Observation of an Oxygen Isotope Effect in $YBa_2Cu_3O_7$

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A small decrease in T_c of 0.3 to 0.5 K is observed when as much as 90% of the ^{16}O in $YBa_2Cu_3O_7$ is substituted with ^{18}O. This result is consistent with our observation that there is an oxygen isotope effect in $La_{1.85}Sr_{0.15}CuO_4$, but in contrast with previous reports that there is no isotope effect for $YBa_2Cu_3O_7$. This new result suggests that phonons play an important role in the electron-pairing mechanism in $YBa_2Cu_3O_7$.

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Since the discovery of superconductivity above 90 K in $YBa_2Cu_3O_7$,[1,2] it has been debated whether the superconductivity in this material is phonon mediated as expected from conventional BCS theory,[3] or whether a different mechanism is involved. Support for a nonphonon mechanism was provided when our group,[4] Batlogg et al.,[5] reported that the superconducting transition temperature, T_c, does not change significantly when ^{16}O is replaced with ^{18}O in $YBa_2Cu_3O_7$. However, more recently we have observed an oxygen isotope effect in samples of $La_{1.85}Sr_{0.15}CuO_4$,[6] $La_{1.85}Ca_{0.15}CuO_4$,[7] and $BaPb_{0.75}Bi_{0.25}O_3$.[7] The shift in T_c to lower temperatures observed for $La_{1.85}Sr_{0.15}CuO_4$ when 75% of the ^{16}O was replaced with ^{18}O varied between 0.3 and 1.0 K depending on the sample. This shift is smaller than what is predicted by conventional BCS theory. The small decrease in T_c for $La_{1.85}Sr_{0.15}CuO_4$ prompted us to reexamine the effect of ^{18}O substitution on the transition temperature of $YBa_2Cu_3O_7$. In this paper, we report the observation of a drop in T_c to lower temperatures by 0.3 to 0.5 K in three different samples of $YBa_2Cu_3O_7$ when as much as 90% of the ^{16}O is replaced by ^{18}O. This shift in the onset of the diamagnetic transition due to ^{18}O substitution was reversible by resubstitution of ^{16}O for ^{18}O.

According to the conventional BCS treatment,[3] T_c should vary as $M^{-\alpha}$, where M is the oxygen mass. This assumes that the frequency of the important phonon mode depends only on the mass of oxygen. For a value of $\alpha = 0.5$, a shift in T_c to lower temperatures by approximately 5 K is predicted for a 90-K superconductor (on the assumption of complete substitution of ^{18}O for ^{16}O). We note that this is the maximum shift expected and that because of the complexity of the structure, i.e., both chains and layers of Cu-O, this prediction is at best tenuous. Although the 0.3- to 0.5-K shift in T_c for $YBa_2Cu_3O_7$ is smaller than the predicted shift, the presence of an oxygen isotope effect demonstrates that phonons play an important role in the electron-pairing mechanism in this material.

Three samples of $YBa_2Cu_3O_7$, referred to below as samples I, II, and III, were synthesized via a nitrate route which has been described previously.[8] This route involved our dissolving stoichiometric ratios of Y_2O_3, $BaCO_3$, and CuO in nitric acid and evaporating the solution to dryness. The resulting powders were decomposed near 800°C in Al_2O_3 crucibles. To ensure homogeneous products, these powders were then ground and fired in air for 48 h at temperatures ranging from 750 to 950°C,

TABLE I. Conditions for isotopic exchange.

Sample	Isotope	Oxygen pressure (Torr)	T_1 (°C)	Time at T_1 (h)	Cooling rate to T_2 (°C/h)	T_2 (°C)	at T_2 (h)	Cooling rate to 25°C (°C/h)
I	^{18}O	650	950	12	...	...	...	155
	^{16}O	650	950	12	...	...	...	155
II	^{18}O	530	900	12	100	500	4	238
	^{16}O	530	900	12	100	500	4	238
II-18[a]	^{16}O	530	900	12	100	500	4	238
III	^{18}O	530	900	12	100	500	4	238
	^{16}O	530	900	12	100	500	4	238
III-18[a]	^{16}O	530	900	12	100	500	4	238

[a]Portion of sample exchanged with ^{18}O was subsequently treated in $^{16}O_2$ to reexchange ^{16}O for ^{18}O.

with four intermediate grindings. The final anneal was in O_2 at 950 °C for 1 h, followed by cooling to 25 °C at 155 °C/h. No impurity phases were detected by powder x-ray diffraction and the samples were all in the orthorhombic phase. The samples were ground and pressed into $\frac{1}{4}$ -in. pellets at 8000 psi for isotopic exchange.

To exchange ^{18}O for ^{16}O, a pellet of the superconductor was wrapped loosely in platinum foil and placed in a degassed quartz tube attached to a glass manifold. The tube and manifold were evacuated to less than 10^{-4} Torr before the introduction of $^{18}O_2$. The volume of the system was sufficient to contain at least 50 times the $^{18}O_2$ needed to exchange all the ^{16}O in the sample. A second portion of each sample was annealed in $^{16}O_2$ under identical conditions. The oxygen pressures and annealing temperatures for the three samples are listed in Table I.

Isotope substitution in these samples was verified by temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR) as described elsewhere.[9] The quantities of $^{18}O_2$, $^{18}O^{16}O$, and $^{16}O_2$ which desorbed from each sample during heating in helium (TPD) and of $H_2{}^{18}O$ and $H_2{}^{16}O$ which desorbed during heating in hydrogen (TPR) were determined to within 3% accuracy by means of a quadrupole mass spectrometer. Since the $YBa_2Cu_3O_7$ was reduced to Y_2O_3, BaO, and Cu metal, only 50% of the oxygen could be analyzed. The fraction of ^{18}O in the samples reported in Table II was calculated on the assumption that the fraction of ^{18}O in the reduction products was the same as the fraction measured in the gases evolved during TPD and TPR.

Meissner-effect measurements on the ^{18}O and ^{16}O portions of the three samples are shown in Figs. 1–4. These measurements were performed on a SHE SQUID magnetometer by cooling of the sample from 100 K in a field of 12 G; the field was calibrated by measurement of the diamagnetism of a superconducting tin sphere. As shown in Figs. 1 and 2, the onset of diamagnetism, T_c(onset), for the ^{16}O portion of sample I occurs at 92.1 K, and the gram susceptibility at 5 K is -5.0×10^{-3} emu/g. The width of the transition for sample I is approximately 14 K, measured from 10% to 90% of the full transition. The diamagnetic onset and the gram susceptibility at 5 K for samples II and III are similar to those
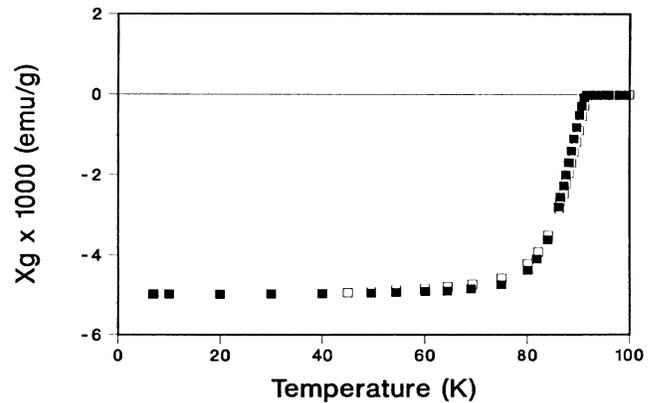

FIG. 1. Magnetic susceptibility of $YBa_2Cu_3O_7$ vs temperature for the ^{16}O (open squares) and ^{18}O (filled squares) portions of sample I.

of sample I, as summarized in Table II. However, the transitions for samples II and III are broader, the susceptibility not becoming constant until below ≈60 K.

Despite the differences between the three samples, Figs. 2–4 clearly show that in each case substitution of ^{18}O for ^{16}O shifts T_c(onset) to lower temperature. As shown in Table II, the magnitude of the shift is sample dependent and varies from 0.3 to 0.5 K. Moreover, the shift in T_c(onset) is reversed by resubstitution of ^{16}O for ^{18}O, as shown in Figs. 3 and 4. The magnetic data near T_c(onset) of samples which were exchanged with ^{18}O and then reexchanged with ^{16}O (filled circles) are nearly identical to the data for the samples which were never exchanged (open squares). The residual ^{18}O after reexchange was 2.0% and 3.3% for samples II and III, respectively.

Although sample inhomogeneities may produce an artificially small shift near the diamagnetic onset, we suggest that this is the best place to measure the shift be-

TABLE II. Summary of oxygen-isotope-shift data for $YBa_2Cu_3O_7$.

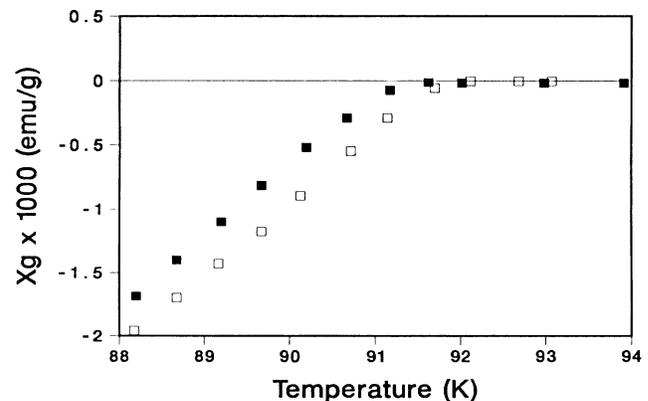| Sample	T_c(onset) ^{16}O (K)	T_c(onset) ^{18}O (K)	T_c(onset) reexchange ^{16}O for ^{18}O (K)	Shift in T_c(onset) (K)	^{18}O (%)
I	92.1	91.6	⋯	0.5	90
II	91.4	91.1	91.4	0.3	75
III	91.5	91.1	91.5	0.4	73

FIG. 2. Magnetic susceptibility of $YBa_2Cu_3O_7$ vs temperature for the ^{16}O (open squares) and ^{18}O (filled squares) portions of sample I near T_c(onset).
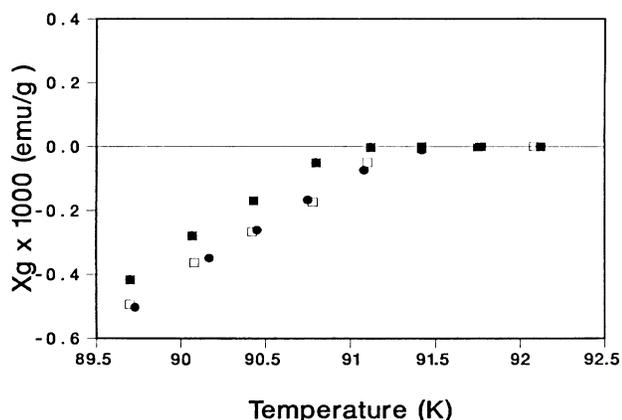
FIG. 3. Magnetic susceptibility of $YBa_2Cu_3O_7$ vs temperature for three portions of sample II: ^{16}O (open squares), ^{18}O (filled squares), and reexchange of ^{16}O for ^{18}O (filled circles).

FIG. 4. Magnetic susceptibility of $YBa_2Cu_3O_7$ vs temperature for three portions of sample III: ^{16}O (open squares), ^{18}O (filled squares), and reexchange of ^{16}O for ^{18}O (filled circles).

cause T_c(onset) is not affected by additional processing, whereas the sharpness of the transition does change with additional processing. Near the midpoint of the transition, the data for the portion of sample III which was resubstituted with ^{16}O starts to deviate from the data for the portion which was never exchanged. Also, just below the midpoint of the transition, the curves for the ^{18}O and ^{16}O portions of samples I and II cross. In contrast, the two curves for sample III never cross. Therefore, while T_c(onset) is reproducible for various samples of $YBa_2Cu_3O_7$ (see Table II), the transition width is sample dependent.

It is important to emphasize that in order to obtain an accurate value for the isotope shift, it is necessary to prepare samples which have very sharp transitions, and which are isotopically pure and homogeneous. If the samples are inhomogeneous and contain regions rich in ^{16}O, then the ^{16}O regions will expel flux at higher temperature than the ^{18}O regions. This would cause the measured shift in T_c(onset) to be artificially small. For the samples investigated here, even though the substitution was at most 90% as measured by TPD and TPR, the relative rates at which ^{16}O and ^{18}O desorbed from the samples as a function of temperature remained constant. This suggests that on a macroscopic scale the ^{18}O was uniformly distributed throughout the sample.

Because the effects of processing conditions on the properties of $YBa_2Cu_3O_7$ are not well understood, it is important that the ^{16}O and ^{18}O samples be processed under identical conditions. This is shown clearly in Tables I and II, where because of different processing conditions, T_c(onset) for the ^{18}O portion of sample I was 0.1 K higher than T_c(onset) for the ^{16}O portion of sample III. In our previous study,[4] we were expecting an isotope shift on the order of several degrees Kelvin. Since such a large shift would be insensitive to slight differences in sample treatments, we simply compared an ^{18}O sample
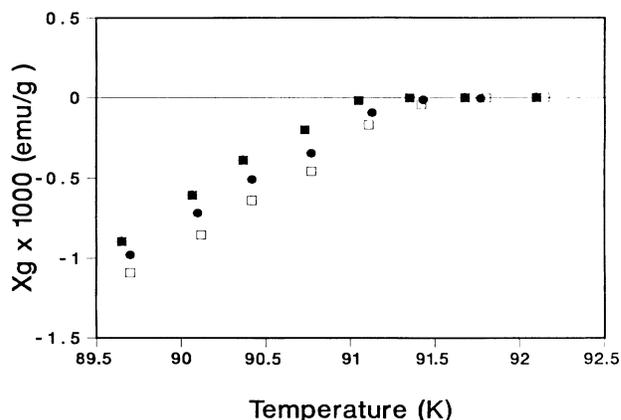
with its parent ^{16}O compound. However, to observe a shift on the order of tenths of a degree Kelvin, the ^{18}O and ^{16}O samples which are being compared must be treated under identical conditions. This would explain why no isotope effect was observed. Also, we note that Batlogg et al.[5] reported 75% substitution at an annealing temperature of only 500 °C. In contrast, we performed the isotope-exchange experiments at 900 to 950 °C.

From the results presented above, we conclude that when as much as 90% of the ^{16}O is replaced by ^{18}O in $YBa_2Cu_3O_7$, T_c is lowered by up to 0.5 K. Thus, phonons play an important role in the electron-pairing mechanism in $YBa_2Cu_3O_7$. This is consistent with our findings for the other high-T_c oxides.[6,7]

[1] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[2] P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassilious, and C. W. Chu, Phys. Rev. Lett. **58**, 911 (1987).

[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957).

[4] L. C. Bourne, M. F. Crommie, A. Zettl, H.-C. zur Loye, S. W. Keller, K. J. Leary, A. M. Stacy, K. J. Chang, M. L. Cohen, and D. E. Morris, Phys. Rev. Lett. **58**, 2337 (1987).

[5] B. Batlogg, R. J. Cava, A. Jayaraman, R. B. van Dover, G. A. Kourouklis, S. Sunshine, D. W. Murphy, L. W. Rupp, H. S. Chen, A. White, K. T. Short, A. M. Mujsce, and E. A.

Rietman, Phys. Rev. Lett. **58**, 2333 (1987).

[6]T. A. Faltens, W. K. Ham, S. W. Keller, K. J. Leary, J. N. Michaels, A. M. Stacy, H.-C. zur Loye, D. E. Morris, T. W. Barbee, III, L. C. Bourne, M. L. Cohen, S. Hoen, and A. Zettl, Phys. Rev. Lett. **59**, 915 (1987).

[7]H.-C. zur Loye, T. A. Faltens, W. K. Ham, S. W. Keller, K. J. Leary, J. N. Michaels, and A. M. Stacy, to be published.

[8]G. F. Holland, R. L. Hoskins, M. A. Dixon, P. D. VerNooy, H.-C. zur Loye, G. Brimhall, D. Sullivan, R. Cormia, H. W. Zandbergen, R. Gronsky, and A. M. Stacy, in *Chemistry of High Temperature Superconductors,* edited by D. L. Nelson, T. F. George, and M. S. Whittingham, American Chemical Society Symposium Series, Vol. 351 (American Chemical Society, Washington, DC, 1987), Chap. 11

[9]S. W. Keller, K. J. Leary, T. A. Faltens, J. N. Michaels, and A. M. Stacy, in Ref. 8, Chap. 12.