Isotope Effect in the High-T_c Superconductors $Ba_2YCu_3O_7$ and $Ba_2EuCu_3O_7$

B. Batlogg, R. J. Cava, A. Jayaraman, R. B. van Dover, G. A. Kourouklis,[(a)] S. Sunshine, D. W. Murphy,
L. W. Rupp, H. S. Chen, A. White, K. T. Short, A. M. Mujsce, and E. A. Rietman
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 24 April 1987)

We have studied the effect of isotopic substitution on the superconducting T_c in the 90-K superconductors $Ba_2YCu_3O_7$ and $Ba_2EuCu_3O_7$ by replacing ^{16}O with the heavier isotope ^{18}O. Samples with approximately 75% of the ^{16}O replaced by ^{18}O were prepared by gas-phase ion exchange. In these samples the phonon frequencies, measured by Raman spectroscopy, are reduced by the expected ~4%. The transition temperatures, however, are found to change by less than 0.2%. This change in T_c is much less than that expected for strongly coupled phonon-mediated superconductivity.

PACS numbers: 74.70.Ya, 63.20.Dj, 74.10.+v, 78.30.−j

It is well known that the effect of isotope substitution on the superconducting transition temperature[1,2] T_c provides the strongest support for the mechanism that phonons are involved in the formation of the superconducting ground state, in the framework of the BCS theory. The need to invoke mechanisms other than phonon-mediated electron pairing has arisen only recently with the discovery of heavy-fermion superconductors[3-5] and now the high-T_c oxide superconductors.[6-14] For the case of high-T_c oxide superconductors, some new mechanisms have already been proposed,[15-19] in addition to the conventional electron-phonon coupling interaction.[20-24] Central to the conventional model are the high frequencies of the Cu—O bond-stretching vibrational modes and their strong coupling to the electronic states at the Fermi level, presumed to be the result of a strong mixture of oxygen p states with the copper d states at the Fermi level (or with the lead-bismuth s states in the case of lead-bismuth oxide systems).[22-25] The high-frequency modes involve the motions of oxygen atoms and thus replacement of ^{16}O by ^{18}O may be expected to modify significantly the vibrational-mode frequencies, which in turn should affect the superconducting T_c. Thus a good test for the conventional model would be a correlation between these vibrational frequencies and the superconducting T_c.

In this Letter we report the results of an isotope-effect study in which at least 75% of the ^{16}O was replaced by ^{18}O in $Ba_2YCu_3O_7$ and $Ba_2EuCu_3O_7$. The high-frequency vibrational modes were characterized by Raman spectroscopy, clearly showing the expected mass-dependent shifts. There is, however, no significant variation in the superconducting T_c. The mass dependence of T_c is generally expressed as $T_c \sim M^{-\alpha}$, where M is the isotopic mass and α is usually close to 0.5 for the full isotope effect. In the present case α is found to be 0 ± 0.02, indicating very little, if any, of an isotope effect.

Isotope-effect studies require well-characterized samples with reproducible crystal chemical properties. For isotopic substitution with ^{18}O we took advantage of the high mobility of oxygen in these compounds at elevated temperatures, which allows for an exchange of oxygen without disruption of the crystal structure. The starting samples were synthesized and annealed in the manner described earlier. Two samples (~2×4 mm^2) were cut from the center of a single sintered disk, which was nominally 10 mm in diameter and 1–2 mm in thickness. For subsequent treatment the samples were placed in two identical quartz ampoules which were connected to manometers and to either a vacuum pump or oxygen containers, as warranted by the treatment procedure. The two quartz ampoules were inserted from opposite ends into the center of the flat hot zone of a tube furnace, to ensure that the two samples received identical thermal treatment. In the first step the samples were heated to 500-550 °C *in vacuo,* held there for 3–12 h, and cooled to 100 °C in ~2 h. The weight loss in this treatment corresponded to a loss of (10 ± 1)% of the oxygen, which is low enough to prevent reduction of Cu below Cu^{2+} and to preserve the basic crystal structure without decomposition. In the second step the samples were heated to 500 °C, the control sample in ^{16}O atmosphere and the test sample in ^{18}O at a pressure of 1 atm, and held at 500 °C for 8–12 h, and then cooled to ~100 °C in ~2 h. In this treatment the oxygen lost in the first step was fully replenished. This cycling could be repeated reproducibly with a total weight loss or gain of (1.65 ± 0.15)%. We found that this technique provided a simple and reliable method to introduce ^{18}O into the test sample, allowing the control sample to be treated in an identical manner with ^{16}O and eliminating the ambiguity that might arise as a result of differing ^{18}O and ^{16}O synthetic conditions. The relative amounts of ^{16}O and ^{18}O were analyzed by mass spectrometry and, for one sample, Rutherford backscattering (RBS). After one cycle of exposure to ^{18}O, it was found that the latter not only filled the vacant sites, but also exchanged ^{16}O present in the sample, resulting in about equal amounts of the two isotopes. This is due to the high mobility of oxygen in the compound and the large concentration gradient when the 50–150-mg sample is surrounded by ~20 cm^3 of ^{18}O. After three exchange cycles,

$(74 \pm 7)\%$ of the ^{16}O was substituted by ^{18}O. A total of seven pairs of $Ba_2YCu_3O_7$ and $Ba_2EuCu_3O_7$ samples, treated to one to three ^{18}O exchange cycles, were studied.

The superconducting transition temperatures were determined by both four-probe-resistance, magnetization, and Meissner-effect measurements. In addition to the aforementioned analysis for ^{18}O, we measured directly the shift of the phonon frequencies by Raman spectroscopy.

We will confine our detailed discussions to $Ba_2EuCu_3O_7$. The average oxygen mass according to RBS and mass-spectrometric analysis increased by $(9.3 \pm 1)\%$ in the compound during the ion exchange. This mass enhancement should shift the vibrational frequencies involving the oxygens by $(4.3 \pm 0.4)\%$. The observed Raman peaks for the ^{16}O and ^{18}O samples are shown in Figs. 1(a) and 1(b), respectively. A detailed description of the experiment and analysis of the spectra will be presented separately. (We would like to mention that the intensity of the highest-frequency line has been observed to be somewhat dependent on sample-handling conditions. Further studies to clarify the origin of this line are in progress.) The Raman data are significant for three reasons. First, the phonon frequencies in the ^{18}O-containing sample are shifted downwards by the expected amount, determined by the ^{18}O:^{16}O ratio. The average $\Delta\omega/\omega$, taken from several experiments, is $-(4.2 \pm 0.5)\%$. The results of the mass-spectroscopy, RBS, and Raman measurements are in good agreement. Second, the downward shift in the frequency of the peaks by the expected amount proves that the observed high-frequency vibrations involve the motion of oxygen atoms. Finally, the peaks in the Raman spectrum, although shifted to lower energies in the ^{18}O sample, are only slightly broadened (by ~20% as compared to the ^{16}O sample). From this we conclude that the isotope ratio is uniform when averaged over the optical penetration depth, which we estimate to be of the order of 1 μm, and that the ^{16}O in the test sample is homogeneously replaced by ^{18}O at least within the optical penetration depth.

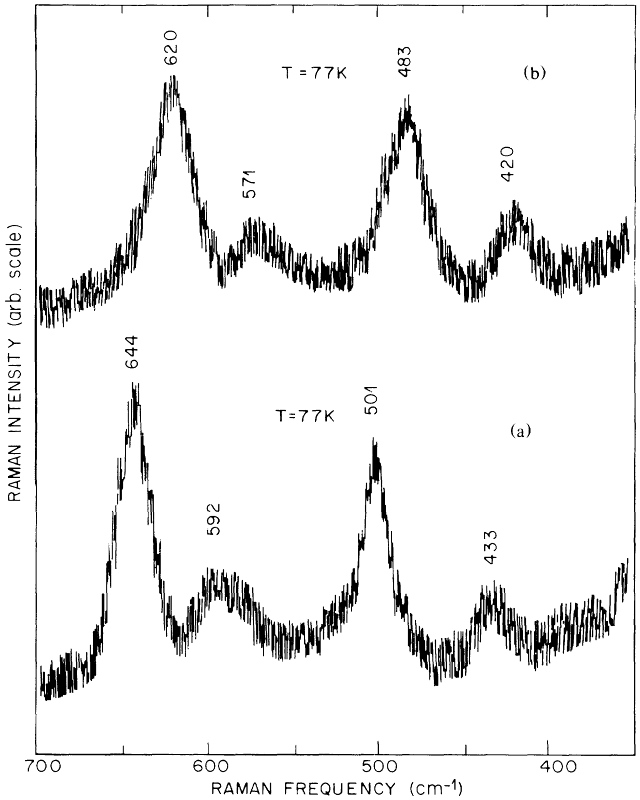

FIG. 1. Raman spectra of superconducting $Ba_2EuCu_3O_7$ at 77 K. (a) Sample containing ^{16}O isotope; (b) sample containing $(74 \pm 7)\%$ ^{18}O. Excitation was with the 488-nm Ar^+ line at a power of ~60 mW and a line focus.

An important experimental point that has to be addressed concerns the possibility of reverse exchange of ^{18}O by ^{16}O when the samples are exposed to air at room temperature. This could produce on the sample an ^{16}O layer a few thousand angstroms thick, with the possibility of shielding the T_c of the ^{18}O-substituted material, thus masking the isotope effect. To check this we have measured the T_c of two ^{18}O-substituted samples handled only in ^{18}O atmosphere, and later in helium or nitrogen atmospheres. These samples displayed the same behavior as those handled in the normal manner.

The transition temperature was measured magnetically by our monitoring the temperature of the flux excluded by the stationary sample in a SQUID magnetometer (Meissner effect) or measuring the dc magnetization. The field was 21 Oe and data were collected during both warming and cooling through T_c, which is necessary in order to correct for the small temperature difference between sample and thermometer (~0.1 K). Typical results are shown in Fig. 2. In none of the samples could we detect a significant (>0.1 K) difference in T_c between the ^{16}O and ^{18}O samples. (Such null results actually led us to adopt the precautionary handling procedures described above.) Resistance measurements required exposure to air and attachment of leads. Thus the derived T_c's were considered less typical for the bulk of the samples, particularly as this method probes the highest-T_c connecting path. We have observed that in these materials resistive T_c's are usually higher by ~0.5-1 K than Meissner-effect T_c's. In two cases the ^{18}O samples had a slightly lower T_c by resistance measurements (0.3-0.4 K), but still higher than the Meissner-effect T_c's, which were equal. This upper bound of a few tenths of a degree is to be compared with 3.7 ± 0.5 K calculated for the full isotope effect on the basis of the measured shift of the phonon frequencies.

Reduced isotope effects have been observed, particularly in transition metals where $\alpha = 0$ is also found for

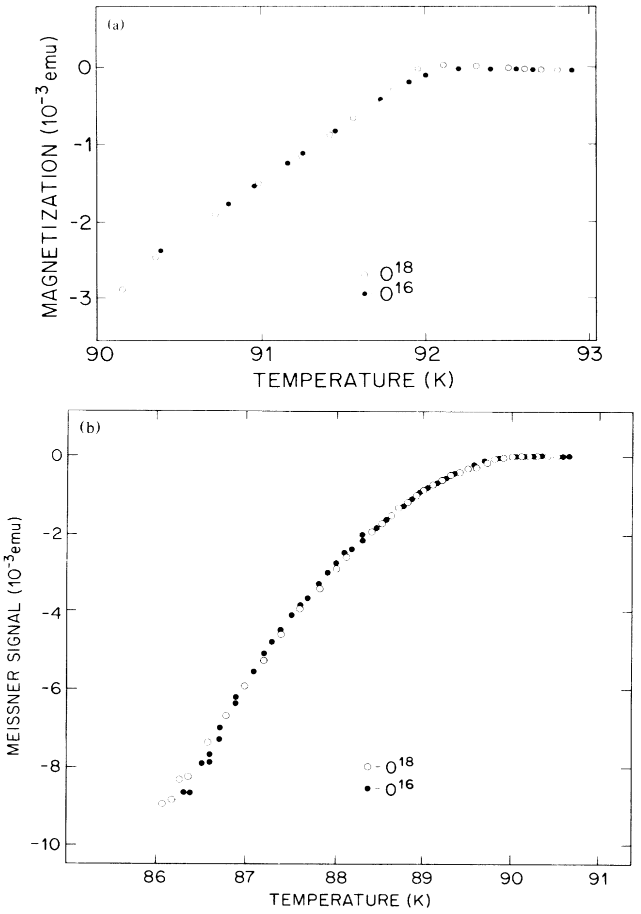

FIG. 2. Magnetic measurements on ^{16}O- and ^{18}O-containing samples. (a) Magnetization of $Ba_2EuCu_3O_7$ and (b) Meissner signal of $Ba_2YCu_3O_7$. For a full isotope effect a T_c difference of 3.7 ± 0.5 K is expected.

Ru[26] and Zr.[27] [The inverse isotope effect in palladium hydride (PdH) is well known.[28]] In a general treatment of T_c in terms of the electron-phonon coupling strength λ and the renormalized Coulomb interaction μ^*, a reduced isotope effect is characteristic of a small λ ($\lambda < 0.3$) with reasonable values for μ^* (< 0.3).[29,30] Detailed model calculations for the transition metals associate the small α's with details of the band structure, resulting in an enhanced μ^*.[31] On the basis of the current understanding of the oxide superconductor materials, and particularly their high T_c compared to their relatively low density of states at the Fermi level,[32] the high T_c's are unlikely to be reached with the weak electron-phonon coupling strength implied by the present isotope-effect results. Therefore, only a combination of large λ's with unprecedented large μ's would explain the absence of an isotope effect within the framework of the traditional electron-phonon theory. No isotope effect, however, is expected from purely electronic mechanisms for superconducting pairing.

We acknowledge discussions with E. Bucher J. P. Remeika, W. Weber, and C. M. Varma, and the contributions of S. M. Zahurak. We also thank P. Weiss, A. M. Schnoltener, and Y. T. Lee for facilitating the availability of ^{18}O.

---

[a] Permanent address: Department of Physics, National Technical University, Zografau Campus, GR15773 Athens, Greece.

[1] E. Maxwell, Phys. Rev. **78**, 477 (1950).

[2] C. Reynolds, B. Serin, W. Wright, and L. Nesbitt, Phys. Rev. **78**, 487 (1950).

[3] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).

[4] H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **50**, 1595 (1983).

[5] G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, Phys. Rev. Lett. **52**, 679 (1984).

[6] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[7] S. Uchida, H. Tagaki, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L1 (1987).

[8] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[9] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[10] 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).

[11] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[12] J. M. Tarascon, L. H. Green, W. R. McKinnon, and G. W. Hull, Phys. Rev. B **35**, 7115 (1987).

[13] P. M. Grant, R. B. Beyers, E. M. Engler, G. Lim, S. S. Parkin, M. L. Ramirez, V. Y. Lee, A. Nazzal, J. E. Vasquez, and R. J. Savoy, Phys. Rev. B **35**, 7242 (1987).

[14] P. Ganguly, A. K. Raychaudhari, K. Sreedhar, and C. N. R. Rao, Pramana **27**, L229 (1987).

[15] P. W. Anderson, Science **235**, 1196 (1987).

[16] C. M. Varma, S. Schmitt-Rink, and E. Abrahams, to be published.

[17] V. Z. Kresin, Phys. Rev. B (to be published).

[18] J. Ruvalds, to be published.

[19] H. Kamimura, Jpn. J. Appl. Phys. (to be published).

[20] W. Weber, Phys. Rev. Lett. **58**, 1371 (1987).

[21] W. Pickett, H. Krakauer, D. A. Papaconstantopoulos, and L. L. Boyer, Phys. Rev. B **35**, 7252 (1987).

[22] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[23] C. L. Fu and A. J. Freeman, Phys. Rev. B (to be published).

[24] K. H. Benneman, to be published.

[25] L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **28**, 4227 (1983).

[26] T. H. Geballe, B. T. Matthias, G. W. Hull, and E. Co-

renzwit, Phys. Rev. Lett. **6**, 275 (1961).

[27] E. Bucher, J. Müller, J. L. Olsen, and C. Palmy, Phys. Lett. **15**, 303 (1965).

[28] B. Stritzker and W. Buckel, Z. Phys. **257**, 1 (1972).

[29] N. N. Bogolubov, Nuovo Cimento **7**, 6, 794 (1958).

[30] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

[31] J. W. Garland, Phys. Rev. Lett. **11**, 114 (1963), and Phys. Rev. **153**, 460 (1967).

[32] See, e.g., B. Batlogg, A. P. Ramirez, R. J. Cava, R. B. van Dover, and E. A. Rietman, Phys. Rev. B **35**, 5340 (1987), and Ref. 11.