Search for Isotope Effect in Superconducting Y-Ba-Cu-O

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An isotope effect has been searched for in the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ through substitution of ^{18}O for ^{16}O. No shift in the superconducting transition temperature T_c is observed by electrical resistivity or magnetic susceptibility measurements. We discuss the implications of this result for mechanisms of superconductivity in the high-T_c oxides.

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The recent discovery of superconductivity above 30 K in $La_{2-x}Ba_xCuO_4$ by Bednorz and Müller[1] has led to enormous success in the development of materials with high superconducting transition temperature T_c. Wu *et al.*[2] were the first to report superconductivity above 90 K in a mixed-phase Y-Ba-Cu-O compound; similar independent findings have since been published by Bourne *et al.*[3] and Hikami, Hirai, and Kagoshima.[4] Structural studies[5,6] indicate that the superconducting phase in these Y-Ba-Cu-O compounds is $YBa_2Cu_3O_{7-\delta}$.

An important feature common to both the layered perovskite K_2NiF_4 structure of $La_{2-x}M_xCuO_4$ (M = Ba, Sr, or Ca) and the distorted oxygen-defect perovskite structure of $RBa_2Cu_3O_{7-\delta}$ (R = Y or some lanthanide rare-earth elements) is the existence of two-dimensional copper-oxygen planes which are the most responsible for the metallic conduction. Band-structure calculations[7,8] demonstrate that the density of states at the Fermi level E_F is due largely to hybridized Cu 3*d* and O 2*p* states. It is therefore expected that vibration of the O ions would be involved if electron-phonon coupling is responsible for the superconductivity. For the La-based materials, it has been suggested[9] that the conventional electron-phonon Bardeen-Cooper-Schrieffer[10] (BCS) superconductivity mechanism is dominant. Strong electron-phonon couplings to O breathing-mode vibrations lead to electron-phonon coupling constants $\lambda \geq 2$ and T_c's on the order of 30–40 K.[9] On the other hand, the high transition temperatures and unusual two-dimensional electronic structure of the superconducting oxides have also provoked theoretical descriptions which lie outside the conventional BCS theory.[11,12]

One of the most suggestive tests for electron-phonon coupling in conventional superconductors is the isotope effect,[13] where T_c is sensitive to ionic mass. In the original BCS treatment,[10] $\alpha = \frac{1}{2}$ where α is defined by

$$\alpha = -\partial(\ln T_c)/\partial(\ln M) = \tfrac{1}{2}(1-\zeta). \qquad (1)$$

Here, ζ is a deviation from the ideal isotope effect where $\alpha = \frac{1}{2}$. The presence of an isotope effect demonstrates an important role played by the phonons in the superconductivity mechanisms.

We have searched for an isotope effect in $YBa_2Cu_3O_{7-\delta}$, by substituting the isotope ^{18}O for ^{16}O. With an estimated 90% of the oxygen sites replaced by ^{18}O (see below), no shift in T_c is observed in either dc electrical resistivity measurements or dc magnetic susceptibility measurements. Our results show $\alpha = 0.0 \pm 0.027$ indicating that, within our experimental resolution, there is no isotope shift for oxygen. We examine this value in the context of conventional BCS theory and other mechanisms for superconductivity.

Samples of $YBa_2Cu_3O_{7-\delta}$ were prepared by solid-state reaction. Fine powders of Y_2O_3, $BaCO_3$, and CuO were mixed in stoichiometric proportions, dissolved in nitric acid, evaporated to dryness, and decomposed at 800 °C. The powder was then reground, pressed into a pellet, sintered in an ^{16}O atmosphere at 950 °C, and finally slow cooled. The uniform parent pellet was then broken into several pieces for subsequent treatment and measurement. Resistivity measurements on the parent specimen indicated a sharp transition to the superconducting state at $T_c = 90$ K (transition midpoint). Powder x-ray diffraction showed that the sample consisted of a single phase.

In order to determine the appropriate conditions for oxygen isotope substitution, a series of careful thermograviometric analysis (TGA) experiments were performed on several $YBa_2Cu_3O_{7-\delta}$ samples from different preparation batches. The time constant for oxygen diffusion was found to be very short, and dependent on temperature and also sample grain size.[14] It was found that oxygen in the sample freely exchanged with oxygen in the surrounding atmosphere at 950 °C. A portion of the original $YBa_2Cu_3O_{7-\delta}$ parent pellet was placed in an ^{18}O atmosphere at 950 °C for 12 h and slow cooled to 200 °C over 6 h; the temperature and reaction time were chosen to ensure maximal ^{18}O exchange with both weakly and tightly bound oxygen sites in the specimen. The isotope exchange takes place without change of the oxidation state of the material, and the superconducting transition remains sharp. A nearly identical treatment was performed on another portion of the parent pellet, with use of an ^{16}O atmosphere. This treated ^{16}O sample was used as the control sample.

Figure 1(a) shows R vs T for the ^{16}O control sample of $YBa_2Cu_3O_{7-\delta}$ near the superconducting transition region. The data indicate a midpoint transition $T_c = 90.0$ K, nearly identical to that determined for the untreated parent pellet. Figure 1(b) shows similar R vs T data for the ^{18}O sample. The midpoint of the transition is at 90.3 K. Within the experimental uncertainty of ~0.3 K (taking into account possible temperature gradients across the measurement probe, and variations of T_c in different portions of the parent pellet), we find[14,15] *no isotope effect* in $YBa_2Cu_3O_{7-\delta}$, i.e., $\alpha = 0.0 \pm 0.027$. A similar conclusion is drawn from a careful comparison of magnetic susceptibility χ measurements of the parent pellet and the treated ^{18}O specimen. In Fig. 2, the χ for an ^{18}O sample is displayed.

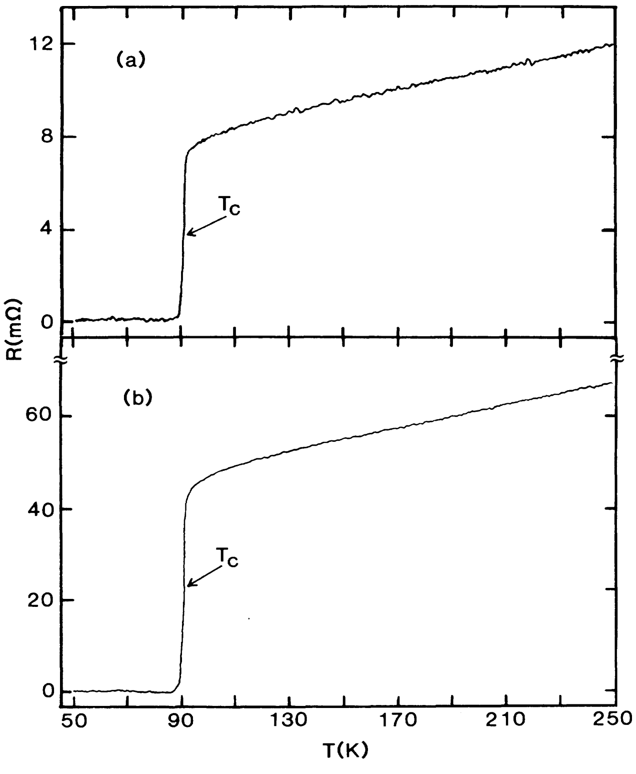

FIG. 1. (a) R vs T for $YBa_2Cu_3O_{7-\delta}$ with ^{16}O. (b) Same as (a) but for ^{18}O. No isotope effect is observed.

Temperature-programmed-desorption measurements (employing a quadrupole mass spectrometer) on the specimens treated in ^{18}O determine how much of the ^{16}O was actually replaced by ^{18}O. A total of 900 μmol/g of O were initially removed from the sample by heating to 800 °C in flowing He. The oxygen desorbed as O_2, with an ^{18}O to ^{16}O ratio of 90%. In addition, small amounts of H_2O, CO_2 and CO desorbed (the samples had been exposed to air). The sample was then heated in flowing H_2, destructively reducing the sample to Y_2O_3, BaO, and CuO, and an additional 4100 μmol/g of O desorbed in the form of H_2O with an isotope ratio of 90%. Of the total amount of oxygen removed from the specimen (50% of the total specimen content), 90% was ^{18}O.

For the La-based oxides, the frequency of the O breathing mode is found to be very high and this high frequency as a prefactor in the T_c equation is suggested to predominate in the high-T_c superconductivity.[7,9] If we make a similar assumption for the Y-based samples studied here, then it is possible to examine the magnitudes of the parameters entering the BCS equation. In this analysis, it is assumed that the oxygen vibrations dominate and comparison is made with transition metals where a reduced and sometimes zero ($\alpha \approx 0$, $\zeta \approx 1$) iso-

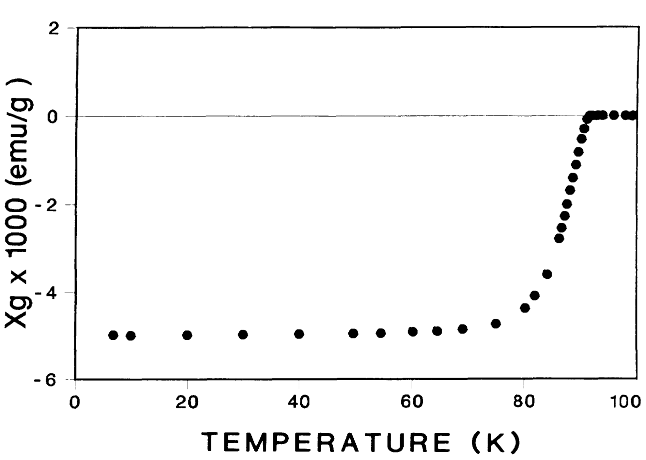

FIG. 2. χ vs T for $YBa_2Cu_3O_{7-\delta}$ with ^{18}O.

tope effect is found[16] as in Ru and Zr. In contrast, for simple (*sp*) BCS superconductors $\zeta \sim 0.1$.

Garland[17] explored the reduced isotope effect for the transition metals. He found that the large and narrow *d*-band density of states changes the effective Coulomb interaction; thus the isotope effect can be absent despite the phonon mechanism being the dominant attractive interaction. If a simple two-square-well model[18] is used within the BCS theory, the parameter ζ is algebraically obtained:

$$\zeta=[\mu^*/(\lambda^*-\mu^*)]^2, \qquad (2)$$

where λ^* $[=\lambda/(1+\lambda)]$ and μ^* are the effective phonon and Coulomb interaction parameters, and λ is the electron-phonon coupling constant. The isotope effect is completely reduced when $\mu^* \gg \lambda^*$ or $\mu^*=\lambda^*/2$. For the Y-Ba-Cu-O system, if we use the measured T_c and assume a Debye temperature $\theta_\text{D} \approx 400$ K, then $\mu^*=0.63$ and $\lambda^*=1.25$ which is an unphysical result. When $\theta_\text{D} \approx 800$ K is used, λ is in the range of 7 while μ^* is about 0.45. We also tested an expression for T_c recently developed by Kresin[19] from the Eliashberg equation in the strong-coupling limit of λ. With the use of the same T_c and θ_D, we found that μ^* is approximately $\lambda/2$ for λ in the range of 10. Since the T_c equation is obtained in the strong-coupling limit of λ, the value for μ^* which yields the zero isotope effect is significantly larger than those found in most superconducting materials, suggesting that the Y-Ba-Cu-O compound has a strong effective Coulomb interaction.

Finally, the present experiments do not rule out nonphonon mechanisms such as the resonating-valence-bond model,[11] the two-dimensional plasmon model,[12] the negative-U mechanism,[20] or other Coulomb-induced attractions. Since these mechanisms are not necessarily related to the ionic mass, the isotope effect may not be expected.

In conclusion, we have found that the oxygen isotope effect is absent in superconducting Y-Ba-Cu-O. This result suggests that although the BCS phonon mechanism may still be appropriate for explaining the high-T_c superconducting behavior of this material, the parameters, θ_D, λ^*, and μ^* would be severely constrained. Hence the absence of an oxygen isotope shift suggests that a nonphonon mechanism may be important in this material.

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