the third exchange, some sample pairs were slowly cooled in their equilibrated exchange atmospheres and annealed for up to 80 h at 350 °C. Other pairs were cooled at rates up to 200 °C/h, without any annealing.

The extent of oxygen exchange was measured in three ways. First, the $^{18}O/^{16}O$ ratio in the vapor above the sample at the end of exchange was measured by mass spectroscopy. Second, the sample weight change due to isotope exchange was determined. Third, following all magnetic and far-infrared measurements, the samples were reduced in vacuum from $YBa_2Cu_3O_7$ to $YBa_2Cu_3O_6$ and the $^{18}O/^{16}O$ ratio of the evolving oxygen was determined by mass spectroscopy. In a typical case, sample *D* in Table I, final exchange gas enrichment was 93%. The ^{18}O sample showed a mass increase of 1.92%, and the ^{16}O sample showed a mass decrease of 0.17%. If the mass increase is

TABLE I. Summary of ^{18}O isotope enrichment and its effect on transition temperature in samples studied.

Sample	Actual ΔT_c (K)	Percentage enriched	α
C	0.20 ± 0.03	94	0.020 ± 0.003
D	0.16 ± 0.02	91	0.016 ± 0.002
E	0.18 ± 0.04	89	0.019 ± 0.004
F	0.13 ± 0.03	92	0.013 ± 0.003
G	0.14 ± 0.05	86	0.015 ± 0.005

assumed to be entirely due to the substitution of ^{18}O for ^{16}O, and all of the oxygen sites have been exchanged, this corresponds to an enrichment of 91%. The measured distribution in the oxygen evolved from the sample during reduction in vacuum was 90% at $YBa_2Cu_3O_7$, and 88% at $YBa_2Cu_3O_{6.5}$.

It has been suggested that in previous work neither the extent of exchange nor the homogeneity of the exchange have been adequately documented.[11] The large mass changes that we have observed can only be explained by exchange on all sites. Furthermore, it seems clear that under these conditions of temperature and pressure, all of the oxygen in the system rapidly reaches equilibrium.

Following magnetic measurements, the samples were pelletized, but not sintered. Far-infrared (FIR) spectroscopy was performed on the samples. The FIR data indicate that all oxygen sites were ^{18}O exchanged, including the O(1) site which has been speculated to be difficult to exchange[11] (Fig. 1). The phonon at 570 cm^{-1} has been attributed to these oxygen ions, while the modes at 276 and 312 cm^{-1} originate in the Cu-O planes. The 194-cm^{-1} mode is largely a Y vibration, and the 155-cm^{-1} mode is a vibration which involves the Cu-O chains.[12] Thus, all four oxygen sites are probed by FIR, and all show substantial shifts. The absolute frequency shift for each mode depends on the amplitude of the oxygen vibration in that mode and may therefore vary from the 6% shift expected for a pure oxygen vibration.

Based on the measurement of the extent of gas exchange and on the results of FIR spectroscopy, we conclude that the samples were homogeneously exchanged to about 90% enrichment on all sample sites.

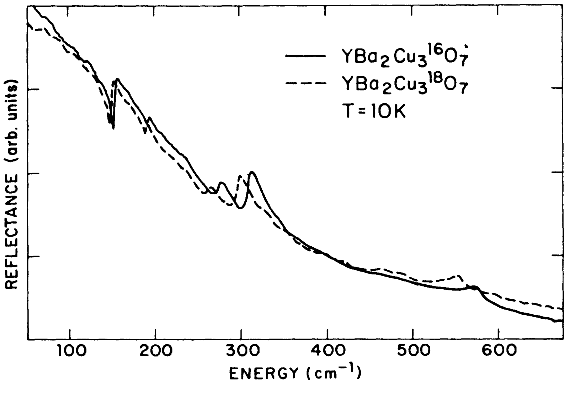

FIG. 1. Far-infrared reflectance vs energy at 10 K for the ^{16}O and ^{18}O portions of sample *D*.

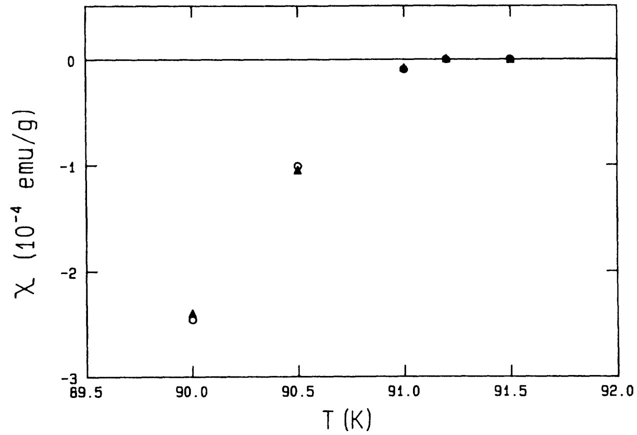

FIG. 2. Magnetic susceptibility of $YBa_2Cu_3O_7$ vs temperature near T_c for the ^{16}O portion of sample *C*, run 1 (filled triangles) and run 2 (open circles).

In order to accurately determine the critical temperature of the samples, Meissner measurement was performed in a SHE 905 superconducting quantum interference device (SQUID) magnetometer. The samples were in the form of a cylinder of powder, 2 mm in diameter and approximately 9 mm in height. The estimated demagnetization factor was 7 ± 1%; our data as shown have not been corrected for demagnetization since the factor is uniform and therefore does not affect our results. Measurements of samples repeated several days apart showed no significant variation in the superconducting transition temperature (Fig. 2).

A typical example of the Meissner effect measured for a pair of samples from 100 down to 7 K is shown in Fig. 3. The Meissner fraction at low temperature is approximately 53% for ^{18}O and 55% for ^{16}O. The gram susceptibility of the two samples differs by about 6%. 2% of the variation is the result of the difference in the densities of the samples due to the replacement in one sample of ^{16}O with heavier ^{18}O. The remaining 4% difference is apparently due to slight variations in sample placement in the

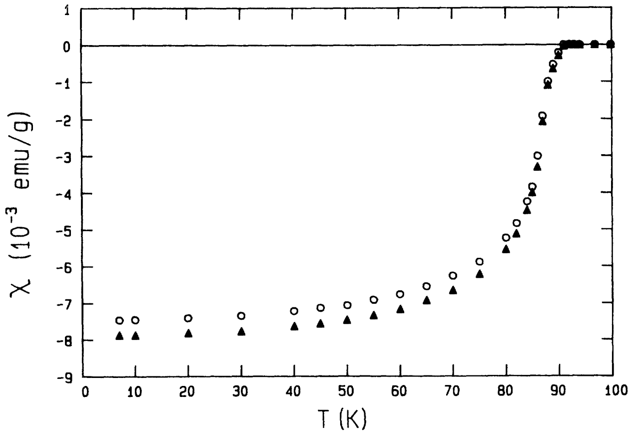

FIG. 3. Magnetic susceptibility of $YBa_2Cu_3O_7$ vs temperature for the ^{16}O (▲) and ^{18}O (○) portions of sample *D*.

SQUID, as it has also been found to occur when the same sample is measured twice. The effect a few percent correction in gram susceptibility could have on the superconducting transition is negligible.

The samples were measured in a field of 20 G. Since the low H_{c1} (Ref. 13) of $YBa_2Cu_3O_7$ affects Meissner measurement even in a small field, Meissner measurement at 5 and 20 G was compared. As can be seen in Fig. 4, the superconducting transitions are slightly sharper for Meissner measurements at 5 G than at 20 G. However, the difference in the transition temperatures between the two samples is not affected by the change in field.

We have determined the change in critical temperature due to isotopic substitution by careful measurement of the Meissner effect is the first degree below T_c. A typical example of this region is the 20-G data shown in Fig. 4(a). In all of our samples, the paired Meissner curves are observed to be parallel in the portion considered, although at larger χ some nonparallel regions were observed.

The results for five pairs are shown in Table I. No significant difference is observed between samples annealed at 350 °C (C,D) and those which were not annealed but rather cooled at 100 °C per hour back to room temperature (E,F,G). Based on these results, we find the overall decrease in transition temperature, for approximately 90% ^{18}O isotope substitution, to be $\Delta T_c = 0.16 \pm 0.06$ K.

In conclusion, we have prepared paired $YBa_2Cu_3O_7$ samples containing ^{16}O and ^{18}O isotopes in carefully controlled conditions. Far-infrared spectroscopy demonstrates that all four oxygen sites contain ^{18}O after isotope exchange. Magnetization measurements show that for 90% ^{18}O isotope substitution, critical temperature decreases by $\Delta T_c = 0.16 \pm 0.06$ K. This corresponds to $\alpha = 0.017 \pm 0.006$. This small isotope shift suggests a nonconventional electron pairing mechanism for $YBa_2Cu_3O_7$.

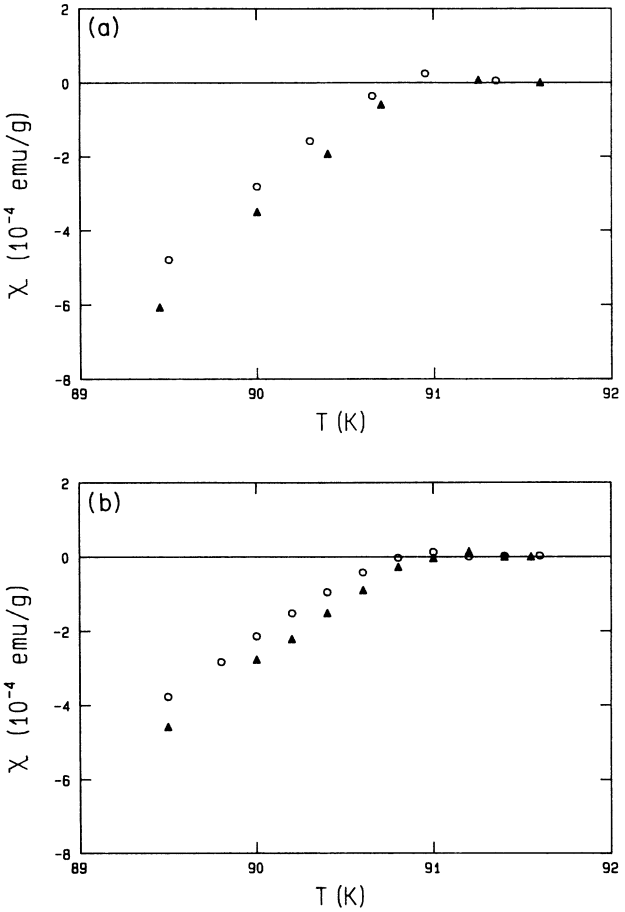

FIG. 4. Magnetic susceptibility of $YBa_2Cu_3O_7$ vs temperature near T_c for the ^{16}O (filled triangles) and ^{18}O (open circles) portions of sample E. (a) shows data taken in a field of 20 G, (b) data from the same sample measured at 5 G.

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