Oxygen Isotope Effect in High-Temperature Oxide Superconductors

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The effect of oxygen isotope substitution on the superconducting transition temperature, T_c, has been measured for $BaBi_{0.25}Pb_{0.75}O_3$ ($T_c \approx 11$ K) and $La_{1.85}Ca_{0.15}CuO_4$ ($T_c \approx 20$ K), and is compared to the shifts observed for $La_{1.85}Sr_{0.15}CuO_4$ ($T_c \approx 37$ K) and $YBa_2Cu_3O_7$ ($T_c \approx 92$ K). For all four materials, the transition temperature is shifted to lower temperature upon substitution of oxygen-18 for oxygen-16. The observed shifts demonstrate that phonons are involved in the electron-pairing mechanism in these oxide superconductors.

THE BEHAVIOR OF MOST KNOWN superconductors is best described by the phonon-mediated Bardeen-Cooper-Schrieffer (BCS) theory (*1*). According to this theory, electron-phonon interactions couple electrons in pairs, and this coupling leads to the superconducting ground state. However, there has been much debate as to whether the electron-pairing mechanism in oxide superconductors (*2–5*) is phonon-mediated. An important test of whether phonons are involved is the measurement of the effect of isotopic substitution on the superconducting transition temperature, T_c. If Coulomb interactions are negligible, T_c should vary as $M^{-\alpha}$, where $\alpha = 0.5$ and M is the reduced mass of the dominant phonon mode. In this report, we show that T_c decreases when ^{18}O is substituted for ^{16}O in $La_{1.85}Ca_{0.15}CuO_4$ and $BaBi_{0.25}Pb_{0.75}O_3$. These results are consistent with our previously reported data for $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$ (*6, 7*); additional data for these two materials are reported here in order to compare the isotope shifts for these four oxides. The observation of an oxygen isotope effect demonstrates that phonons are involved in the electron-pairing mechanism in these oxides but does not rule out the possibility that additional mechanisms also may be involved.

Several different synthesis routes were used to prepare the various oxide superconductors. The $YBa_2Cu_3O_7$ sample was synthesized with a nitrate route that has been described previously (*8*). Samples of $La_{1.85}Sr_{0.15}CuO_4$ and $La_{1.85}Ca_{0.15}CuO_4$ were prepared by coprecipitation of the metals as oxalates (*6*). The $BaBi_{0.25}Pb_{0.75}O_3$ superconductor was prepared by firing stoichiometric amounts of previously ground $BaCO_3$, PbO, and Bi_2O_3 in O_2 at 850°C for 72 hours with three intermediate grindings, followed by quenching to room temperature. Powder x-ray diffraction was used to verify that each superconductor sample consisted of a single phase.

Exchange of ^{18}O for ^{16}O in each material was accomplished as follows. A pressed pellet of each superconductor was wrapped loosely in platinum foil, placed in a degassed quartz tube attached to a glass manifold, and evacuated to less than 10^{-4} torr. After evacuation, the pellets of the copper oxides were annealed in $^{18}O_2$ for 20 hours at 950°C, and the pellet of $BaBi_{0.25}Pb_{0.75}O_3$ was annealed at 800°C for 20 hours. The $^{18}O_2$ pressure was 650 torr for $YBa_2Cu_3O_7$ and 530 torr for the other three oxides. In each case, the amount of $^{18}O_2$ introduced was at least 50 times the amount required to exchange all of the ^{16}O in the sample. A second pellet of each superconductor, referred to below as a control sample, was annealed in $^{16}O_2$ under similar conditions. For $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$, a static $^{16}O_2$ atmosphere was used, and the annealing conditions were identical to those used for the isotope exchange. For the $La_{1.85}Ca_{0.15}CuO_4$ and $BaBi_{0.25}Pb_{0.75}O_3$, $^{16}O_2$ flowed over the sample at 10 cm^3/min [standard temperature and pressure (STP)]. Thus the oxygen pressures used to anneal the ^{16}O and ^{18}O portions of these two samples were different, 530 torr versus 760 torr, respectively. However, we have shown that this has no noticeable effect on T_c (*6*).

The fraction of ^{18}O in each sample after isotope exchange was determined by temperature-programmed desorption (TPD) and reduction (TPR) as has been described previously (*9, 10*). In a typical experiment, a 25-mg sample was placed into a reactor, evacuated at room temperature, and then heated at 0.5 K/sec to 1073 K in 100 cm^3 (STP) of helium per minute. This procedure removed H_2O, CO, and CO_2, which were incorporated in the samples during exposure to air, and which interfere with the measurement of the isotope ratio (*9*). In the case of $YBa_2Cu_3O_7$, approximately 0.5 oxygen atom per formula unit also was removed during heating in helium. After cooling to room temperature in helium, the sample was heated a second time at 0.5 K per second to 1223 K in 200 cm^3 (STP) of hydrogen per minute. During heating, the hydrogen reacted with oxygen in the samples, producing water that desorbed. By monitoring the effluent from the reactor with a calibrated UTI model 100 C quadrupole mass spectrometer, we could determine the relative amounts of $H_2{}^{18}O$ and $H_2{}^{16}O$ that desorbed to within 3% accuracy (*10*). From the relative amounts of $H_2{}^{18}O$ to $H_2{}^{16}O$ produced by the reduction of the samples, the fraction of ^{18}O in the samples was determined.

Measurements by TPR showed that the amount of ^{18}O exchanged ranged from 60% in $BaBi_{0.25}Pb_{0.75}O_3$ to 75% for $La_{1.85}Sr_{0.15}CuO_4$. We should note that the reduction procedure reduced the superconductors not to their respective metals but rather to mixtures of metals and stable oxides. For example, reduction of $BaBi_{0.25}Pb_{0.75}O_3$ removed 2.0 oxygen atoms per formula unit leaving BaO, lead metal, and bismuth metal. The ratios of ^{18}O to ^{16}O in the isotope-exchanged samples are given in Table 1. In each case it was assumed that the oxygen isotope ratio in the gases that are evolved during TPR was the same as the isotope ratio of the oxygen remaining in the reduction products. This assumption is consistent with the observation that the relative rates at which ^{18}O and ^{16}O desorb from each sample as a function of temperature remained constant. This strongly suggests that on a macroscopic scale ^{18}O was uniformly distributed throughout the samples.

We determined the effect of oxygen isotope substitution on T_c by measuring the

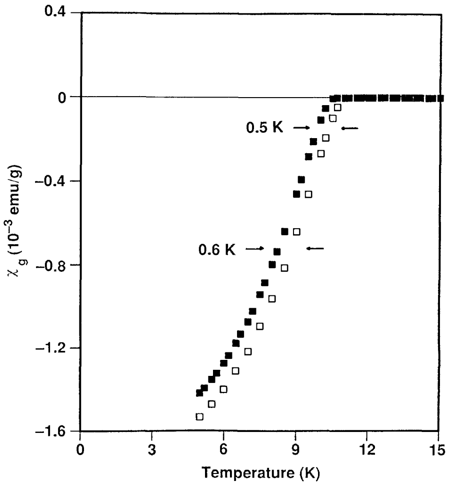

Fig. 1. Magnetic susceptibility versus temperature for the ^{18}O (■) and ^{16}O (□) portions of $BaBi_{0.75}Pb_{0.25}O_3$.

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magnetic susceptibility of each sample as a function of temperature. If the magnitude of the Coulomb interactions in the different oxides does not vary substantially, then we would expect from BCS theory that the shift in T_c should increase as T_c increases. Thus we would expect the largest isotope effect in $YBa_2Cu_3O_7$ ($T_c \approx 92$ K), and the smallest effect in $BaBi_{0.25}Pb_{0.75}O_3$ ($T_c \approx 13$ K). However, as shown below, the observed decrease in T_c is approximately the same for all these oxides when ^{18}O is substituted for ^{16}O.

We performed the magnetic measurements on a superconducting quantum interference device (SQUID) magnetometer by cooling the samples from above T_c in a field of 12 G. The magnetic susceptibility (χ_g) obtained for the ^{18}O and ^{16}O portions of each sample is shown in Figs. 1 to 4, and the results are summarized in Table 1. In each figure, a 15 K temperature range is shown so that the magnitudes of the isotope shifts for the four oxides can be compared directly. The magnitude of the isotope shift expected from BCS theory also is listed in Table 1, assuming $\alpha = 0.5$, M = mass of oxygen, and 100% exchange of ^{18}O for ^{16}O.

The magnetic data obtained for the ^{18}O and ^{16}O portions of $BaBi_{0.25}Pb_{0.75}O_3$ are shown in Fig. 1. The diamagnetic onset, T_c(onset), for the ^{16}O portion of the material is approximately 11.0 K, whereas T_c(onset) for the portion containing 60% ^{18}O is 10.5 K. Thus we observe a decrease in T_c(onset) of 0.5 K when ^{18}O is partially substituted for ^{16}O in this material. The magnitude of the isotope shift increases to 0.6 K at 50% of the full diamagnetic transition. This 0.5 to 0.6 K shift in T_c is comparable to that predicted by BCS theory for a sample with 100% ^{18}O substitution.

Another oxide superconductor with a somewhat higher transition temperature than $BaBi_{0.25}Pb_{0.75}O_3$ is $La_{1.85}Ca_{0.15}CuO_4$, which has an onset temperature of about 20 K. The magnetic data for the ^{18}O and ^{16}O portions of the $La_{1.85}Ca_{0.15}CuO_4$ sample are shown in Fig. 2. The magnitude of the shift varies from 1.3 K when measured at 10% of the full diamagnetic transition to 1.6 K at 50% of the full transition. These shifts are slightly larger than expected from BCS theory. However, the ^{18}O and ^{16}O portions of this sample do not exhibit the same diamagnetism at 5 K; therefore, it is likely that the actual shift is smaller. In all the other sets of samples, the diamagnetism measured at 5 K for the ^{18}O and ^{16}O portions was nearly identical.

Although $La_{1.85}Ca_{0.15}CuO_4$ has the same structure as $La_{1.85}Sr_{0.15}CuO_4$, the latter material has a T_c(onset) near 37 K. Therefore, we expect to observe a larger isotope shift in $La_{1.85}Sr_{0.15}CuO_4$ than in $La_{1.85}Ca_{0.15}CuO_4$. The magnetic data for the ^{18}O and ^{16}O portions of $La_{1.85}Sr_{0.15}CuO_4$ are shown in Fig. 3. Preliminary data for this sample were reported in figure 3 of (*6*). These measurements show an isotope shift of approximately 0.5 K at 10% of the full diamagnetic transition. The isotope shift increases to roughly 1.0 K near 50% of the full transition. Thus, even though T_c is almost twice as high for $La_{1.85}Sr_{0.15}CuO_4$ as for $La_{1.85}Ca_{0.15}CuO_4$, we do not observe an increase in the magnitude of the isotope shift.

$YBa_2Cu_3O_7$ not only has a much higher superconducting transition temperature than $La_{1.85}Sr_{0.15}CuO_4$, but it also has an unusual crystal structure. Copper atoms are found in Cu-O chains sandwiched between Cu-O layers. Initial reports suggested that there is no shift in T_c for $YBa_2Cu_3O_7$ when ^{18}O is substituted for ^{16}O (*11, 12*). However, a closer investigation revealed that there is indeed a shift in T_c when ^{18}O is substituted for ^{16}O in $YBa_2Cu_3O_7$ (*7*). To compare with the three "low T_c" oxides discussed above, we have plotted new magnetic measurements for a sample of $YBa_2Cu_3O_7$ over a 15 K temperature range in Fig. 4. The shift in T_c varies from 0.5 K at 10% of the full diamagnetic transition to 0.9 K at 50%. Moreover, this shift in T_c is reversible by resubstitution of ^{16}O for ^{18}O (*7*). This reversibility demonstrates that the shift in T_c is caused by the difference in the mass of the isotopes rather than by an artifact of the thermal treatment. It is significant that although this material has a superconducting

Table 1. Effect of ^{18}O substitution on the magnetism of oxide superconductors.

Compound	T_c(onset)* (K)	ΔT_c*† (K)	Meissner*‡ effect (%)	Isotope shift§ (K)	Isotope shift‖ (K)	BCS shift¶ (K)	^{18}O (%)
$BaPb_{0.75}Bi_{0.25}O_3$	11.0	6	21	0.5	0.6	0.63	60
$La_{1.85}Ca_{0.15}CuO_4$	20.6	10	23	1.3	1.6	1.14	75
$La_{1.85}Sr_{0.15}CuO_4$	37.0	14	12	0.5	1.0	2.10	75
$YBa_2Cu_3O_7$	91.1	29	63	0.5	0.9	5.21	67

*Data for control samples with ^{16}O. †Transition width measured from 10 to 90% of the full diamagnetic transition. ‡Calculated from the gram susceptibility assuming the theoretical density of 6.3 g/cm^3 for $YBa_2Cu_3O_7$, 8.4 g/cm^3 for $BaPb_{0.75}Bi_{0.25}O_3$, and 7.0 g/cm^3 for the two lanthanum compounds. §Shift in T_c as a result of ^{18}O substitution measured at 10% of the transition. ‖Shift in T_c as a result of ^{18}O substitution measured at 50% of the transition. ¶Shift in T_c predicted by BCS theory for $\alpha = 0.5$ and 100% substitution of ^{18}O.

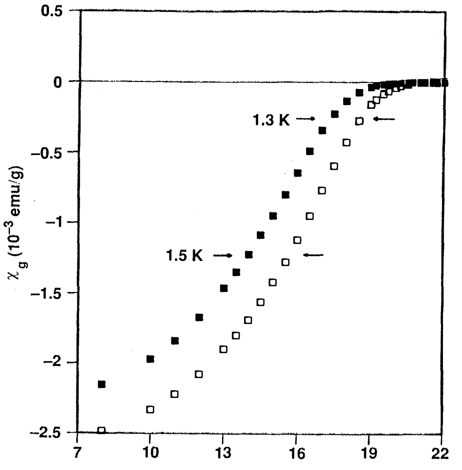

Fig. 2. Magnetic susceptibility versus temperature for the ^{18}O (■) and ^{16}O (□) portions of $La_{1.85}Ca_{0.15}CuO_4$.

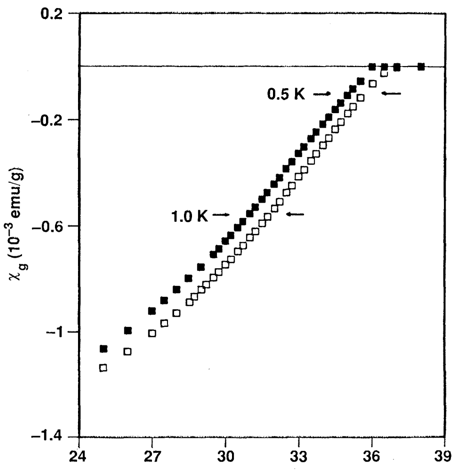

Fig. 3. Magnetic susceptibility versus temperature for the ^{18}O (■) and ^{16}O (□) portions of $La_{1.85}Sr_{0.15}CuO_4$.

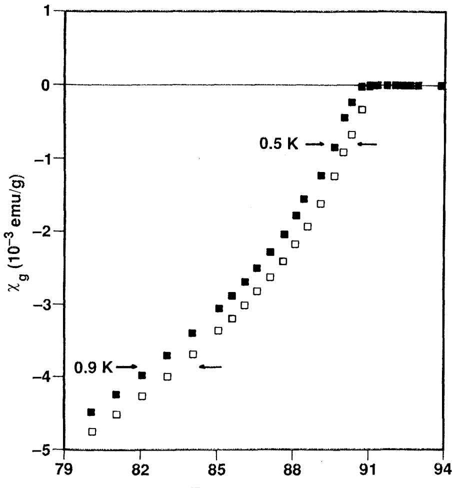

Fig. 4. Magnetic susceptibility versus temperature for the ^{18}O (■) and the ^{16}O (□) portions of $YBa_2Cu_3O_7$.

transition temperature of near 90 K, the magnitude of the isotope shift is approximately the same as for $BaBi_{0.25}Pb_{0.75}O_3$, which has a T_c of only 11 K.

Measurements of the magnetic susceptibility of superconductors are sensitive to sample orientation in the magnetometer. Therefore, to verify that our data were not affected by sample orientation, that is, demagnetization effects, we conducted the following worst-case experiment. Magnetic data were collected for a pellet of $La_{1.85}Sr_{0.15}CuO_4$ when it was oriented perpendicular and parallel to the applied field. Although we did observe a small effect due to orientation on the measured susceptibility, it was small relative to the isotope shifts observed. Moreover, the diamagnetic onset does not depend on orientation. Therefore, we conclude that the isotope shifts are not produced by experimental artifacts.

Although it is possible to demonstrate the existence of an oxygen isotope effect, it is difficult to quantify the shift in T_c. This is because the diamagnetic transitions are relatively broad, and the magnitude of the shift is temperature-dependent. Furthermore, the samples are not isotopically pure, and it is not necessarily correct to assume a linear extrapolation to obtain the isotope effect for a sample with 100% ^{18}O. To measure the isotope shift quantitatively, one would need two samples, one with 100% ^{18}O and one with 100% ^{16}O, both showing identical Meissner effects and transition widths of at most 1 K.

Unless phonons are involved in the electron-pairing mechanism in these oxide superconductors, there is no reason for the superconducting transition temperatures to depend on the mass of oxygen. Therefore, the observation of an isotope effect confirms that phonons are involved in the electron-pairing mechanism in these oxide superconductors. It is significant that the magnitudes of the shifts in T_c when ^{18}O is substituted for ^{16}O are similar for all the samples. This is in contrast to what is predicted by BCS theory, assuming that Coulomb interactions do not vary substantially. It is possible that the Coulomb repulsion between electrons is larger in $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ than in $BaBi_{0.25}Pb_{0.75}O_3$, which would explain why smaller oxygen isotope effects are observed in the former samples. On the other hand, although phonons are definitely involved in the electron-pairing mechanism, there is a possibility of an additional interaction, several of which already have been proposed (*13–16*).

REFERENCES AND NOTES

1. J. Bardeen, L. N. Cooper, J. R. Schrieffer, *Phys. Rev.* **106**, 162 (1957).
2. A. W. Sleight, J. L. Gillson, P. E. Bierstedt, *Solid State Commun.* **17**, 27 (1975).
3. J. G. Bednorz and K. A. Müller, *Z. Phys.* **B84**, 189 (1986).
4. M. K. Wu *et al.*, *Phys. Rev. Lett.* **58**, 908 (1987).
5. P. H. Hor *et al.*, *ibid.*, p. 911.
6. T. F. Faltens *et al.*, *ibid.* **59**, 915 (1987).
7. K. J. Leary *et al.*, *ibid.*, p. 1236.
8. G. F. Holland *et al.*, *ACS Symp. Ser.* **351**, 102 (1987).
9. S. W. Keller, K. J. Leary, A. M. Stacy, J. M. Michaels, *Mater. Lett.* **5**, 357 (1987).
10. S. W. Keller *et al.*, *ACS Symp. Ser.* **351**, 114 (1987).
11. B. Batlogg *et al.*, *Phys. Rev. Lett.* **58**, 2333 (1987).
12. L. C. Bourne *et al.*, *ibid.*, p. 2337.
13. V. L. Ginzburg, *Usp. Fiz. Nauk* **101**, 185 (1970) [*Sov. Phys. Usp.* **13**, 335 (1970)].
14. D. Allender, J. Bray, J. Bardeen, *Phys. Rev. B* **7**, 1020 (1973).
15. D. Davis, H. Gutfreund, W. A. Little, *ibid.* **13**, 4766 (1976).
16. A. W. Sleight, *ACS Symp. Ser.* **351**, 2 (1987).
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Spectrophotometry of Pluto-Charon Mutual Events: Individual Spectra of Pluto and Charon

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Time-resolved spectra of the 3 March and 4 April 1987 mutual events of Pluto and its satellite Charon were obtained with spectral coverage from 5,500 to 10,000 angstroms with 25 angstrom spectral resolution. Since both events were total occultations of Charon by Pluto, spectra were obtained of the anti-Charon–facing hemisphere of Pluto, with no contribution from Charon during totality. On 4 April, a combined spectrum of Pluto and Charon immediately before first contact was also obtained. The spectrum of the Pluto-facing hemisphere of Charon was extracted by differencing the pre-event and totality spectra. The spectra were reduced to reflectances by ratioing them to spectra of solar analog stars. Charon has a featureless reflectance spectrum, with no evidence of methane absorption. Charon's reflectance appears neutral in color and corresponds to a geometric albedo of ~0.37 at 6000 angstroms. The Pluto reflectance spectrum displays methane absorption bands at 7300, 7900, 8400, 8600, and 8900 angstroms and is red in color, with a geometric albedo of ~0.56 at 6000 angstroms. The signal-to-noise ratios of the eclipse spectra were not high enough to unambiguously identify the weaker methane band at 6200 angstroms.

PLUTO AND ITS SATELLITE CHARON are the best example of a double planet in our solar system because of Charon's relatively large size compared to that of Pluto. Current estimates of the radii of the two bodies are 1210 and 590 km for Pluto and Charon, respectively (*1*). Thus, the presence of Charon accounts for nearly 20% of the total area of the Pluto-Charon system visible from Earth. However, the Pluto-Charon system is currently about 30 times farther from the sun than Earth. Consequently, the angular separation of the two bodies as seen from Earth is less than 1 arc sec, which is too small for any Earth-based instruments to resolve. Until recently, therefore, spectroscopic studies of Pluto and Charon have been limited to studies of the combined light from the two bodies.

The only features that have been identified in combined spectra of Pluto-Charon are a result of the presence of methane (CH_4), which displays characteristic absorption bands throughout the visible and near-infrared spectrum. Since the discovery of CH_4 on Pluto-Charon (*2*), researchers have attempted to model its distribution and state. Cruikshank *et al.* (*2*) interpreted their infrared photometry of Pluto-Charon as evidence for a CH_4 frost. Fink *et al.* (*3*) made the first high-quality observations of the CH_4 absorption bands in the region from 5,000 to 10,000 Å. They modeled the observed spectrum by assuming that the absorptions occurred within a CH_4 atmosphere and found that the weak bands (6200, 7900, and 8400 Å) displayed a linear relation between band depth and CH_4 abundance for the band depths present in the observed spectra. However, models of the strong bands (7300 and 8900 Å) displayed little variation in band depth with CH_4 abundance for the observed band depths. Fink *et al.* (*3*) argued that the saturation of the strong bands demonstrated the presence of a CH_4 atmosphere on Pluto (Charon's spectrum was ignored in their models) since

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