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Small oxygen isotope shift in $YBa_2Cu_3O_7$

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We find the oxygen isotope shift in $YBa_2Cu_3O_7$ is 0.18 ± 0.04 K with ~85% ^{18}O substitution, in disagreement with a recent published result. The methods used to measure a small shift in T_c of a ceramic oxide superconductor are discussed: sample preparation, reversible isotope substitution, measurement at low field, and control of temperature drift. We find $\alpha = 0.019 \pm 0.005$ in the relation $T_c \propto M^{-\alpha}$.

The discovery of superconductivity in $La_{1.85}Sr_{0.15}CuO_4$ at temperatures above 30 K by Bednorz and Müller,[1] and in $YBa_2Cu_3O_7$ at temperatures above 90 K by Wu *et al.*,[2] and the hope that this may lead to materials with still higher transition temperatures, has triggered a flood of theoretical and experimental research. Several suggestions have been made to explain the underlying electron-electron interaction which is responsible for the extraordinarily high critical temperatures of these compounds. In the earlier known elemental superconductors, the importance of phonon-mediated[3] electron pairing was established by the isotope shift,[4] the change in critical temperature with ionic mass. In the original BCS theory[5] $T_c \propto M^{-\alpha}$ with $\alpha = \frac{1}{2}$. In the high-temperature oxide superconductors, motion of the oxygen ions is dominant in the high-frequency phonon modes which have been suggested[6] as the cause of the high T_c. A nonzero value of α could indicate a significant role for phonon-mediated coupling in this material.

We have undertaken a careful measurement of the oxygen isotope shift in $YBa_2Cu_3O_7$, and find $\alpha = 0.019 \pm 0.005$. This is in conflict with the claim by Leary *et al.*[7] of a shift of 0.3–0.5 K (with 75–90% ^{18}O substitution), which implies $0.037 \leq \alpha \leq 0.051$. Our result is consistent with upper limits reported earlier by Bourne *et al.*[8] and by Batlogg *et al.*[9] (see Fig. 1). Our value supports the conclusion of Ref. 10 regarding the inapplicability of isotropic three-dimensional phonon-mediated electron pairing for $YBa_2Cu_3O_7$.

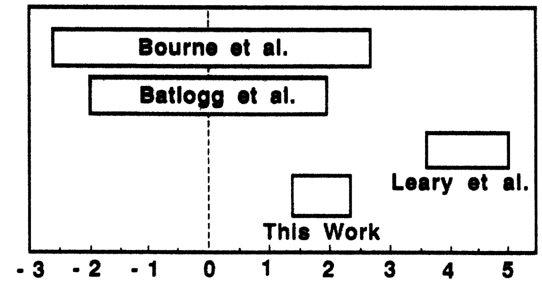

FIG. 1. Reported values of α in the expression $T_c \propto M^{-\alpha}$. Our result: $\alpha = 0.019 \pm 0.005$ is consistent with the limits placed by Bourne *et al.* (Ref. 8) and by Batlogg *et al.* (Ref. 9), but are in conflict with the results claimed by Leary *et al.* (Ref. 7).

Our method is similar to that described in Refs. 7, 8, and 11, but special precautions were taken to reliably measure the small isotope shift. Oxygen isotope substitution in $YBa_2Cu_3O_7$ was accomplished by gas-phase diffusion.[11] This permitted reversible substitution in the same sample, thus avoiding errors caused by sample-to-sample differences. Samples with sharp transitions were prepared, and measurements were made in a small field (3 Oe) to minimize broadening of the diamagnetic transition by flux penetration close to T_c. Temperature drift of sample versus thermometer in the SQUID susceptometer was minimized and corrections were made for the residual drift.

Sharp diamagnetic transitions were obtained in samples prepared by solid-state reaction, using the heat-treatment process described below. Stochiometric quantities of Y_2O_3, $BaCO_3$, and CuO powders (all Aesar 99.999% except $BaCO_3$ 99.99%) were mixed thoroughly and calcined in flowing oxygen (4 h at 850 °C, 12 h at 930 °C, cooled at 115 °C/h to 700 °C, held 1 h, cooled at 60 °C/h to 450 °C, and furnace cooled at 220 °C/h). The reacted mixture was finely ground in an agate morter and pestle, pressed into 6-mm-diameter tablets at 75 kg/mm^2, and sintered in flowing oxygen (15 h at 930 °C, cooled at 115 °C/h to 700 °C, held 1 h, cooled at 60 °C/h to 450 °C, and furnace cooled at 220 °C/h). Calcining and sintering was carried out in alumina boats, lined with gold foil to minimize contamination. No reaction with the gold was observed. X-ray powder diffractometry indicated that the material was single phase and that unreacted ingredients were absent. Our samples, which were porous to facilitate isotope exchange, had sintered density of 4.8 g/cm^3, ~75% of the ideal density calculated from the lattice parameters. The grain size was ~2 μm by scanning electron microscopy (SEM). Careful storage of the samples proved necessary to maintain sample quality. Preliminary experiments showed that our porous samples deteriorate if stored in a dessicator containing ambient air and silica gel; the transition broadened by a factor of 2 in a period of one week. We then adopted the practice of storing the samples under vacuum (~0.2 Torr), with P_2O_5 in the container; this proved effective in preserving sharp superconducting transitions.

For the isotope shift measurements, two pieces, called *A* and *B*, were broken off from the same pellet, and underwent identical simultaneous thermal treatment during the diffusion process, which was carried out in a tube furnace. *A* and *B* were weighed on a microbalance, wrapped loosely in gold foil, and placed in parallel 7-mm-i.d. quartz tubes connected to 1064 cm^3 reservoirs. *A* was heated in an $^{18}O_2$-enriched atmosphere (92% ^{18}O+8% ^{16}O), and *B* in $^{16}O_2$ (~99.6% ^{16}O+~0.2% ^{18}O).[12] The reservoirs were outgassed and evacuated to $< 10^{-2}$ Torr, then filled to 759 Torr with their respective oxygen isotopes. The pressures were identical within one Torr. At the diffusion temperature (930 °C), the pressures in both sample tubes were 767 Torr. Atmospheric pressure was also 767 Torr. *A* and *B* were within 1 cm of each other at the center of the furnace during the heat treatment, which followed the same thermal program described above for sintering. The weight change of *A* relative to *B* was +1.77%, corresponding to 88% ^{18}O content in *A*. (*A* gained 1.645%, while *B* lost 0.124% as a result of the annealing schedule.) After measuring the superconducting of *A* and *B* (see below), a small chip was broken off from each for further tests. Since the initial ^{18}O content of the gas was only 92%, we estimate that oxygen from the reservoir replaced ~96% of the oxygen originally present, indicating that oxygen in all sites was almost completely exchanged.

To separate the real isotope shift from any intrinsic difference in transition temperatures caused by sample nonuniformity, the remaining portions of *A* and *B* were again diffused, but with the opposite isotopes: *B* in an ^{18}O-rich atmosphere (~90% ^{18}O+10% ^{16}O), and *A* in the $^{16}O_2$ atmosphere. The procedure was the same as before, but the filling pressures were 753 ± 1 Torr, and increased to 762 Torr upon heating to 930 °C. The same thermal program for diffusion was repeated. Weight changes indicated that *B* was now ^{18}O enriched, while *A* was depleted as expected, with an 83% higher ^{18}O fraction in *B* than in *A*. Taking into account ~4% residual ^{18}O expected in *A*, the replacement of oxygen in the sample by oxygen in the gas was again ~96% complete. The particle size and microstructure was again examined by scanning electron microscopy and appeared unchanged.

To observe a sharp diamagnetic transition, the measurements must be made in a very small magnetic field. At temperatures just below T_c, the lower critical field $H_{c1} < H_m$ the measuring field, since $H_{c1} \propto [1-(T/T_c)^2]$, which goes to zero at T_c. Flux expulsion is incomplete and the transition is broadened. In Refs. 7 and 8, measurements were made at 12 Oe; in Ref. 9 the field was 21 Oe. In a 12 Oe field $H_m > H_{c1}$ within ~1.5 K of T_c since $H_{c1} \approx 120$ Oe at 76 K in $YBa_2Cu_3O_7$.[13] At $H_m = 3$ Oe the range is ~0.4 K. A sample was measured at two fields. At 10.3 Oe the transition width (to $\frac{1}{2}$ the low temperature value of χ) was 1.8 K; at 3 Oe the width was only 1 K. All measurements reported below were of Meissner diamagnetism cooling through T_c in a constant 2.7 or 3.0 Oe. The measurements were made on the same SHE Model VTS-805 SQUID magnetometer used in Refs. 7 and 8.

Temperature drift of sample versus thermometer must be minimized. (The thermometer of the SHE magnetometer is in the He gas stream, and not in thermal contact with the sample.) When the transition of a single sample was measured repeatedly, T_c appeared to vary up to 0.3 K over ~6 h when the liquid-helium (LHe) level was as low as 40%. This may be the source of the relatively large temperature differences between samples reported in Ref. 7 and interpreted as an isotope shift. Further experiments showed that thermometer versus sample temperature drift is minimized when the LHe level is high. Thereafter, the susceptometer was filled before starting, and the LHe level remained between 100% and 90% throughout the measurements. The He gas flow was maintained at 450 ± 25 cm^3/min during all measurements.

The small residual drift was measured by alternating samples *A* and *B* and measuring the transition repeatedly, eight times within 16 h. One run for each sample was made over a larger range to determine the shape of the curve down to low temperature. Figure 2(a) shows the results for several runs, selected for clarity. The transition temperature of sample *A* (^{18}O enriched) is clearly ~0.2 K lower than that of B (^{16}O). Table I gives the results for all eight runs. Measurements were made at intervals of ~0.2 K, about the same as the difference in T_c of the two samples. For this reason, the susceptibility of *B* was nearly the same as that of *A* at the next measuring temperature. The demagnetization curves were interpolated to

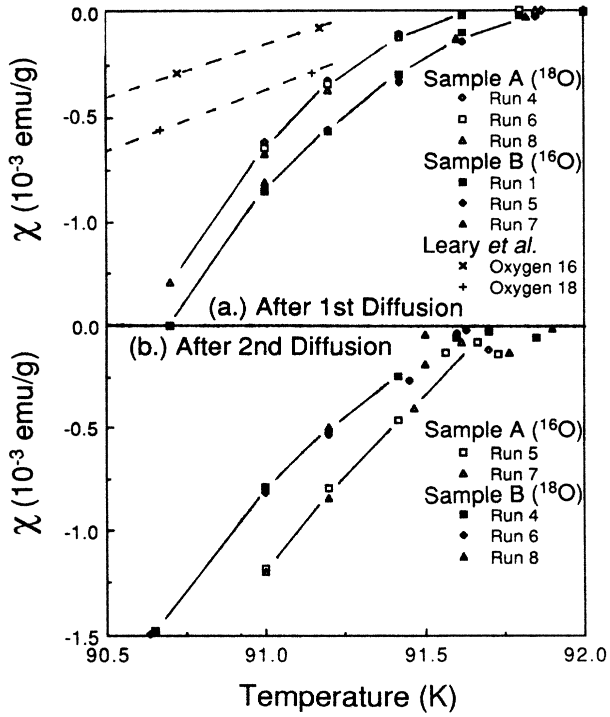

FIG. 2. (a) Transition temperatures of two samples *A* and *B* broken from the same pellet, after isotopic substitution by gas phase diffusion. *A* contains ~88% ^{18}O, while *B* has ~100% ^{16}O. Several runs are plotted. The transition temperature of *A* is clearly ~0.2 K lower than *B*. Data points from Fig. 1 of Leary *et al.* (Ref. 7) are included for comparison. (b) Transitions of the same samples, but following rediffusion with the opposite isotope (i.e., *B* in ^{18}O and *A* in ^{16}O). Now the ^{18}O fraction in *B* is ~83% greater than in *A*, and the transition temperature of *B* is lower, confirming that the difference is due to the isotope effect.

TABLE I. Superconducting transition temperature shift with oxygen isotope substitution. Samples B (^{16}O) and A (^{18}O) were measured alternately. Temperatures are given at which the Meissner diamagnetic susceptibility reached each of three values. The transition of A (^{18}O enriched) is at lower temperature than B (^{16}O).

Run	Sample	Time (h)	Temperature (K) at which the χ vs T curve crosses the indicated χ (emu/g)		
			$\chi = -1.2\times10^{-4}$	$\chi = -3.2\times10^{-4}$	$\chi = -6.0\times10^{-4}$
1	$B(^{16}\mathrm{O})$	1	91.60	91.40	91.17
2	$A(^{18}\mathrm{O})$	3	91.31	91.13	90.97
3	$B(^{16}\mathrm{O})$	5.5	91.59	91.40	91.12
4	$A(^{18}\mathrm{O})$	7.5	91.40	91.20	91.01
5	$B(^{16}\mathrm{O})$	10.75	91.61	91.43	91.16
6	$A(^{18}\mathrm{O})$	12	91.42	91.22	91.02
7	$B(^{16}\mathrm{O})$	14	91.66	91.42	91.16
8	$A(^{18}\mathrm{O})$	15	91.43	91.24	91.04
	Average of all runs				
	$\langle B(^{16}\mathrm{O})\rangle$	7.81	91.61	91.42	91.15
	$\langle A(^{18}\mathrm{O})\rangle$	9.37	91.39	91.20	91.01
	$[\langle B\rangle - \langle A\rangle]$	−1.56	0.23	0.22	0.14
Estimated drift rate (deg/h)[a]			0.006	0.005	0.003
Drift correction (deg)[b]			0.009	0.008	0.005
Corrected temperature difference (deg) $(\langle B\rangle - \langle A\rangle +$drift correction)			0.24	0.23	0.15
Corresponding value of α				0.023	0.015

[a] Slope from linear interpolation of runs 1–8 at one value of χ, after shifting sample A temperatures by $[\langle B\rangle - \langle A\rangle]$.

[b] Estimated drift rate × average time difference of 1.56 h.

give the temperature at each of three susceptibility values $\chi = -1.2\times10^{-4}$, -3.2×10^{-4}, and -6.0×10^{-4} emu/g, chosen because they lie near the measured data points. Since the curves of the two samples are not exactly parallel, the temperature shift between samples was determined separately for each column in Table I, by averaging the runs. The results are given in the row marked $[\langle B\rangle - \langle A\rangle]$. A small temperature drift is indicated by the monotonic change of temperature at the same χ for different runs of the same sample. Because measurements of A were made $\sim$1.56 h later than B, a drift correction was necessary. An estimated drift rate was computed separately for each χ by linear interpolation of the temperature of runs 1–8, after shifting the temperatures of sample A by $[\langle B\rangle - \langle A\rangle]$. The drift correction was <0.01 K. The values of corrected temperature differences between A and B are given in Table I, with the values for $\chi = -3.2\times10^{-4}$ and -6.0×10^{-4} emu/g underlined; the value for $\chi = -1.2\times10^{-4}$, though consistent, is considered less accurate because of low S/N at such a small χ.

After reverse diffusion of the samples, B is enriched in ^{18}O and A contains mainly ^{16}O. The transitions were again measured, with the same procedure and precautions. The results for several runs are shown in Fig. 2(b). The transition temperatures of the two samples are now reversed; T_c of sample B is now lower than A, confirming that the difference is due to the isotope effect. The results for all eight runs are given in Table II. The chosen values of χ lie near the measured data points, and are different from Table I. The temperature shift between samples was determined separately for each column in the table. The temperature drift is somewhat greater than during the previous measurements, especially during the first three runs. The corrected values of temperature difference between A and B are given in Table II, with the values for $\chi = -4.5\times10^{-4}$ and $\chi = -8.0\times10^{-4}$ emu/g underlined; the value for $\chi = -14\times10^{-4}$ emu/g is considered less reliable since the demagnetization curves are not parallel for large χ. An alternative analysis of the data in Table II was also made, excluding runs 1 and 2 because of the larger drift rate. This analysis gives smaller drift corrections of 0.004, 0.012, and 0.001 K, and slightly raises the values of the corrected temperature shift to 0.16, 0.19, and 0.23 K, but the increases are small compared to the scatter in the values given in Tables I and II.

The Meissner demagnetization curves of A and B are not parallel at large χ; the curve for A is steeper and reaches a limiting value of -38×10^{-4} emu/g at $\sim$85 K, while the limiting value for B is -34×10^{-4} emu/g, reached at $\sim$82 K. For these measurements, the two samples were sanded down to similar shapes, and orientation was kept constant in subsequent measurements. The screening-current susceptibility χ_{sc} was measured by increasing the field from 3 to 33 Oe while the sample was held at 25 K; A and B differed by only 4%, showing that the demagnetizing factors are similar. The Meissner diamagnetization at 25 K was 19.3% of χ_{sc} in A, while it was 17.9% in B. The difference in slope of A and B in Fig. 2(b) is unexplained. For determining the isotope shift the measured χ values were used without corrections.

An intrinsic difference in T_c between samples would result in a different temperature offset between samples after the second diffusion, compared to that observed after

TABLE II. Superconducting transition temperature shift after second diffusion (sample B in ^{18}O and sample A in ^{16}O). Temperatures for three values of χ are given. The transition of B is now at lower temperature than A, confirming that the shift is due to an isotope effect.

			Temperature (K) at which the χ vs T curve crosses the indicated χ (emu/g)		
Run	Sample	Time (h)	$\chi = -4.5\times10^{-4}$	$\chi = -8.0\times10^{-4}$	$\chi = -14\times10^{-4}$
1	$A(^{16}O)$	1	91.20	91.04	90.81
2	$B(^{18}O)$	3	91.20	90.95	90.65
3	$A(^{16}O)$	6	91.38	91.13	90.90
4	$B(^{16}O)$	7.5	91.25	90.99	90.68
5	$A(^{16}O)$	9.5	91.42	91.19	90.91
6	$B(^{18}O)$	11	91.28	91.01	90.67
7	$A(^{16}O)$	12.5	91.44	91.23	90.91
8	$B(^{18}O)$	15	91.23	91.00	90.68
	Average of all runs				
	$\langle A(^{16}O)\rangle$	7.25	91.36	91.15	90.88
	$\langle B(^{18}O)\rangle$	9.13	91.24	90.99	90.67
	$[\langle A\rangle - \langle B\rangle]$	−1.88	0.12	0.16	0.21
Estimated drift rate (deg/h)[a]			0.011	0.009	0.005
Drift correction (deg)[b]			0.021	0.017	0.009
Corrected temperature difference (deg) $(\langle A\rangle - \langle B\rangle + \text{drift correction})$			0.14	0.18	0.22
Corresponding value of α			0.016	0.020	

[a] Slope from linear interpolation of runs 1–8 at one value of χ, after shifting sample B temperatures by $[\langle A\rangle - \langle B\rangle]$.

[b] Estimated drift rate × average time difference of 1.88 h.

the first. By averaging the underlined values from each table, subtracting one average from the other, and dividing the difference by two, we estimate the difference in T_c of A and B is <0.02 K when they contain the same isotope (<0.01 K if runs 1 and 2 in Table II are deleted). The underlined values of corrected temperature difference were used to calculate values of α, which are given in the last line of each table.

Two possible causes of systematic error in this work have not been entirely excluded, although they are not expected to be significant. (1) A change in T_c might be caused by a difference in trace gas content of the ^{18}O and ^{16}O gases used for diffusion, and could mimic an isotope shift since it would be correlated with isotope. (2) Isotope diffusion was done at 930 °C, above the orthorhombic-tetragonal phase transition, but if any variation of T_c resulted it would be uncorrelated with isotope. In conclusion, a small oxygen isotope shift has been observed and measured in $YBa_2Cu_3O_7$. Considering the spread of measurements and possible systematic errors, we find $\alpha = 0.019 \pm 0.005$.

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