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Oxygen isotope study of $YBa_2Cu_3O_7$

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The magnitude of the oxygen isotope effect in the high-T_c superconductor $YBa_2Cu_3O_7$ has been determined by substitution of ^{18}O for ^{16}O. A series of cross exchanges was performed on high-quality polycrystalline specimens to eliminate uncertainties due to sample heat treatments and sample inhomogeneities. Magnetic measurements suggest a relative isotope shift for the bulk material of -0.17 ± 0.03 K at 80% ^{18}O substitution, yielding $\alpha_{\text{bulk}} = 0.019 \pm 0.004$ where $T_c \sim M^{-\alpha}$ and M is the oxygen mass. Resistivity measurements in freshly prepared specimens reveal filamentary superconductivity 1 or 2 K above the bulk superconducting transition temperature. The isotope shift associated with the filamentary superconductivity is similar to but slightly larger than the bulk shift: $\alpha_{\text{fil}} = 0.028 \pm 0.003$. The filamentary superconductivity is time dependent and disappears several months after sample preparation. We show that the above values of α are inconsistent with the standard three-dimensional phonon-mediated Bardeen-Cooper-Schrieffer theory, and discuss implications for alternative possibilities.

I. INTRODUCTION

The spectacularly high transition temperatures of the newly discovered classes of oxide superconductors[1-3] have resulted in suggestions that the superconductivity in these materials may be fundamentally very different from that of the "conventional" superconductors. The Bardeen-Cooper-Schrieffer (BCS)[4] theory of phonon-mediated electron pairing may not be adequate to explain superconductivity within these new materials. Shapiro step experiments[5] on $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$, which exploit intrinsic ac Josephson effects within polycrystalline specimens, have clearly indicated that a fundamental charge $q = 2e$ is associated with the superconducting state. Although most researchers believe that this result demonstrates that electron pairing does occur, the specific pairing mechanism (phonon or nonphonon) is generally considered to be an open question.

The dependence of the superconducting transition temperature T_c on isotopic mass M in the host lattice has been one of the most revealing tests for phonon-mediated pairing. The original isotope effect experiments[6] in elemental mercury showed that $T_c \sim M^{-\alpha}$, with $\alpha = 0.5$. This discovery provided one of the important clues which resulted in the BCS theory of superconductivity. According to the simple BCS model, T_c is directly proportional to the Debye frequency ω_D, which in turn varies as $M^{-0.5}$ in an ideal harmonic solid. When the electron-phonon interaction and the Coulomb repulsion are treated separately in a two-square-well model[7] within BCS theory, α may be reduced from 0.5 and assume negative values. However, within this model α cannot be greater than $+0.5$.[8] Indeed, isotope studies in conventional superconductors find α ranging from 0.5 (mercury) to -2.2 (α-uranium).[9] Interestingly, for zirconium and ruthenium, $\alpha = 0$, which can be shown to be consistent with phonon-mediated electron pairing if one assumes a two-square-well model and takes into account specific normal-state and superconducting properties of the individual materials.

Recently, several studies have been performed to examine isotope effects in oxide superconductors. The first experiments[10,11] involved oxygen isotope substitution in $YBa_2Cu_3O_7$, and found no or very little shift, with $\alpha \cong 0.0 \pm 0.03$. This small value of α is not easily explained within the standard two square well model if $T_c \sim 90$ K, and is thus suggestive of a nonphonon pairing mechanism. Later studies,[12-14] on the other hand, indicated that for oxygen isotope substitution in $YBa_2Cu_3O_7$ α might be as large as 0.12, or even greater than 3.5. Hence, the findings to date are contradictory. Since different pairing mechanisms yield different values of α, it is important to establish the magnitude of the isotope shift.

We report here on a detailed study of the oxygen isotope effect in $YBa_2Cu_3O_7$, where up to 94% of the ^{16}O in the sample was replaced by ^{18}O. Multiple cross exchanges of oxygen isotopes were performed in high-quality sample-control pairs to eliminate T_c shifts not associated with isotopic mass. Time-dependent effects were also studied by monitoring transition temperatures for various isotopically substituted samples over a period of five months.

We find that a small but finite oxygen isotope effect occurs in $YBa_2Cu_3O_7$. Magnetic measurements indicate that for the bulk material $\alpha_{\text{bulk}} = 0.019 \pm 0.004$. Resistivity measurements in freshly prepared samples show evidence for filamentary superconductivity occurring 1–2 K above the bulk superconducting transition temperature. The isotope shift associated with the filamentary superconductivity is similar to but slightly larger than the bulk shift: $\alpha_{\text{fil}}=0.028\pm0.003$. The transition temperature for filamentary superconductivity is not stable, but decays smoothly toward the bulk transition temperature over a period of several months. Our observed values of α are within the error limits of several previous $YBa_2Cu_3O_7$ oxygen isotope studies,[10,11,15,16] but are inconsistent with other findings.[12–14] We show that our values of α cannot be explained within a standard three-dimensional phonon-mediated pairing model, and we examine other possible mechanisms.

The remainder of this paper is organized as follows: In Sec. II we review previous isotope-effect studies in high-T_c oxide superconductors, with emphasis on $YBa_2Cu_3O_7$. Section III gives details on sample preparation, isotopic exchange, T_c measurement, and isotopic content analysis relevant to the present study. Our isotope shift results are presented in Sec. IV, and discussed in Sec. V. A conclusion follows in Sec. VI.

II. BACKGROUND OF HIGH-T_c ISOTOPE STUDIES

The first isotope studies on high-T_c oxide superconductors were oxygen isotope substitution experiments performed on the $YBa_2Cu_3O_7$ structure. Batlogg *et al.*[10] substituted ^{18}O isotopes in $YBa_2Cu_3O_7$ and in $EuBa_2Cu_3O_7$ by heating samples to 550 °C in vacuum, removing approximately 10% of the oxygen, and heating again in an $^{18}O_2$ atmosphere. After 3 cycles, 74% ± 7% of the ^{16}O had been substituted with ^{18}O, as determined by Rutherford backscattering spectroscopy. They observed resistive shifts of -0.3 to -0.4 K in T_c, but observed no shifts in the magnetization data and, therefore, set a limit on the isotope shift of $\alpha=0.0\pm0.02$. A Raman line at 500 cm^{-1} that was assigned[17] to the O(1) site which bridges the inequivalent Cu atoms gave isotope shifts of about 4% demonstrating that at least some of the phonon modes were isotope shifted. Bourne *et al.*[11] substituted ^{18}O for ^{16}O in $YBa_2Cu_3O_7$ by heating a sample at 950 °C in an ^{18}O atmosphere. An identical heat treatment was performed in ^{16}O on another sample derived from the same parent pellet. The oxygen isotope content was measured with temperature-programmed desorption and with 50% (random) removal of the total oxygen content; 90% of the desorbed oxygen was found to be ^{18}O. Within an experimental uncertainty of ±0.3 K, no isotope effect was observed in both magnetization and resistivity measurements, yielding $\alpha=0.0\pm0.027$.

Leary *et al.*[12] reported a finite oxygen isotope shift in $YBa_2Cu_3O_7$. Using a gas-exchange technique similar to that of Bourne *et al.*, they obtained ^{18}O enrichments of 73%–90% (determined by thermally programmed desorption), and identified shifts in T_c of -0.3 to -0.5 K from magnetization data. The shifts in T_c were reversed in one sample and partially reversed in a second sample by resubstituting ^{16}O for the ^{18}O. The same group later reported magnetization data[13] suggestive of ^{18}O isotope shifts of -0.5 to -0.9 K for 67% ^{18}O enrichment, yielding $\alpha=0.07$–0.12. The isotope shifts determined by this group lie outside the original error limits set by Batlogg *et al.* and Bourne *et al.*

Morris *et al.*[15] attempted to reduce the error limits of the oxygen isotope effect in $YBa_2Cu_3O_7$. Since an applied magnetic field was found to substantially increase the measured transition width, they used applied field values of only 3 Oe during the magnetization measurement. A high-temperature gas-exchange technique was again used to substitute ^{18}O for ^{16}O. After measuring the T_c's, the isotope species of the two samples were reversed with another high-temperature gas exchange treatment and the T_c's were again determined. With ^{18}O isotope enrichments of approximately 88% (estimated from sample weight changes), α was found to be 0.019 ± 0.005. The error limits were estimated from variations in ΔT_c at different points in the susceptibility versus temperature curves and from variations between the two annealing runs.

Lopdrup *et al.*[18] also performed gas-phase oxygen-isotope-exchange studies on $YBa_2Cu_3O_7$. Samples containing up to 95% ^{18}O enrichment (determined by thermally programmed desorption measurements) were initially reported[18] to have T_c's as much as 1 K lower than the corresponding ^{16}O samples, but subsequent work[16,19] revised these shifts to about -0.2 K, again giving $\alpha\approx0.02$. One sample prepared with 98% enriched $^{18}O_2$ gas was found to have 97% ^{18}O enrichment.

Reports have also emerged of extremely large oxygen isotope shifts in $YBa_2Cu_3O_7$. Ott *et al.*[14] prepared oxygen-isotope-enriched $YBa_2Cu_3O_7$ samples by dissolving Y, Cu, and $BaC^{16}O_3$ in ^{18}O- or ^{17}O-enriched HNO_3. The resistive midpoint transition temperatures were 93 K for the ^{16}O samples, 77 K for samples with ^{17}O, and 59 K for samples with 95% ^{18}O. The sample quality decreased dramatically with decreasing T_c's, with magnetic-susceptibility measurements showing transition widths of 40 K or more for the lower T_c's. A brief heat treatment in ^{16}O increased T_c from 59 to 77 K for an ^{18}O sample and from 77 to 90 K for an ^{17}O sample. The large T_c shifts reported by Ott *et al.* correspond to $\alpha\approx3.5$.

In $YBa_2Cu_3O_7$, isotope experiments have also been performed on the other atomic sites. In general, these experiments are less easily controlled since it is not possible to reversibly exchange isotopes on the Y, Ba, or Cu sites for a given sample. A new sample must be prepared for each isotopic species. Bourne, Zettl, Barbee, and Cohen[20] prepared $YBa_2Cu_3O_7$ with different Ba and Cu isotopes through a solid-state reaction process using Y_2O_3, $BaCO_3$, and CuO. HNO_3 was used to dissolve and mix the precalcined powder to yield sharp transitions. CuO with 99.6% ^{65}Cu and CuO with 99.7% ^{63}Cu were used for one pair of samples; $BaCO_3$ with 78.8% ^{135}Ba and $BaCO_3$ with 99.7% ^{138}Ba were used for another pair of samples. Through resistivity measurements the isotope shift was determined to be less than 0.2 K for Cu ($\alpha=0.0\pm0.07$) and less than 0.1 K for Ba ($\alpha=0.0\pm0.1$). Quan *et al.*[21] placed similar bounds on the isotope shift for Cu ($\Delta T_c=0.0\pm0.2$ K) using both ac susceptibility and resistivity to characterize the transition. Hidaka, Matsui, and Nakagawa[22] studied the effects of ^{134}Ba (85% pure) substitution for naturally occurring Ba (70% ^{138}Ba). With an inductive technique, they determined that there was no isotope shift within 0.15 K.

Although no experiments have been reported for different Y isotopes in $YBa_2Cu_3O_7$, the Y site has been substituted by a host of other rare-earth elements with very different masses.[23] Some T_c dependence on rare-earth species is observed, but there is no correlation between T_c and the ion mass. Hence, no obvious isotope effect is observed.

Oxygen isotope studies have also been performed on several high-T_c oxides distinct from the $YBa_2Cu_3O_7$ structure. For $La_{1.85}Sr_{0.15}CuO_4$, Cohen, Morris, Stacy, and Zettl,[24] Batlogg *et al.*,[25] Faltens *et al.*,[26] zur Loye *et al.*,[13] and Bourne *et al.*[27] have reported significant shifts for 70%–80% ^{18}O enrichment corresponding to α between 0.1 and 0.2. For $La_{1.85}Ca_{0.15}CuO_4$, zur Loye *et al.* report shifts of -1.3 to -1.6 K with 75% ^{18}O enrichment, yielding $\alpha = 0.73-0.90$; the same group has reported oxygen isotope shifts corresponding to similar large values of α for $BaPb_{0.75}Bi_{0.25}O_3$. Values of α greater than 0.5 have never before been observed for any superconductor, and such values are inexplicable within conventional BCS theory, regardless of the value of T_c. Batlogg *et al.*,[28] on the other hand, report $\alpha = 0.22 \pm 0.03$ for oxygen isotope substitution in $BaPb_{0.75}Bi_{0.25}O_3$.

Recent studies of oxygen isotope substitution in Bi-Sr-Ca-Cu-O indicate $\alpha = 0.026$ and 0.048 for the $T_c = 110$ and 85 K phases, respectively.[29]

Thus, despite much work, the determination of more precise estimates of the magnitude of the isotope effect in most high-T_c oxide superconductors is still an important area of research. Part of the difficulty in achieving this goal is in producing sufficiently well-characterized samples with sharp and reproducible transitions. Some ambiguity may even arise from data interpretation. For example, in deducing the finite oxygen isotope shift of -0.5 K in $YBa_2Cu_3O_7$, Leary *et al.*[12] compare magnetization curves which differ by the quoted amount near the transition onset, but cross near the transition midpoint (suggestive of a zero isotope effect with large error bars).

Reliable determination of α with small error limits necessitates careful control of sample preparation, measurement, and data interpretation. In the present study of the oxygen isotope effect in $YBa_2Cu_3O_7$, we have attempted to lower the error limits for each of these contributions.

III. EXPERIMENT

A. Sample preparation

Polycrystalline samples of $YBa_2Cu_3O_7$ were produced by the solid-state reaction of high purity (99.999%) powders of Y_2O_3, $BaCO_3$, and CuO. All grinding was done in an agate mortar in a nitrogen-filled glove box to maintain high purity and to reduce the deleterious effects of water vapor. The precalcining and subsequent sintering heat treatments used gold foil as a substrate to minimize contamination. The mixed powders were heated to 850 °C, held for 15 h, then cooled over 8 h to room temperature. The resulting blackened powder was reground and calcined at 930 °C for 15 h then cooled to room temperature over 9 h. This powder was reground, pelletized, and sintered at 930 °C for 15 h then cooled over 9 h. After the final heat cycle the pellets were stored with a desiccant, P_2O_5, in vials and the vials were kept in an evacuated desiccator.

Samples of $YBa_2Cu_3O_7$ produced by the above procedure were characterized by magnetic-susceptibility and dc resistivity measurements. T_c's were typically near 92 K with sharp transitions. Full magnetic transition widths were 2–3 K, with 50% Meissner signals.

B. Isotope exchange and measurement technique

The isotope exchange was achieved with a high-temperature gas-diffusion technique and after each exchange the samples were characterized magnetically and resistively. To reduce the effects of any existing sample inhomogeneities in the initial samples or differences (unrelated to isotopic species) introduced during the high temperature exchange process, we designed an experimental procedure which averaged out such deviations. As outlined in Fig. 1, four $YBa_2Cu_3O_7$ pellets (two pairs) of nearly identical weights were chosen and each pellet underwent several oxygen isotope exchanges. Within each pair, one sample was designated primarily for resistive tests (R_a or R_b) and one sample was designated primarily for magnetic tests (M_a or M_b).

To accomplish isotopic exchange, the samples were placed on platinum boats in identical quartz tubes. The quartz tubes were placed side-by-side and equidistant from the coils of a small tube furnace. The quartz tubes were coupled to similar static gas reservoirs containing 99.99% pure ^{16}O and 95% (occasionally 99%) enriched ^{18}O, respectively. At room temperature the pressures in the two reservoirs were 740 Torr and during the exchange, they would rise to 750 Torr. In each of the first three exchanges, the samples were heated to 950 °C over 2 h, held for 10 h, cooled to 300 °C over 9 h, then cooled in the oven to room temperature. In one test, the ^{16}O and ^{18}O gases were switched between reservoirs to ensure that no asymmetries existed in the isotope exchange apparatus; none were found.

After each exchange, a small chip was removed from each of the two samples designated for resistance measurements (R_a and R_b). The chips were mounted in the standard four-probe resistance measurement configuration with silver paint contacts, and placed side-by-side on a solid copper probe in close proximity to a calibrated diode thermometer. The samples were cooled with a helium gas flow system. The resistance versus temperature curve for each sample did not change when the sample positions on the copper probe were interchanged, indicating negligible thermal gradients across the copper probe. Each resistance measurement at a given temperature was performed with forward and then reversed dc current (typically 1 mA) to ensure freedom from thermal electromotive forces.

We measured the magnetic susceptibility (usually of samples M_a and M_b) using a modified SHE model VTS-805 superconducting quantum interference device (SQUID) magnetometer. The modifications allowed the sample temperature to be regulated with greater precision

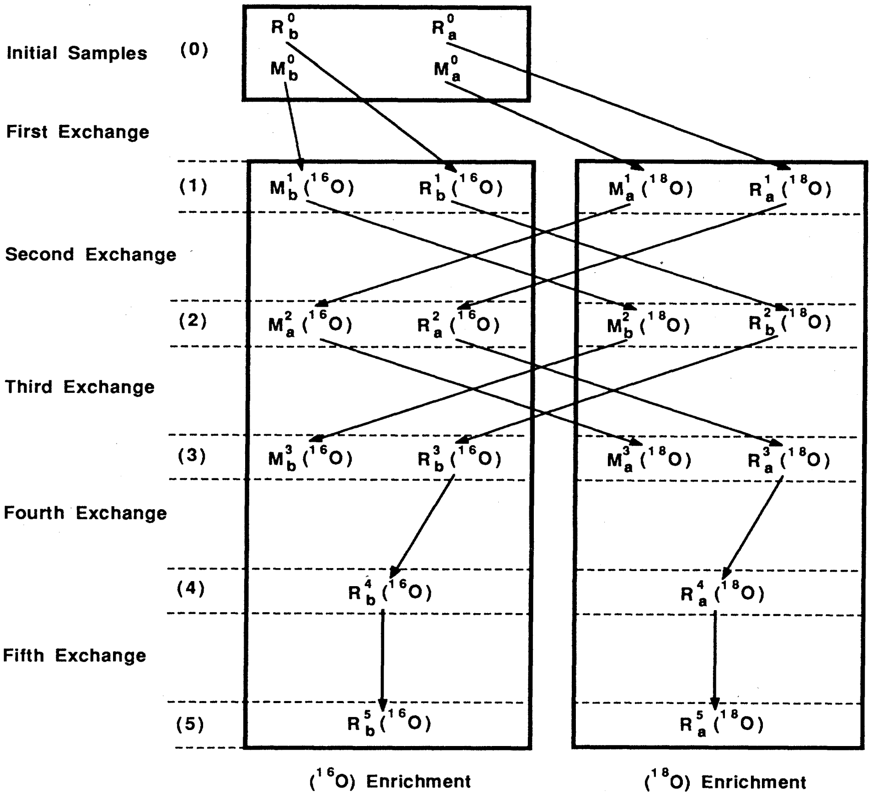

FIG. 1. Schematic of ^{16}O and ^{18}O isotope exchange. R and M refer to samples used for resistive and magnetic tests, respectively. Subscripts differentiate between different samples and superscripts refer to the last exchange that the sample has undergone. The numbers in parentheses refer to the associated curves in Figs. 2 and 3.

and determined with greater accuracy than possible with the standard magnetometer configuration. Samples M_a and M_b were kept geometrically intact throughout the series of isotopic exchanges and magnetic measurements to avoid errors from changing the geometrical demagnetization factors for the samples. To remove temperature gradients within the sample tube, we stabilized the system at a temperature slightly above the transition for 30 min. A computer controlled the slow downward temperature drift (0.01 K/min) for the samples in the magnetometer and recorded their magnetization typically 12 times per 0.1°. Subsequent tests have verified that the temperature of the samples was accurate to 0.05 K and repeatable between runs to 0.03 K. The magnetic field was typically 2–3 Oe and was calibrated before each run by measuring the magnetization of a small superconducting tin sphere. The susceptibility of a given sample at $T=40$ K, well below the transition, varied by as much as 10% between repeated magnetization measurements due to flux-trapping effects, but the susceptibility curves for any given sample at higher temperatures near T_c were found to be repeatable.

Isotopic determination was done both by weighing the samples before and after the exchange and by the more accurate method of laser-assisted ion mass analysis (LIMA). In the LIMA technique, a 4-eV laser vaporizes and ionizes a small portion of the sample. Constituents of the resulting plasma are driven through a time of flight spectrometer, thus determining (within approximately 1% or 2% accuracy) relative isotopic content of the sample. The samples were examined at different locations across their surface, and as a function of depth into the bulk. No evidence for inhomogeneous isotopic enhancement was found. For analysis purposes, we shall use the LIMA results for the isotopic enrichment, which agree to within $\sim 10\%$ of those determined by sample weight changes.

IV. RESULTS

Figure 2 shows the results of resistive and magnetic measurements for the pure and isotopically exchanged $YBa_2Cu_3O_7$ samples. Graphs (0) show $R(T)$ and $\chi(T)$ for the samples as initially prepared. Graphs (1)–(3) show resistive and magnetic data for the sample sets following the first, second, and third exchanges, respectively (see Fig. 1). Ideally, the sample data plotted together should be identical in (0), and the curves for ^{16}O and ^{18}O enriched pellets in (1) should reflect directly any oxygen isotope shift. The curve for a given sample would then be expected to switch between the ^{16}O and ^{18}O positions in subsequent frames after each isotope exchange step. This ideal situation is not realized in Fig. 2 because the initial samples already show slightly different T_c's. Nevertheless, for each sample, both resistive and magnetic measurements exhibit a clear pattern of oscillation between a

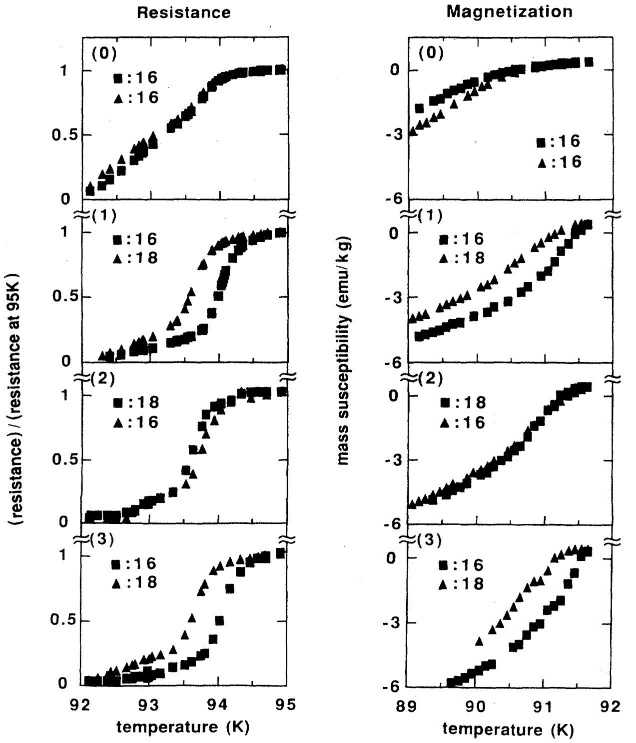

FIG. 2. Resistance vs temperature for samples R_a and R_b, and magnetization vs temperature for samples M_a and M_b: (0) immediately after initial preparation of the samples; (1) after the first isotopic exchange; (2) after the second exchange; (3) after the third exchange.

higher value of T_c for ^{16}O enrichment and a lower value of T_c for ^{18}O enrichment as one progresses from graphs (0) to (3).

Tables I and II summarize the isotope shift information drawn from the data illustrated in Fig. 2. For resistance samples R_a and R_b, the transition temperature was taken to be the temperature midway between the temperatures where the sample resistance was 90% and 50% of the normal state resistance at 95.05 K. For magnetization samples M_a and M_b measured after the second or third exchange, the transition temperature was taken to be the temperature midway between the temperatures where the sample magnetization was 10% and 50% of the superconducting state magnetization at 89.55 K. After initial preparation the onset temperature of the transition for the magnetization samples is about a degree lower than the onset after the samples had one or more exchanges; the transition temperatures after initial preparation were accordingly normalized to 88.45 K for the magnetization samples. We chose not to normalize the magnetization measurements to the values of the magnetic moment at lower temperatures because flux trapping was found to contaminate the measurements well below the transition temperature. Using these definitions of T_c, Table I gives the change in transition temperature for each sample after each isotopic exchange relative to its transition temperature before the exchange. The change in transition temperature could in principle be due to both an isotope effect and the annealing cycle; by subtracting the change in transition temperature for the ^{18}O sample from the change for the ^{16}O sample the effects of the annealing cycle are canceled. The relative T_c shift must be divided by two for the second and third exchanges to obtain the net shift since these are cross exchanges. The spread is the variation of the relative T_c shift over half the transition width according to the above definitions. The results of the LIMA measurements of isotopic enrichment are also shown in the table.

The resistive and magnetic data taken after the second and third exchanges are most appropriate for extracting a net isotope shift. The exchanges are both cross exchanges, and the data reveal sharp transitions and consistent ^{18}O isotope enrichments of approximately 80%. From Table I we determine from resistance measurements a net oxygen isotope shift in $YBa_2Cu_3O_7$ of -0.25 ± 0.02 K, and from magnetization measurements a net shift of -0.17 ± 0.03 K. In Sec. V below, we extrapolate these shifts to full oxygen isotope substitution and determine corresponding values of α.

After the three isotope exchanges discussed above, two additional exchanges were performed to increase the relative ^{18}O content of a particular specimen (sample R_a) as much as possible. The additional exchange sequences are also shown in Fig. 1. In the fourth exchange, the ~95% enriched ^{18}O from the third exchange experiment was reused in the ^{18}O arm of the exchange apparatus, and the samples were held at 950 °C for 25 h and cooled to 300 °C over 9 h. In the fifth exchange, the samples were held at

TABLE I. Isotope shift information for resistance samples.

		R_a			R_b		Relative
	ΔT_c (K)	Spread (K)	% Isotope enrichment	ΔT_c (K)	Spread (K)	% Isotope enrichment	T_c shift (K)
After first exchange	+0.303	0.205	75.3 (^{18}O)	+0.601	0.183	100 (^{16}O)	+0.298
After second exchange	+0.150	0.003	84.6 (^{16}O)	−0.379	0.007	73.3 (^{18}O)	+0.265
After third exchange	−0.017	0.084	84.3 (^{18}O)	+0.440	0.010	88.9 (^{16}O)	+0.229

TABLE II. Isotope shift information for magnetization samples.

	M_a		M_b		Relative
	ΔT_c (K)	Spread (K)	ΔT_c (K)	Spread (K)	T_c shift (K)
After first exchange	+0.285	0.065	+0.640	0.210	+0.355
After second exchange	+0.030	0.010	−0.255	0.015	+0.143
After third exchange	−0.095	0.045	+0.295	0.005	+0.195

950 °C for 40 h before cooling to 300 °C over 9 h, and the purity of the ^{18}O exchange gas was increased to 99% enrichment.

The results of the fourth and fifth exchanges are shown in Fig. 3, together with the results of the third exchange. The third exchange data, Fig. 3, graph (3), correspond to 84% enrichment of the ^{18}O sample. The isotopic enrichment for the ^{18}O sample after the fourth exchange was increased to 91%, and to 94% after the fifth exchange. Figure 3 shows a similar isotope shift between ^{16}O and ^{18}O samples following the fourth and fifth exchanges as was observed following the third exchange. This suggests that the few ^{16}O atoms which remain in the $YBa_2Cu_3O_7$ lattice in a typical ^{18}O substitution experiment do not by some unusual mechanism mask a large intrinsic isotope shift.

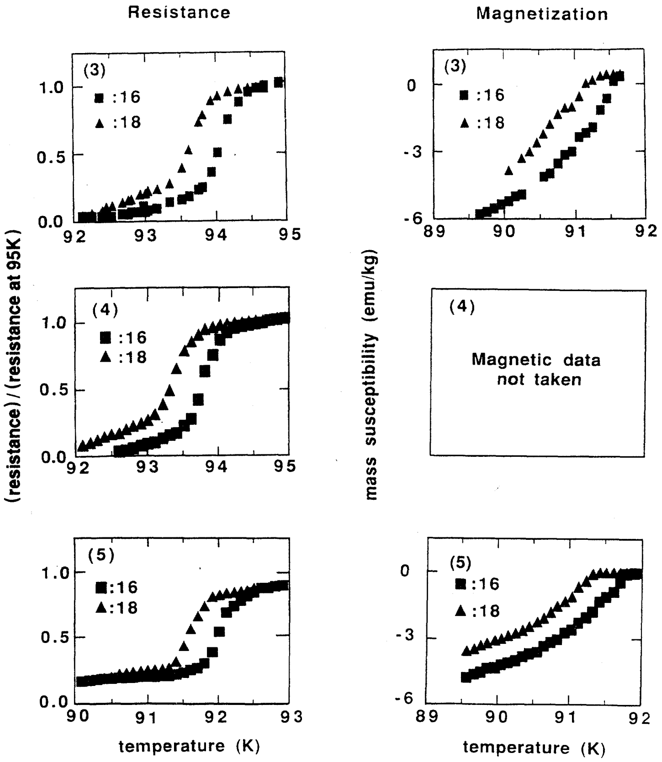

FIG. 3. Resistive and magnetic transitions of oxygen exchanged samples: (3) after third exchange, one week after initial production of the samples; (4) after fourth exchange, one month later; (5) after fifth exchange, five months after initial production. The magnetization measurement (3) was performed on samples M_a^3 and M_b^3 while (5) was performed on samples R_a^5 and R_b^5.

The data of Figs. 2 and 3 also illustrate interesting time-dependent phenomena. Although the isotope exchanges and measurements of Fig. 2 were all performed within several weeks of the initial sample synthesis, the measurements described in Fig. 3 span a period of five months. In Fig. 3, the data in graph (3) were recorded on fresh samples, two weeks after initial synthesis. The data of graphs (4) and (5) were recorded one and one half and five months after initial synthesis, respectively.

Figure 2 shows that the superconducting transition temperature determined resistively is consistently between 1 and 2 K higher than that determined magnetically for the corresponding sample. We identify the magnetic transition temperature as representing T_c for the bulk material. The higher resistive transitions are taken as evidence for filamentary superconductivity above T_c (bulk). Figure 3 shows that the bulk superconducting transition temperature is relatively time independent: the magnetization graphs (3) and (5) have nearly identical onset temperatures for a given isotope, even though the measurements were taken five months apart. On the other hand, the resistance data of Fig. 3 show a steady decrease in T_c with time. For example, the ^{16}O sample has a T_c near 94 K in graph (3), and a T_c near 92 K in graph (5). The later T_c corresponds to that determined magnetically for the same specimen. This indicates that the filamentary superconductivity is time dependent and disappears after several months. The resistive and magnetic transition temperatures coincide thereafter.

Apparently, resistive measurements near T_c test a small portion of the material (estimated from our magnetic data to be less than 0.3% volume fraction of the specimen) which is compositionally different from the bulk and undergoes "degradation" faster than the bulk. Over the span of five months, the bulk properties remained constant while the resistive transition shifted steadily downward. It seems likely that the filamentary superconductivity is restricted to regions of high oxygen or impurity mobility such as those between grains or within a small distance of the grain boundaries. Figures 2 and 3 and Table I show, however, that the filamentary superconductivity experiences an oxygen isotope shift similar to that of the bulk $YBa_2Cu_3O_7$ and that the relative shift remains constant in time.

V. DISCUSSION

A. Discussion of α

The results of our oxygen isotope cross-exchange experiments described in Fig. 2 and Tables I and II unequivocally demonstrate a small but finite superconducting transition temperature shift between ^{16}O and ^{18}O samples of $YBa_2Cu_3O_7$. The calculation of the appropriate α for full oxygen substitution from the observed T_c shifts is not immediately obvious for two reasons. First, our experiments did not achieve 100% ^{18}O replacement for ^{16}O, and second, oxygen constitutes only 54% of the total number of atomic sites in $YBa_2Cu_3O_7$. The first problem can be corrected by extrapolating our measured T_c shifts to 100% oxygen isotope replacement. The second complication must be addressed when comparison is made between our measured α and that predicted by various models.

Of the four inequivalent oxygen sites within the $YBa_2Cu_3O_7$ unit cell, one [O(1)] is singly occupied and three [O(2), O(3), O(4)] are doubly occupied. It is desired to extrapolate the measured T_c shift to an effective shift (and α) which would occur with complete substitution at each of the four sites. For each site, there will be a different shift of the transition temperature with complete ^{16}O to ^{18}O exchange. If there were nonuniform substitution of oxygen atoms, then a site on which T_c were particularly dependent could be left unsubstituted. For the chain site [O(1)] to be left unsubstituted, the sample must contain less than 86% ^{18}O, and for any other site, no more than 72% could be exchanged. With our 91% and 94% exchange achieved in the fourth and fifth exchanges, at least half of any particular site must have been substituted. From the constancy of the relative shifts, we deduce that incomplete substitution is not a serious concern in our isotope shift determination.

At least two methods can be used to extrapolate the measured T_c shifts to 100% isotopic substitution. In one method, one assumes that the mass that enters into $T_c \propto M^{-\alpha}$ is in fact an average over all similar sites; thus, for 75% ^{18}O substitution, a mass of 17.5 is used. Alternatively, one can divide the shift by the isotopic ratio (number of ^{18}O atoms)/(total number of oxygen atoms), to normalize the shift to 100% substitution. In practice, these two methods differ in the calculated value of α by only a few percent, less than the typical experimental error. Here, we use the latter method.

To determine α for the bulk material, we use the averaged shift obtained from magnetic measurements at approximately 80% ^{18}O enrichment: $\Delta T_c = -0.17 \pm 0.03$ K, with $T_c = 92$ K. This leads to an effective $YBa_2Cu_3O_7$ oxygen isotope exponent of $\alpha_{\text{bulk}} = 0.019 \pm 0.004$. The resistive data for similar ^{18}O enrichment yield an oxygen isotope effect relevant to the filamentary superconductivity in $YBa_2Cu_3O_7$. From $\Delta T_c = -0.25 \pm 0.02$ K and $T_c = 94$ K, we find $\alpha_{\text{fil}} = 0.028 \pm 0.003$. Hence, the isotope effect for the bulk material and that for the filamentary regions are very similar, and this suggests that the bulk and filamentary regions are structurally similar. Our value of α_{bulk} lies within the original error limits set by Batlogg *et al.*[10] and Bourne *et al.*[11] for oxygen isotope substitution in bulk $YBa_2Cu_3O_7$. Figure 4 gives a graphic summary of oxygen isotope effects reported to date for $YBa_2Cu_3O_7$.

Interpretation of the isotope shift is less straightforward in compounds than in elemental solids. Anharmonic and zero-point motion effects can cause anomalous changes in T_c upon isotopic substitution. In PdH, for example, substitution of D or T for H results in a substantial increase in T_c and a large negative value for α.[30] Even in the absence of these effects, the meaning of α in the relationship $T_c \propto M^{-\alpha}$ is not obvious. In superconducting compounds, α is conventionally expressed as $\alpha = \sum \alpha_i$ and $T_c \propto \prod M_i^{-\alpha_i}$ where M_i is the mass of the atom in the ith position within the unit cell. Since different lattice positions contribute to the phonon spectrum in different ways, the various α_i are unlikely to be equal. To perform a theoretical calculation of α_i, it would be necessary to know how each lattice site affects each portion of the phonon spectrum and which phonons were active in binding the electrons. More simply, an effective α' can be calculated by assuming an equal scaling of all atomic masses M_i by a factor γ: $M_i' = \gamma M_i$. The phonon spectrum will then scale in frequency as $\omega' = \omega/\gamma^{1/2}$, and the resulting shift in T_c can be used to define $\alpha' = -\Delta \ln T_c / \Delta \ln M = -\Delta \ln T_c / \ln \gamma$. The above definition of α_i ensures that in the limit of infinitesimal mass changes, $\alpha' = \sum \alpha_i$.

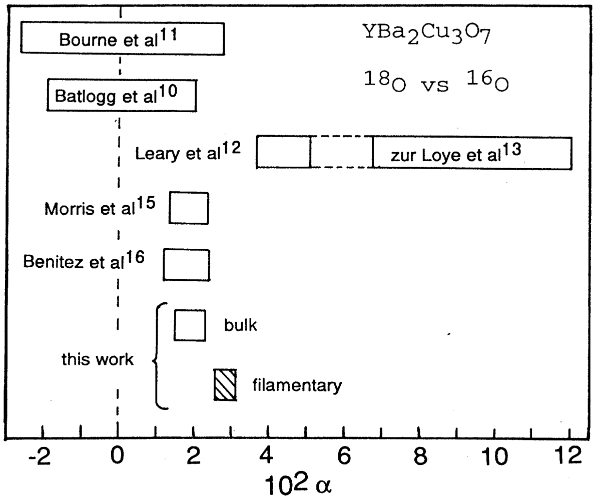

FIG. 4. Graphical plot of the reported values of the oxygen isotope exponent α in $YBa_2Cu_3O_7$. The appropriate reference is noted alongside the first author of a particular experiment.

In the particular case of oxygen substitution at the four inequivalent sites in $YBa_2Cu_3O_7$, we expect the resulting oxygen isotope exponent $\alpha_O = \alpha_{O(1)} + \alpha_{O(2)} + \alpha_{O(3)} + \alpha_{O(4)}$ to be nearly equal to the theoretically derived α' since oxygen is much lighter than the other elements. A one-square-well BCS model will not describe this compound since experiments with Ba,[20,22] Cu,[20,21] and rare earth elements[23] have shown that $\alpha' = \alpha_Y + \alpha_{Ba} + \alpha_{Cu} + \alpha_O < 0.5$.

The small observed value of α and the high-$T_c \sim 90$ K suggest the possibility that the electron pairing mechanism in $YBa_2Cu_3O_7$ differs from that of low transition temperature superconductors. We first examine the consequences of the observed isotope shift for three-dimensional BCS phonon-mediated pairing. We then discuss alternative models.

B. BCS theory

To test the applicability of the standard isotropic three-dimensional phonon-mediated model of superconductivity to $YBa_2Cu_3O_7$, we calculate transition temperatures and isotope shifts from the electron-phonon interaction spectrum $\alpha^2F(\omega)$ and the Coulomb repulsion parameter μ^* using the Matsubara representation[31] of the Eliashberg theory.[32] The isotope effect exponent α is not related to the electron-phonon matrix element which is also represented by an α in $\alpha^2F(\omega)$. We consider several different models of the electron-phonon interaction spectrum $\alpha^2F(\omega)$ to test the dependence of the isotope shift α on $\alpha^2F(\omega)$.

We consider a simple model of oxygen isotope substitution in which only the high-frequency peaks in $\alpha^2F(\omega)$ are shifted, and assume that the repulsive Coulomb interaction μ is independent of isotopic mass. Hence, the calculated isotope effects are obtained by simulating the change in the frequency of the phonons arising from the substitution of one isotope for another.

Since shifting the entire $\alpha^2F(\omega)$ spectrum would be appropriate only for calculating the isotope effect in the case of an elemental superconductor, we have also calculated the shifts resulting from shifting only the high-frequency half of $\alpha^2F(\omega)$ as a simple approximation for oxygen substitution. Figure 5 shows the calculated isotope effects for shifting the entire $\alpha^2F(\omega)$ spectrum. We find that the calculated values of the isotope effect are independent of the shape of $\alpha^2F(\omega)$ for small values of μ^* and exhibit only a small amount of scatter for extremely large values of μ^*, where μ^* is the renormalized Coulomb interaction evaluated at the root-mean-square phonon frequency. Therefore, we expect that small differences between our model spectra and the actual $\alpha^2F(\omega)$ in $YBa_2Cu_3O_7$ will not affect the calculated values of the isotope shifts significantly.

Using electron-phonon spectra similar to those presented in experimental data, we have calculated the isotope effect in $YBa_2Cu_3O_7$ with the goal of determining whether a standard phonon-mediated pairing in three dimensions can be responsible for superconductivity in the ceramic oxides. From the results presented above, we assume the following values for $YBa_2Cu_3O_7$: $\alpha = 0.023 \pm 0.008$ and $T_c \approx 93$ K.

For $YBa_2Cu_3O_7$, the experimental results appear to exclude a solely harmonic phonon-mediated isotropic three-dimensional model. Figure 6 shows the results for $YBa_2Cu_3O_7$, with the $T_c = 93$ K isotherm and the lines of constant $\alpha \approx 0.023 \pm 0.008$. When the entire spectrum is shifted, no values of the parameters λ and μ^* will yield the necessary values of α and T_c. When we consider a simulated oxygen substitution by shifting only the high-frequency phonon modes, we find that the intersection of the T_c isotherm and the constant-α line occurs for unphysically large $\lambda > 30$. We therefore conclude that our standard three-dimensional harmonic phonon-mediated model is incapable of describing superconductivity in $YBa_2Cu_3O_7$.

C. Variations on electron-phonon coupling

Several attempts have been made to explain the experimental results by changing features of the standard isotropic three-dimensional model. The idea of reduced dimensionality, based on the one-dimensional chains or two-dimensional planes occurring in high-T_c superconductors, could possibly explain both the high-T_c and small α seen. Labbe and Bok[33] have proposed a two-dimensional model where the Fermi energy occurs near a logarithmic divergence (van Hove singularity) in the electronic density of states, resulting in a large λ and a small α, since the relevant energy scale is the width of the peak in the density of states rather than ω_D.

A second variation on the standard model is the con-

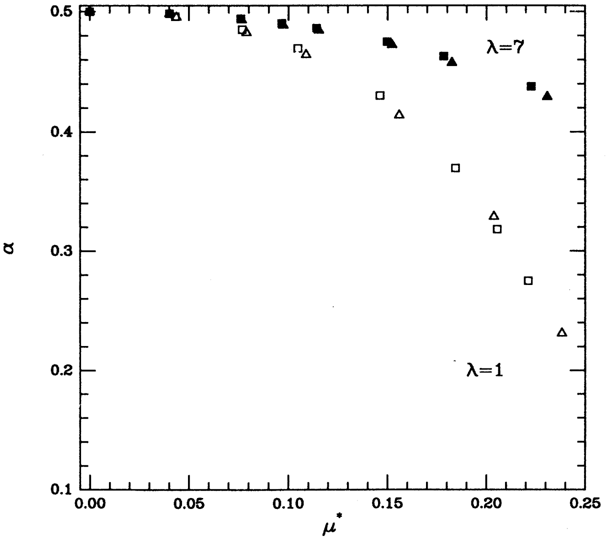

FIG. 5. Values of α calculated for $\lambda = 1$ (open symbols) and $\lambda = 7$ (filled symbols) using an Einstein phonon spectrum (squares) and a model $La_{1.85}Sr_{0.15}CuO_4$ spectrum (triangles). At constant λ, the values of α are nearly independent of the shape of the phonon spectrum.

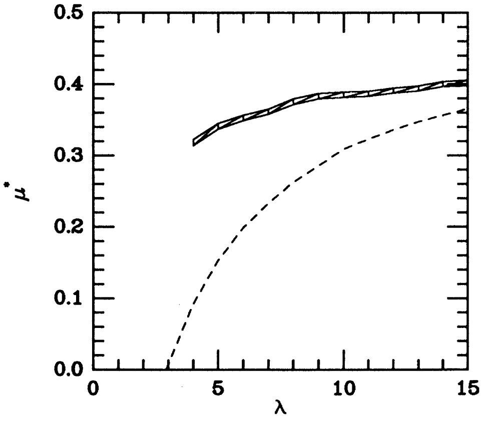

FIG. 6. Values of λ and μ^* for which $T_c = 93$ K from numerical calculations (dashed curve). The shaded area represents solutions with $\alpha = 0.023 \pm 0.008$ found numerically by shifting only the phonon spectrum peaks corresponding to oxygen vibrations. An intersection of the solid curve with the shaded area would indicate values of λ and μ^* consistent with phonon-mediated superconductivity in $YBa_2Cu_3O_7$.

sideration of anharmonic effects, perhaps due to defects or zero-point motion. Hardy and Flocken[34] calculate that λ may be increased dramatically if the oxygen atoms vibrate within a double-well potential, but such a mechanism should not suppress the isotope shift α. Phillips[35] considers a model based on ordered oxygen defects where the defects move so as to optimize T_c. Near a maximum of T_c, the isotope shift should be nearly zero as seen in $YBa_2Cu_3O_7$. Fisher[36] has commented that the effect of the change in zero-point motion on the Cu-O hopping parameter due to isotopic substitution could itself account for the observed shift in T_c in the oxide superconductors.

D. Nonphonon mechanisms

Many proposed explanations of high-T_c superconductivity[37–39] explain the experimental results by considering an additional non-phonon-mediated coupling between electrons. These new coupling mechanisms are mediated by electronic excitations (such as plasmons, excitons, etc.) which are independent of isotopic mass and of much higher energy than phonons; therefore, the combination of high T_c and small α can be satisfied easily within these models. Cohen *et al.*[38] examine a three square-well model with renormalization and calculate T_c and α. With the inclusion of higher-energy nonphonon interactions, they find possible agreement with the observed values of T_c and α for $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$ and speculate that the differences between the materials could be explained solely by changing the strength of the nonphonon interactions. A recent measurement[28] of $\alpha = 0.22 \pm 0.03$ for Pb-Bi-Ba-O is nearly in agreement with predictions by Cohen Cohen, and Cohen.[38]

VI. CONCLUSION

Our results conclusively show that there exists a small but finite oxygen isotope shift in $YBa_2Cu_3O_7$. In samples with ^{18}O substituted for ^{16}O at approximately 80% of the atomic sites, magnetic measurements indicate a shift $\Delta T_c(\text{bulk}) = -0.17 \pm 0.03$ K. dc resistance measurements on similar samples show a transition temperature 1–2 K higher than the bulk transition temperature, suggesting that filaments of a distinct material are present in the samples. The isotope shift for these filaments is $\Delta T_c = -0.24 \pm 0.02$ K. After adjusting these values for full oxygen substitution, we find, respectively, for the bulk and filamentary superconductivity $\alpha_{\text{bulk}} = 0.019 \pm 0.004$ and $\alpha_{\text{fil}} = 0.028 \pm 0.003$, where $T_c \propto M^{-\alpha}$. These results are within the error limits of several previous $YBa_2Cu_3O_7$ oxygen isotope studies,[10,11,15,16] but are inconsistent with other reports.[12–14]

We find that the small values of α and high T_c reported here can only be explained within the standard three-dimensional phonon-mediated BCS theory if an unphysically large electron-phonon coupling constant λ is used. It appears that additional features (such as anisotropy, anharmonicity, or an additional nonphonon interaction) will be necessary to explain superconductivity in $YBa_2Cu_3O_7$.

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

[2] 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).

[3] H. Maeda, Y. Tanaka, M. Fukuton, and T. Asano, Jpn. J. Appl. Phys. Lett. **27**, L209 (1988).

[4] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957); **108**, 1175 (1957).

[5] D. Estève, J. M. Martinis, C. Urbina, M. H. Devoret, G. Collin, P. Monod, and A. Revcolevschi, Europhys. Lett. **3**, 1237 (1987).

[6] E. Maxwell, Phys. Rev. **78**, 477 (1950); C. A. Reynolds, B. Serin, W. H. Wright, and L. B. Nesbitt, *ibid.* **78**, 487 (1950).

[7] N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (Consultants Bureau, Inc., New York, 1959), Sec. 6.3.

[8] J. C. Swihart, Phys. Rev. **116**, 45 (1959).

[9] R. Meservey and B. B. Schwartz, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), p. 126.

[10] 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); **60**, 754 (1988).

[11] L. C. Bourne, M. F. Crommie, A. Zettl, Hans-Conrad zur Loye, S. W. Keller, K. L. Leary, Angelica M. Stacy, and Don Morris, Phys. Rev. Lett. **58**, 2337 (1987).

[12] Kevin J. Leary, Hans-Conrad zur Loye, Steven W. Keller, Tanya A. Faltens, William K. Ham, James N. Michaels, and Angelica M. Stacy, Phys. Rev. Lett. **59**, 1236 (1987).

[13] Hans-Conrad zur Loye, Kevin J. Leary, Steven W. Keller, William K. Ham, Tanya A. Faltens, James N. Michaels, and Angelica M. Stacy, Science **238**, 1558 (1987).

[14] K. C. Ott, J. L. Smith, J. O. Willis, R. M. Aikin, E. Garcia, M. Goldblatt, W. B. Hutchinson, G. H. Kwei, C. B. Pierce, J. F. Smith, J. D. Thompson, and T. E. Walker (unpublished).

[15] Donald E. Morris, Randy M. Kuroda, Andrea G. Markelz, Janice H. Nickel, and John Y. T. Wei, Phys. Rev. B **37**, 5936 (1988).

[16] E. L. Benitez, J. J. Lin, S. J. Poon, W. E. Farneth, M. K. Crawford, and E. M. McCaron, Phys. Rev. B **38**, 5025 (1988).

[17] G. A. Kourouklis, A. Jayaraman, B. Batlogg, R. J. Cava, M.

Stavola, D. M. Krol, E. A. Rietman, and L. F. Schneemeyer, Phys. Rev. B **36**, 8320 (1987).

[18] E. Lopdrup, M. Crawford, W. E. Farneth, R. K. Bordia, E. M. McCarron, and S. J. Poon, Bull. Am. Phys. Soc. **33**, 558 (1988).

[19] E. Lopdrup (private communication).

[20] L. C. Bourne, A. Zettl, T. W. Barbee III, and Marvin L. Cohen, Phys. Rev. B **36**, 3990 (1987).

[21] Lin Quan (C. Lin), Wei Yu-nian, Yan Qi-wei, Chen Geng-hua, Zhang-zin, Ning Tai-gang, Ni Yong-ming, Yang Qian-sheng, Liu Chao-xin, Ning Tai-shang, Zhao Jin-Kue, Shao You-yu, Han Shun-hui, and Li Jing-yuan, Solid State Commun. **65**, 869 (1988).

[22] Takehiko Hidaka, Toshimi Matsui, and Yoshihiko Nakagawa, Jpn. J. Appl. Phys. **27**, L553 (1988).

[23] Z. Fisk, J. D. Thompson, E. Zirngiebl, J. L. Smith, and S.-W. Cheong, Solid State Commun. **62**, 743 (1987).

[24] M. L. Cohen, D. E. Morris, A. Stacy, and A. Zettl, in *Novel Superconductivity,* edited by V. Kresin and S. Wolf (Plenum, New York, 1987), p. 733.

[25] B. Batlogg, G. Kourouklis, W. Weber, R. J. Cava, A. Jayaraman, A. E. White, K. T. Short, L. W. Rupp, and E. A. Rietman, Phys. Rev. Lett. **59**, 912 (1987).

[26] Tanya A. Faltens, William K. Ham, Steven W. Keller, Kevin J. Leary, James N. Michaels, Angelica M. Stacy, Hans-Conrad zur Loye, Donald E. Morris, T. W. Barbee III, L. C. Bourne, Marvin L. Cohen, S. Hoen, and A. Zettl, Phys. Rev. Lett. **59**, 915 (1987).

[27] L. C. Bourne, S. Hoen, M. F. Crommie, W. N. Creager, A. Zettl, M. L. Cohen, L. Bernadez, J. Kinney, and D. E. Morris, Solid State Commun. **67**, 707 (1988).

[28] B. Batlogg, R. J. Cava, and M. Stavalo, Phys. Rev. B **60**, 754 (1988).

[29] H. Katayama-Yoshida, T. Hirooka, A. Oyamada, Y. Okabe, T. Takahashi, T. Sasaki, A. Ochiai, T. Suzuki, A. J. Mascarenhas, J. I. Pankove, T. F. Ciszek, S. K. Deb, R. B. Goldfarb, and Youngkang Li (unpublished).

[30] T. Stoskiewisc, Phys. Status Solidi A **11**, K123 (1972); B. Stratzker and W. Buckel, Z. Phys. **257**, 1 (1972); J. E. Schirber, J. M. Mintz, and W. Wall, Solid State Commun. **52**, 837 (1984).

[31] G. Bergmann and D. Rainer, Z. Phys. **263**, 59 (1973).

[32] G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **38**, 966 (1960) [Sov. Phys. JETP **11**, 696 (1960)].

[33] J. Labbe and J. Bok, Europhys. Lett. **3**, 1225 (1987); J. Labbe and J. Friedel, J. Phys. (Paris) **27**, 303 (1966).

[34] J. R. Hardy and J. W. Flocken, Phys. Rev. Lett. **60**, 2191 (1988).

[35] J. C. Phillips, Phys. Rev. Lett. **59**, 1856 (1987).

[36] Daniel S. Fisher, A. J. Millis, B. Shraiman, and R. N. Bhatt, Phys. Rev. Lett. **61**, 482 (1988).

[37] B. Ashauer, W. Lee, D. Rainer, and J. Rammer, Physica B **148**, 243 (1987).

[38] R. W. Cohen, M. H. Cohen, and M. L. Cohen (unpublished).

[39] F. Marsiglio, R. Akis, and J. P. Carbotte, Solid State Commun. **64**, 905 (1987).