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Observation of an oxygen isotope effect in superconducting $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$

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The oxygen isotope effect was studied in the system $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ for x=0.2, 0.3, 0.4, and 0.5. It is found that the oxygen isotope exponent α increases with increasing x and therefore decreasing transition temperature T_c. For the highest Pr concentrations α tends toward α=0.5. The value of the isotope exponent depends on the concentration of mobile holes. The lower this concentration is, the larger becomes the isotope exponent.

The isotope effect has played an important role in establishing the electron-phonon interaction as the dominant attractive interaction in conventional superconductors. Initial studies of the isotope effect in high-T_c superconductors found that the effect is either absent or very small.[1-5] Together with the exceptionally large transition temperatures near 100 K, these results have generally been taken as evidence that new interactions rather than the electron-phonon interaction are responsible for superconductivity in these materials.[6] Our earlier oxygen-isotope-effect studies[7] on $YBa_2Cu_3O_{7-\delta}$ found a small but finite effect, up to 2 to 3 times larger than previous work, but still small. Large isotope effects were observed in $La_{2-x}Sr_xCuO_4$ as a function of Sr doping by Crawford *et al.*[8]

Substitution of the rare-earth ion Pr into the 91-K superconductor $YBa_2Cu_3O_{7-\delta}$ according to the formula $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ leads to superconductors for the substitution range $0 \leq x \leq 0.55$.[9,10] Pr substitution occurs predominantly on the Y site. There is, however, evidence from x-ray-absorption spectroscopy that a small fraction of Pr substitutes for Cu in the Cu(2) (plane) site.[11] In this Brief Report we are reporting on our results for the oxygen isotope effect in this system for substitution levels between x =0.2 and 0.5. A short report on this work has already been given.[12]

The depression of T_c by Pr substitution is still not fully understood. Initially, it was assumed that Pr enters the compounds with a valence between 3 and 4, reducing the concentration of hole carriers. This evidence was based on the Pr magnetic moment obtained from susceptibility measurements.[9,10,13-18] Specific-heat measurements were also interpreted in this way.[13] Direct evidence of a reduced hole concentration was obtained from Hall-effect measurements[14] and is also evident from the larger penetration depth in these compounds, obtained from muon-spin relaxation.[19,20] In Ref. 15 a detailed study comparing hole filling due to Pr with hole production due to Ca led to a valence of Pr of about 3.9. It was found that hole filling is only one of two factors affecting T_c, the second being pair breaking by the Pr magnetic moments due to hybridization of Pr 4f with the hole conduction band.[15,21] Other work, however, found evidence only for trivalent Pr; from H_{c2} determinations,[21] studies of oxygen-deficient compounds,[22] x-ray-absorption spectroscopy,[11,23] and electron-energy-loss spectroscopy.[24] In Ref. 24 it was concluded that Pr does not fill holes, but that mobile holes become localized. Hole localization is claimed to take place at the Ba site from x-ray photoemission studies as well as polarized Raman scattering.[25,26] Theoretical evidence for Pr^{3+} in $PrBa_2Cu_3O_7$ has also been published.[27]

Samples were prepared for x =0.2, 0.3, 0.4, and 0.5 from high-purity Y_2O_3, Pr_6O_{11}, $BaCO_3$, and CuO. The powders were calcined in air in alumina crucibles for 125 h at 905 °C with three intermediate grindings. The calcined powders were always quenched to room temperature. We then prepared from these calcined powders three similar pellets of about 280 mg weight and 6.35 mm diameter. The three comparison samples for a particular Pr concentration were sintered in a closed processing system, using flowing $^{16}O_2$ (for two pellets) and flowing $^{18}O_2$ for the third pellet. The circulating oxygen gas was constantly purified by passing it through liquid O_2 traps.[7] We sintered at 935 °C for 7 h, oven cooled to 450 °C, held at 450, 350, and 250 °C each for 10 h, and then oven cooled to room temperature. The sintering conditions were designed to lead essentially to full oxygenization, $\delta \lesssim 0.1$. We also tried a longer sintering process for a set of comparison samples at x =0.3; these were sintered for 2 days at 950 °C and then held at 450 °C for 3.5 days and at 350 and 250 °C for 12 h each. These samples did not show qualitatively different behavior from the standard anneal samples, apart from an isotope shift about 14% larger and a slightly sharper transition. In view of these results, it is unlikely that differences in total oxygen concentration are responsible for the observed isotope shift.

^{18}O concentrations in the substituted samples were obtained from secondary-ion-mass spectroscopy (SIMS) and were in the range 72–86 %.

X-ray powder analysis showed a phase isomorphous to $YBa_2Cu_3O_{7-\delta}$. The lattice parameters increased approximately linearly with increasing Pr concentration.

Meissner fractions were obtained from field-cooled shielding curves at 20 Oe, using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. We find Meissner fractions of 24% ($x=0.2$), 21% ($x=0.3$), 17% ($x=0.4$), and 7% ($x=0.5$). No allowance for demagnetization was made. These fractions are lower values for the amount of superconducting phase present. Pr substitution is known to lead to smaller Meissner fractions.[21]

The transition was observed resistively by a four-point resistance measurement and, magnetically, through low-field dc magnetization and ac susceptibility measurements. We found in all cases a lower transition for the ^{18}O substituted samples. The relative as well as the absolute shift increases with increasing Pr concentration.

In Fig. 1(a) we show the resistive transitions. The transitions are broadened compared to resistive transitions in pure $YBa_2Cu_3O_7$; this is commonly observed in the Pr-substituted system. The transition temperature and width in this system vary with different preparation conditions, as can be seen from the spread of data in the literature.[9,10,13,15] Our data fall, however, well within this range. Isotope shifts were taken at the $R=0$ point. The differences in the resistive transition temperature are given in Table I. Isotope exponents α, obtained from $\alpha=-d\ln T_c/d\ln m$ and based only on the oxygen mass, are also given in Table I. We quote both α, obtained by using the actual observed ΔT_c, as well as α', corrected to 100% ^{18}O substitution. The latter values should be treated with caution, since the isotope effect is probably not linear in ^{18}O concentration.

Back exchange was done for the samples with $x=0.3$. The original ^{18}O sample was sintered in $^{16}O_2$, and the original ^{16}O sample was sintered in $^{18}O_2$, using the same (short) sintering program as before. Resistance measurements were taken after one and two back-exchange treatments. We found that the isotope effect reversed itself. (The data are shown in Table I and Fig. 3 and are in good agreement with the other data.)

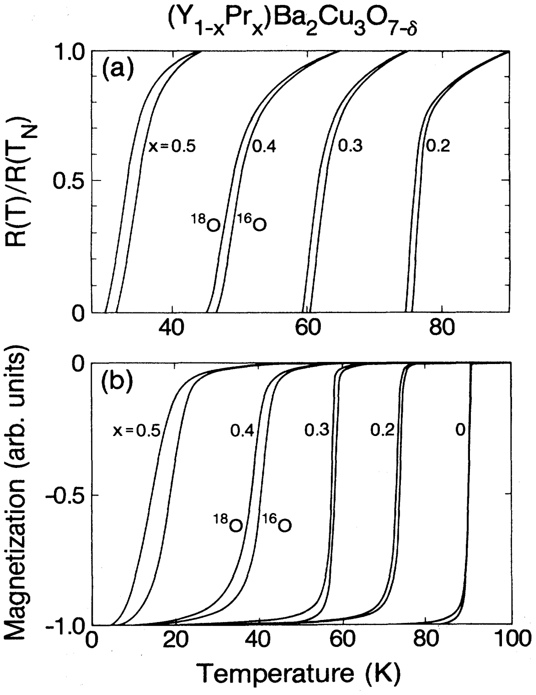

FIG. 1. (a) Resistive transition for four comparison sets of $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$. The ^{18}O concentrations are $x=0.2$ (84.6%), 0.3 (79.0%), 0.4 (85.5%), and 0.5 (85.9%). Normalization temperatures are $x=0.2$ ($T_N=90$ K), 0.3 ($T_N=85$ K), 0.4 ($T_N=65$ K), and 0.5 ($T_N=45$ K). (b) Zero-field-cooled dc magnetization in a field of 0.1 Oe for the samples shown in (a). A typical $x=0$ transition is included. Note the different temperature scales in (a) and (b).

Magnetically, we observed the transitions in a noncom-

TABLE I. Properties of ^{18}O-substituted $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$.

x (at. %)	^{18}O conc. (at. %)	$T_c^{R=0}$ (K)	$\Delta T_{c,\mathrm{res}}$ (K)	$\Delta T_{c,\mathrm{mag}}$[a] (K)	α_{res}[b]	α_{mag}[b]	α'_{res}[c]	α'_{mag}[c]
20	0.2	75.6						
20	84.6		0.80	0.68	0.09	0.08	0.11	0.09
30	0.2	60.4						
30	79.0		1.07	1.25	0.15	0.17	0.19	0.22
30[d]	0.2	60.0						
30[d]	72.1		1.16		0.17		0.23	
30[e]	0.2	54.3						
30[e]	83.2		1.42		0.23		0.28	
40	0.2	46.2						
40	85.5		1.50	1.60	0.27	0.29	0.32	0.34
50	0.2	30.6						
50	85.9		1.65	1.70	0.45	0.49	0.53	0.57

[a] At shielding level corresponding to zero-resistance temperature of the ^{16}O sample.

[b] Oxygen isotope exponent for the measured isotope shifts.

[c] Oxygen isotope exponent normalized to 100% ^{18}O concentration.

[d] Long annealing.

[e] Back exchange twice.

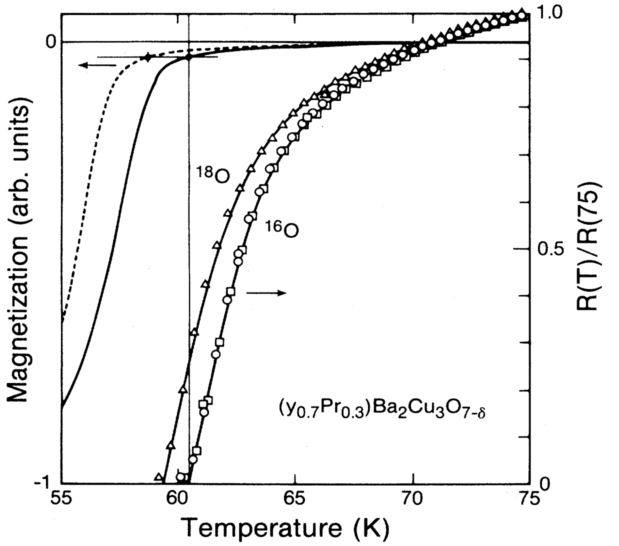

FIG. 2. Low-field dc magnetization (0.1 Oe) and resistive transition for a sample triplet of $(Y_{0.7}Pr_{0.3})Ba_2Cu_3O_{7-\delta}$. Squares and circles: sintered in $^{16}O_2$; triangles: sintered in $^{18}O_2$. The resistance was normalized at $T_N=75$ K. The method used to obtain the shielding level for comparison of the magnetic transitions is shown.

mercial SQUID magnetometer through low-field dc magnetization (0.1 Oe) and low-field ac susceptibility (0.01 Oe, 160 Hz). In Fig. 1(b) we show the normalized zero-field-cooled dc magnetization taken from small flakes broken off from the sintered pellets. These flakes have irregular shapes which affect the form of the magnetic transition curve through demagnetization effects. Nevertheless, the transitions are quite sharp compared with published data.[13,15,21] The transition temperature is normally taken at the onset of shielding, which usually corresponds to the extrapolated $R=0$ point in the resistive transition. We note, however, that with Pr-substituted samples the magnetic transitions measured with high resolution show a long tail at very small shielding levels. This tail becomes more pronounced with increasing Pr concentration. The same effect is observed for finely powdered samples obtained by crushing small pieces of the pellets under acetone.

The magnetic and resistive transitions are compared in Fig. 2 for $x=0.3$ samples. We note that a linear extrapolation of the resistive transition to $R=0$ corresponds to a temperature where the bulk of the magnetic transition begins. The diamagnetic signal at that temperature is small enough to make demagnetiztaion effects unimportant. These observations apply to all the Pr-substituted samples. We have chosen, therefore, this extrapolation to $R=0$ as the transition temperature T_c. Results for the magnetically observed transitions are also included in Table I.

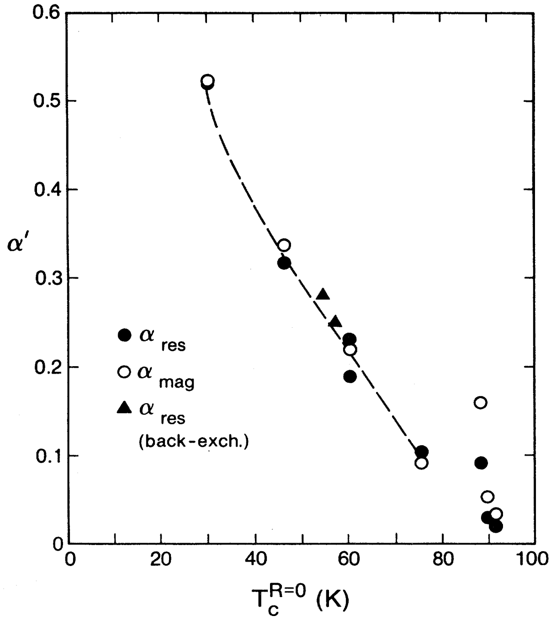

FIG. 3. Oxygen isotope exponent α' as a function of transition temperature, normalized for 100% ^{18}O concentration. The data near 90 K represent the various oxygen isotope exponents obtained in our earlier work (Ref. 7) on $YBa_2Cu_3O_{7-\delta}$. The spread of these data is connected with different preparation conditions.

For purposes of comparison with the data on $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$, we have also investigated the oxygen isotope effect in Ca-substituted superconductors of composition $(Y_{0.8-y}Pr_{0.2}Ca_y)Ba_2Cu_3O_{7-\delta}$, for $y=0$, 0.05, 0.10, and 0.20. Preliminary results show that the transition temperature goes through a maximum, as reported already by Neumeier *et al.*[15] and that the isotope effect becomes smaller with increasing Ca concentration. Preliminary results are given in Table II; a more comprehensive report will be published later.

TABLE II. Oxygen isotope effects in $(Y_{0.8-y}Pr_{0.2}Ca_y)Ba_2Cu_3O_{7-\delta}$.[a]

Ca conc. (at. %)	^{18}O conc. (at. %)	$T_c^{R=0}$ (K)	$\Delta T_{c,\text{res}}$ (K)	α_{res}[b]	α'_{res}[c]
0		71.0	0.90	0.10	
5	84	73.6	0.76	0.09	0.11
10	78	77.8	0.47	0.05	0.06
20	76	71.2	0.42	0.05	0.07

[a] The comparison samples in this table were produced using different calcining and sintering conditions than those in Table I.

[b] Oxygen isotope exponent for the measured isotope shift.

[c] Oxygen isotope exponent normalized to 100% ^{18}O concentration.

The results show that the isotopic transition-temperature shift increases with increasing Pr concentration in $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$. We see from Fig. 3 that the oxygen isotope exponent increases smoothly with falling transition temperature, i.e., increasing Pr concentration. Because of the uncertainties in the extrapolation to 100% ^{18}O concentration, the slight rise of α' above 0.5 for $x=0.5$ should not be taken too seriously. For $x \rightarrow 0$ the isotope exponent extrapolates well toward the small values found in unsubstituted $YBa_2Cu_3O_7$ (Refs. 1–5 and 7, and references therein).

The explanation of the observed effect is naturally intimately connected with our understanding of the Pr-substituted system. The most recent work[24] identifies hole localization and pair breaking due to the Pr moment and Pr 4f-hole band hybridization as responsible for the decrease in transition temperature. In order to distinguish which of these two effects is responsible for the increased isotope effect, we turn to the results on the Ca-substituted $(Y_{0.8-y}Pr_{0.2}Ca_y)Ba_2Cu_3O_{7-\delta}$ system (Table II). Ca substitution does not effect the pair breaking, but it increases the hole concentration. We found that Ca substitution drastically reduces the isotope effect, down to values typical for unsubstituted $YBa_2Cu_3O_7$. It is clear, therefore, that the pair-breaking mechanism has no influence on the isotope effect and that it is the concentration of mobile holes that affects α. It is, moreover, clear from the Ca results that the transition temperature is not the only variable determining α. We estimated the hole concentration for given Pr and Ca concentrations using the analysis of Neumeier *et al.*[15] We found that the main correlation of the isotope effect is with the concentration of mobile holes. The lower this concentration is, the larger becomes the isotope exponent α. These findings are quite similar to those obtained by Crawford *et al.*[8] on the system $La_{2-x}Sr_xCuO_4$.

In Refs. 24 and 25 it was shown that increasing x in the Pr system leads to an increase in the Ba-O(4) distance [O(4)=apical oxygen], as well as an increase in the c-axis O(4) vibration frequency. This mode shows strong electron-phonon interaction,[26,28] and the localization of holes in the Ba 5d orbitals is strongly dependent on the Ba-O(4) distance. The isotope effect may then work indirectly by influencing the amount of localization. The importance of coupling via the apical O(4) oxygen in high-T_c superconductors was pointed out by Bishop *et al.*[29] and by Müller.[30]

A somewhat related analysis was given by Tsuei *et al.*[31] In their work it is shown that the combination of a two-dimensional van Hove singularity in the hole density of states combined with BCS phonon-mediated pairing can lead to substantial oxygen isotope exponents, even exceeding 0.5. This analysis also assumes coupling via the apical oxygen. These authors show that α should become small near the peak in T_c as function of hole concentration and increase away from the T_c peak. Our results agree with this, as α increases with falling T_c in the Pr system. We find, however, in the Pr-Ca system that α remains small as the peak in T_c is passed toward larger hole concentrations. According to Tsuei *et al.*,[31] this result may be a consequence of a nonsymmetric density of states near the van Hove singularity. Similar calculations were published by Schachinger, Greeson, and Carbotte.[32]

A connection between the micromorphology of high-T_c superconductors (in particular, $YBa_2Cu_3O_7$) and the isotope effect was given by Phillips.[33,34] The calculations lead to a general reduction in the isotope effect with increasing transition temperature.

In conclusion, we find a substantial oxygen isotope effect in the system $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$. Lattice vibrations, particularly those dominated by oxygen, apparently play an important role in the behavior of high-T_c superconductors.

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