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Complete absence of isotope effect in $YBa_2Cu_3O_7$: Consequences for phonon-mediated superconductivity

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$YBa_2Cu_3O_7$ has been prepared with enriched ^{135}Ba, ^{138}Ba, ^{63}Cu, and ^{65}Cu isotopes. The superconducting transition temperature T_c is found to be insensitive to the mass of the Ba and Cu atoms. This result, when combined with earlier findings of no T_c shift for oxygen-isotope substitution or rare-earth substitution, demonstrates the complete absence of an isotope effect in $YBa_2Cu_3O_7$. The consequences of these results for the applicability of phonon-mediated electron pairing mechanisms are discussed.

One of the central questions pertaining to the recently discovered high-T_c superconducting oxides such as La-Ba-Cu-O (Ref. 1) and Y-Ba-Cu-O (Ref. 2) is the superconductivity mechanism. In "conventional" superconductors, the electron-electron attraction is mediated by phonons, leading almost always to a sensitive dependence of transition temperature T_c on the phonon frequency, or equivalently, on the mass of the crystal ions. In the original Bardeen-Cooper-Schrieffer (BCS) treatment of superconductivity,[3] $T_c \propto M^{-\alpha}$, where M is the ionic mass and $\alpha = \frac{1}{2}$. The isotope effect has been studied extensively in a wide range of superconducting materials, and experimentally α is typically in the range 0.2–0.5.[4]

In the $YBa_2Cu_3O_7$ system, substitution[5] of a host of rare-earth elements (with significantly different masses) on the Y sites has little or no effect on T_c. It was also recently demonstrated[6] that substitution of the isotope ^{18}O for ^{16}O has no measurable effect on T_c. The lack of an oxygen-isotope effect in $YBa_2Cu_3O_7$ is surprising if the assumption is made[7] that the high-frequency Cu-O vibrational modes couple strongly to the electronic states at the Fermi level E_F and dominate the superconductivity. On the other hand, the lack of an oxygen-isotope effect does not preclude that other phonon modes in the system play a key role in the superconductivity mechanism.

We have explored the sensitivity of T_c in $YBa_2Cu_3O_7$ to changes in the Ba and Cu phonon frequencies by isotopic substitution on the Ba and Cu sites. No difference in T_c is observed between samples prepared exclusively with ^{135}Ba and ^{138}Ba; a similar finding holds for ^{63}Cu vs ^{65}Cu. These observations demonstrate conclusively the complete lack of a significant isotope effect in $YBa_2Cu_3O_7$.

Samples of $YBa_2Cu_3O_7$ were prepared by various solid-state reaction methods using Y_2O_3, $BaCO_3$, and CuO. CuO with 99.6% ^{65}Cu and CuO with 99.7% ^{63}Cu enrichment were used for one pair of samples, and $BaCO_3$ with 78.8% ^{135}Ba and $BaCO_3$ with 99.7% ^{138}Ba were used for another pair of samples.

In previous synthesis routes to $YBa_2Cu_3O_7$, we have observed differences in T_c of up to several degrees for samples prepared by similar but not identical preparation methods. In order to eliminate such uncertainties, the samples used in the present study were prepared simultaneously in pairs under identical conditions for each pair. Fine powders of the starting materials were thoroughly mixed and reacted at 850 °C for several hours under flowing oxygen. The reacted powder was then dissolved in HNO_3, evaporated to dryness, and decomposed at 500 °C. The resulting compounds were reground and heated at temperatures of up to 850 °C under flowing oxygen, with several intermediate cooling and regrinding steps. The final powders were pressed into pellets and heated at 950 °C in oxygen for 12 h, followed by slow cooling. Test samples of nonenriched $YBa_2Cu_3O_7$ prepared in the above manner had T_c's of approximately 90 K with full transition widths of less than 2 K. Different samples produced side by side in the heating and cooling steps had T_c's differing by no more than approximately 0.2 K. T_c's were determined by standard four-probe resistivity measurements employing silver-paint contacts. The samples were cooled in a helium-gas flow cryostat.

Figure 1 shows sample resistance R versus temperature T for samples prepared with different copper isotopes. The sample prepared with ^{63}Cu has a transition tempera-

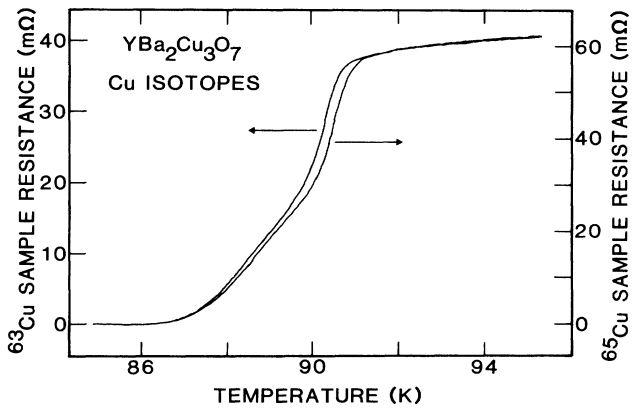

FIG. 1. R vs T for $YBa_2Cu_3O_7$ prepared with ^{63}Cu and ^{65}Cu. No isotope effect is observed.

ture (midpoint) $T_c = 89.70$ K, while the sample prepared with ^{65}Cu has $T_c = 89.90$ K. For Cu isotopes, we thus find $T_c(^{65}Cu) - T_c(^{63}Cu) = 0.2$ K. A similar shift is found if the onset temperature T_c^0 is used as the relevant transition temperature. A second and nearly identical set of experiments for Cu isotopes found a similarly small shift but of opposite sign.

Figure 2 shows resistance data for samples prepared from the two different Ba isotopes. The data indicate (midpoint) transition temperatures $T_c = 91.85$ K and $T_c = 91.95$ K for ^{135}Ba and ^{138}Ba, respectively. Hence, for the Ba isotopes we find $T_c(^{138}Ba) - T_c(^{135}Ba) = 0.1$ K. As with the Cu isotopes, we find no significant shift in T_c by Ba isotope substitution. It is interesting to note that the Ba isotope samples shown in Fig. 2 have T_c's approximately 2 K higher than the T_c's corresponding to the Cu isotope samples. This difference is due only to the slightly different annealing conditions for the two sets of samples. ^{135}Ba and ^{138}Ba isotope samples prepared using exactly the same conditions as were used for the Cu samples of Fig. 1 were found to have T_c's near 90.0 K, again with no significant shift between the Ba samples.

For $\alpha = 0.5$, T_c is expected to decrease by 1.0 and 1.4 K for the Ba and Cu substitutions, respectively. However, our experiments demonstrate that there exists no isotope shift for either Cu within 0.2 K or Ba within 0.1 K in $YBa_2Cu_3O_7$. Within these limits, we find for Cu isotopes $\alpha = 0 \pm 0.07$ and for Ba isotopes $\alpha = 0 \pm 0.10$.

The lack of an isotope effect in $YBa_2Cu_3O_7$ for each of the elements may be examined in the context of conventional phonon-mediated electron pairing within the BCS theory. Here, we consider the possibility of obtaining the observed null isotope shift for various strengths of the electron-phonon coupling λ. It is convenient to consider three ranges of phonon coupling: $\lambda < 1.25$, $\lambda > 15$, and $1.25 < \lambda < 15$. Within these ranges, we consider the limits on the parameters of the electron-electron interaction that arise from the constraints of the observed T_c and the lack of an observed isotope effect.

For $\lambda < 1.25$, two square-well solutions for T_c and α can be obtained analytically. The McMillan[8] equation is representative of these solutions which have the generic form

$$T_c \propto \omega_D \exp[-1/(\lambda^* - \mu^*)] \; ; \qquad \alpha = \tfrac{1}{2}\left[1 - \left(\frac{\mu^*}{\lambda^* - \mu^*}\right)^2\right] , \tag{1}$$

where $\lambda^* = \lambda/(1+\lambda)$, μ^* is the renormalized Coulomb interaction, and ω_D is the phonon cutoff frequency. The parameter $\alpha \to 0$ as $\mu^* \to \lambda^*/2$ or $\mu^* \gg \lambda^*$ (unphysical in a two square-well BCS phonon model). For $\lambda < 1.25$, this condition cannot be satisfied if $T_c = 90$ K even for the largest λ in this range.

In the range $\lambda > 15$, Kresin, Gutfreund, and Little[9] used a 2×2 matrix equation in the Matsubara representation and found the Allen-Dynes result[10] $T_c = 0.18\lambda_{\rm eff}^{1/2}\Omega$, where Ω is the phonon frequency in an Einstein spectrum, and

$$\lambda_{\rm eff} = \lambda[1.2(1 + 2.23\mu^* + 1.08\mu^{*2})^{1/2} - 0.2 + 1.24\mu^{*2}]^{-1} . \tag{2}$$

Solutions of this equation where the Einstein spectrum is assumed to represent an "average" phonon frequency yield $\alpha \approx 0$ and $T_c = 90$ K for unphysically large values of λ and μ^*.

An analytic expression for T_c in the range $1.25 < \lambda < 15$ can be obtained if a constant spectral function of the following form is used:

$$\alpha^2 F(\omega) = \begin{cases} \lambda/2, & \text{if } 0 < \omega < \Omega_{\rm max}, \\ 0, & \text{otherwise.} \end{cases} \tag{3}$$

This model with $\mu^* = 0$ yields

$$T_c = \Omega_{\rm max}(e^{2/\lambda} - 1)^{-1/2}/(2\pi) \tag{4}$$

if only a 1×1 Matsubara matrix is used.[10] This equation has the same form as a numerical fit introduced by Kresin[11] for arbitrary λ. As shown in Fig. 3, Eq. (4) gives

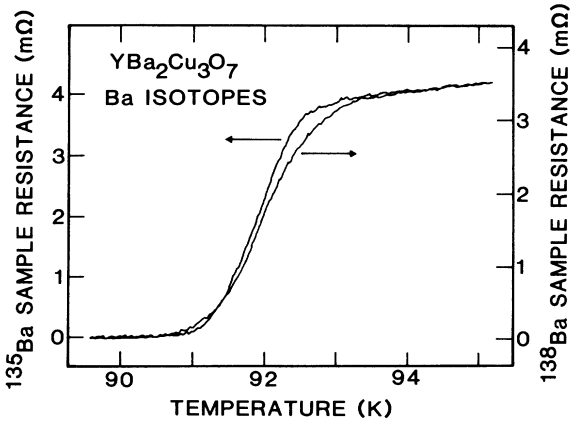

FIG. 2. R vs T for $YBa_2Cu_3O_7$ prepared with ^{135}Ba and ^{138}Ba. No isotope effect is observed.

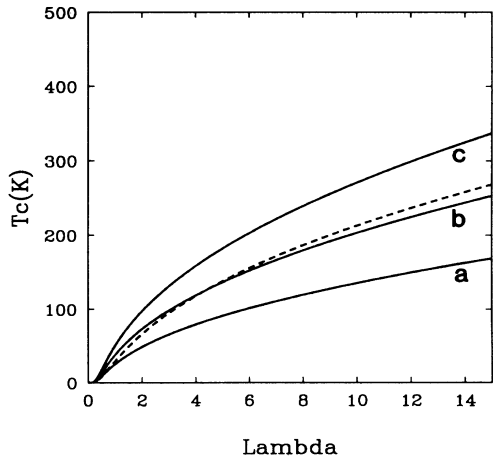

FIG. 3. T_c vs λ calculated numerically (broken curve), and from the equation derived in the text (solid curves); (a) $\Omega_{\rm max} = 400$ K, (b) $\Omega_{\rm max} = 600$ K, (c) $\Omega_{\rm max} = 800$ K.

a reasonable representation of $T_c(\lambda)$ for $\mu^*=0$ over a large range of λ. Comparison of Eq. (4) for $\Omega_{max}=400$, 600, and 800 K is made with the numerical solution using the phonon spectrum described below.

Since Eq. (4) is not valid for large μ^*, we resort to a numerical solution of the Eliashberg equations to search for an $\alpha=0$ and $T_c=90$ K solution. To do this, we have used a model phonon spectrum based on the Raman data on $YBa_2Cu_3O_7$ of Hemley and Mao[12] assuming a constant electron-phonon interaction. The Eliashberg equations were solved in the Matsubara representation using large enough matrices to ensure convergence. We calculated the isotope effect in this range of λ by assuming the functional form $T_c \propto \omega_D g(\lambda,\mu^*)$, where g is evaluated numerically. In this case, the isotope effect is given by

$$\alpha=\frac{1}{2}\left[1+\mu^{*2}\frac{d\ln g(\lambda,\mu^*)}{d\mu^*}\right]. \quad (5)$$

Within this model, we find solutions to the Eliashberg equations with $T_c=90$ K for all $\lambda \geq 2.9$. However, when the entire phonon spectrum is shifted to simulate the effect of isotope substitution, we find no numerical solution that can yield $\alpha=0$ and T_c near 90 K. Therefore, we simulate the substitution of a single element (Ba, Cu, or O) by shifting only a portion of the phonon spectrum. For Ba or Cu substitution, solutions with $T_c=90$ K and α within the experimental limits exist. A solution for the oxygen-isotope shift places more stringent constraints on λ and μ^* as will be discussed here. For ^{18}O substitution, the high-frequency phonon peaks seen by Batlogg *et al.*[6] are shifted. Using these shifts, we find a solution with $\alpha=0\pm0.02$ but $\lambda>30$. We note that since the phonon density of states is taken from Raman spectra, only a subset of phonon modes is used. Figure 4 shows the isotherm for $T_c=90$ K and the area within which $\alpha=0\pm0.02$ for simulated oxygen substitution. At large λ, the value of μ^* for $\alpha=0$ appears to saturate in agreement with the previous discussion for the strong-coupling limit. As is shown in Fig. 4, when shifting only ^{18}O peaks there are no solutions with $T_c=90$ K and $\alpha=0$ for $\lambda<15$. For $\lambda>15$, a solution can be found at $\lambda\approx35$ with $\mu^*\approx0.47$.

We have found that the complete absence of an isotope effect observed in the high-T_c compound $YBa_2Cu_3O_7$ can still be explained within conventional phonon-mediated electron pairing using a model that simulates the effect of substituting isotopes of a single element. However, the values of λ and μ^* which reproduce the experimental results are restricted to unphysical ranges. Hence, it is unlikely that superconductivity in $YBa_2Cu_3O_7$ can be explained by solely phonon-induced electron pairing unless material properties are considered.[13] We also note that because the Raman spectrum was used in the calculation, long-wavelength phonons are over represented.

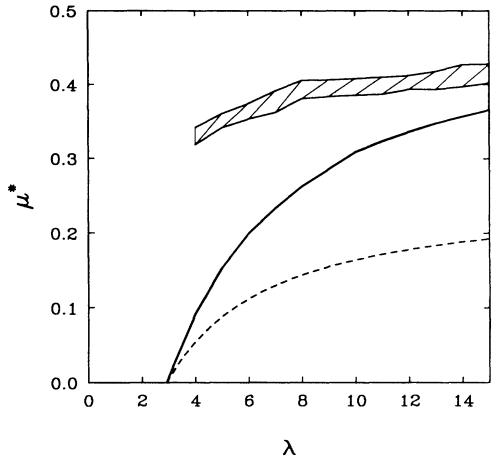

FIG. 4. Values of λ and μ^* for which $T_c=90$ K from numerical calculations (solid curve) and from a two square-well model (dashed curve). The shaded area represents solutions with $\alpha=0\pm0.02$ found numerically by shifting only the phonon spectrum peaks corresponding to oxygen vibrations. An intersection of the solid curve with the shaded area would indicate values of λ and μ^* consistent with phonon-mediated superconductivity in $YBa_2Cu_3O_7$.

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