

Sizable oxygen isotope effects in the electron-doped $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$

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Oxygen isotope effects have been investigated in the electron-doped $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. We find the exponent of oxygen isotope effect $\alpha_O = 0.08 \pm 0.01$. The sizable oxygen isotope effect in this electron-doped system indicates that the electron-phonon interaction plays an important role in the pairing mechanism.

The pairing mechanism responsible for superconductivity in the high- T_c cuprates is still controversial. Experiments to address this fundamental question have been focused on the hole-doped superconductors. The hole-doped superconductors have many unusual properties in both normal and superconducting states (e.g., linear T dependence of resistivity; very short coherence length). The very short coherence length will lead to a strong critical fluctuation, so a mean-field, or equivalently a BCS treatment proves insufficient.¹ In contrast, the electron-doped cuprates like $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ (NCCO) exhibit rather conventional behavior (e.g., T^2 -like dependence of resistivity;² s -wave pairing state;³ relatively long coherence length;³ a simple one-band electronic structure with Luttinger Fermi surface^{4,5}). These unique and conventional properties make the electron-doped cuprate an attractive candidate for detailed investigations to extract the microscopic pairing mechanism for high- T_c superconductivity.

One way to assess the importance of the electron-phonon interaction in the pairing mechanism is an isotope effect experiment. There have been many reports on the isotope effects in the hole-doped cuprates.⁶⁻¹⁴ Due to the complicated electronic and lattice structures in the hole-doped cuprates, these isotope results could be explained by several theoretical models, and cannot give an exclusive test for the pairing mechanism. In contrast, to our knowledge there have been only two reports on the oxygen isotope effects in the electron-doped cuprates, because of experimental difficulty. The oxygen isotope effect in the electron-doped cuprate was reported by Onoda *et al.*¹⁵ These authors found that $0.07 \leq \alpha_O \leq 0.15$ for NCCO with $T_c \sim 23.6$ K. On the other hand, Batlogg *et al.*¹⁶ reported a small or zero oxygen isotope effect ($\alpha_O \leq 0.05$) in NCCO with $T_c \sim 24.5$ K. These isotope results contradict each other, and cannot be used to assess the role of electron-phonon interaction in the pairing mechanism.

Since a reliable isotope-effect result for the electron-doped cuprate is important to clarify the pairing mechanism of high- T_c superconductivity, we develop a feasible experimental technique to investigate the oxygen isotope effects in the electron-doped $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. We find the exponent of oxygen isotope effect $\alpha_O = 0.08 \pm 0.01$. The sizable oxygen isotope effect in this

electron-doped system indicates that the electron-phonon interaction plays an important role in the pairing mechanism.

Samples of $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ were prepared by conventional solid state reaction using Pr_6O_{11} , CeO_2 , and CuO . The powders were mixed and ground thoroughly under isopropyl alcohol, and then pressed into pellets, fired in air at 1000°C for ~ 48 h with one intermediate grinding. The pellets were ground again, pressed into pellets, and annealed in air at 900°C for 12 h, and in flowing nitrogen at 950°C for 12 h, then at 1000°C for 20 h. The cooling time from 1000°C to room temperature was ~ 15 minutes.

Each pellet was broken in half, and the halves were subjected to the ^{16}O and ^{18}O isotope diffusion, which was conducted in two parallel quartz tubes separated by about 2 cm.⁹ Samples were at identical temperatures, and nearly identical oxygen pressures (difference $< 1\%$) throughout the diffusion process. The electronic pressure transducer gauges for the ^{16}O and ^{18}O sides were calibrated at the desired pressures for diffusion. The oxygen isotope diffusion was done at the temperature of 900°C and oxygen pressure of about 0.7 bar for 90 h in experiment 1, and for 135 h in experiment 2. The isotope-exchanged sample pairs were annealed in vacuum (~ 50 millitorr) at 900°C . During vacuum annealing, the samples were placed in the two parallel quartz tubes which were connected together and had identical pressure. With continuously pumping of the system, the vacuum was nearly unchanged during annealing. The vacuum-annealing time is 7 h in experiment 1, and 4 h in experiment 2. The cooling time from 900°C to 500°C is $\sim 2-3$ minutes. The samples were furnace cooled from 500°C to room temperature. Back exchange was carried out at 900°C for 40 h in flowing $^{16}\text{O}_2$ on the samples of experiment 2. The final vacuum annealing was done for the back-exchanged samples in a similar way. The above vacuum-annealing procedure has been successfully used for the ^{16}O and ^{18}O samples of La_2CuO_4 . These samples have equal oxygen contents within ± 0.0001 oxygen per unit cell as shown by x-ray diffraction result. The oxygen isotope enrichments were determined by weight changes of both ^{16}O and ^{18}O samples. The ^{18}O samples have $\sim 83\%$ ^{18}O , 17% ^{16}O in experiment 1; $\sim 88\%$ ^{18}O , 12% ^{16}O in experiment 2; and $\sim 30\%$ ^{18}O , 70% ^{16}O after back ex-

change.

The susceptibility was measured in a commercial superconducting quantum interference device (SQUID). The Meissner effect was measured in a field of 4 Oe. All the samples were well aligned in nearly the same direction (along axis parallel to the field) during each measurement. The samples were held at 40 K in the field for ~ 5 minutes, and then cooled directly to 5 K. The cooling rates for all the measurements were similar. The data were collected during warming. The magnetic field was kept unchanged throughout the whole series of measurements except for the back-exchanged samples which were measured at a later time in a 5 Oe nominal field.

In Figs. 1(a) and 1(b), we show the Meissner susceptibility for the ^{16}O and ^{18}O samples in experiments 1 and 2. At low temperatures, the Meissner fractions for the ^{16}O and ^{18}O samples are nearly equal within $\pm 1.5\%$, in contrast to the results of the hole-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ where the Meissner fractions of the ^{16}O samples are always larger than ^{18}O samples by $\sim 5\text{--}8\%$.¹⁷

Plotted in Figs. 2(a) and 2(b) is the normalized susceptibility near T_c for the ^{16}O and ^{18}O samples in experiments 1 and 2. For experiment 1, the T_c of the ^{18}O sample is ~ 0.14 K lower than the ^{16}O sample, corresponding to

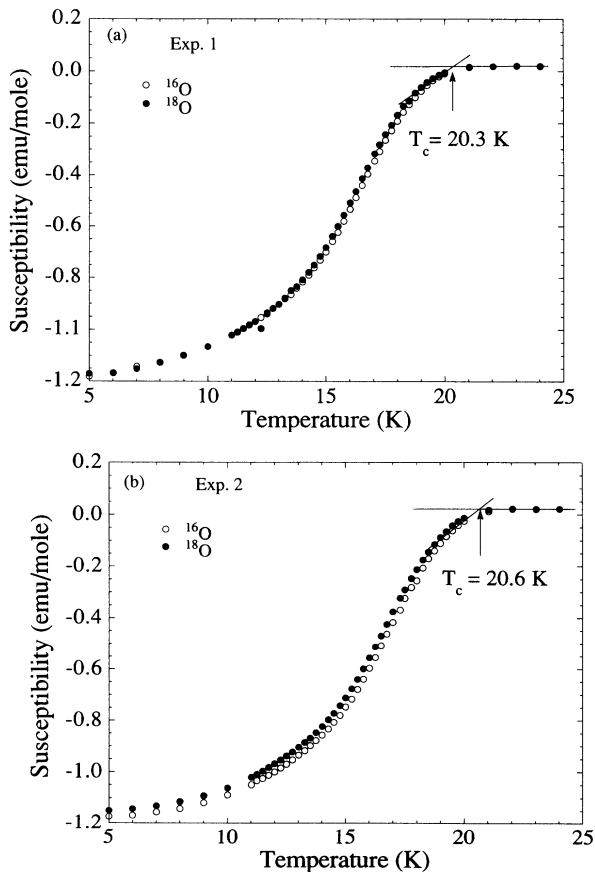


FIG. 1. The Meissner effects for the samples of $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{O}_{4-y}$ after isotope exchange (a) for experiment 1; (b) for experiment 2. The data were not corrected by demagnetization factors. The low-temperature Meissner fractions for the sample pairs are the same within $\pm 1.5\%$.

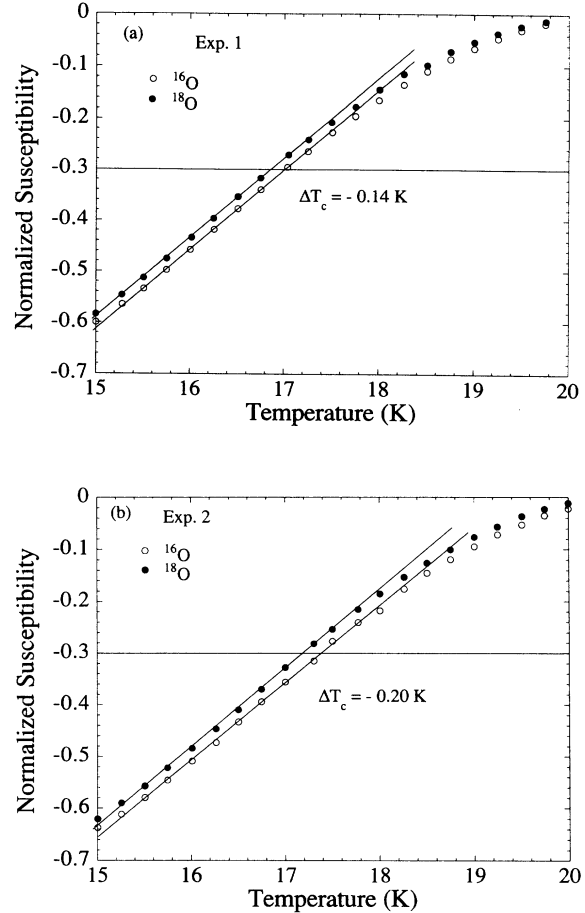


FIG. 2. The renormalized Meissner susceptibility near T_c for the ^{16}O and ^{18}O samples (a) for experiment 1; (b) for experiment 2. The oxygen isotope exponents are 0.07 for experiment 1, and 0.09 for experiment 2.

$\alpha_O = -d \ln T_c / d \ln M \sim 0.07$. For experiment 2, the T_c of the ^{18}O sample is ~ 0.20 K lower than the ^{16}O sample, corresponding to $\alpha_O \sim 0.09$. So, the oxygen isotope exponent for $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is $\sim 0.08 \pm 0.01$, in reasonable agreement with the result of Onoda *et al.*¹⁵

We show, in Figs. 3(a) and 3(b), the results of Meissner susceptibility before isotope exchange. The sample pairs have nearly the same Meissner fraction and equal T_c before isotope exchange. This implies that the starting pellets of the ^{16}O and ^{18}O samples have the same composition and oxygen content. Plotted in Fig. 3(c) is the normalized susceptibility near T_c after back exchange for experiment 2. After back exchange, the ^{18}O atoms in the ^{18}O sample were partially exchanged back to ^{16}O (the ^{18}O enrichment was changed from $\sim 88\%$ to $\sim 30\%$), and the isotope shift in T_c was changed from 0.20 to 0.10 K. This result indicates that the observed isotope shift is reversible and real.

The observed oxygen isotope effect is sizable, but $\alpha_O \ll 0.5$. The reduced isotope effect does not necessarily mean a break-down of conventional phonon-mediated pairing mechanism. This could be due to a large Coulomb pseudopotential μ^* . Since the ratio $E_F / \langle \omega \rangle$ in

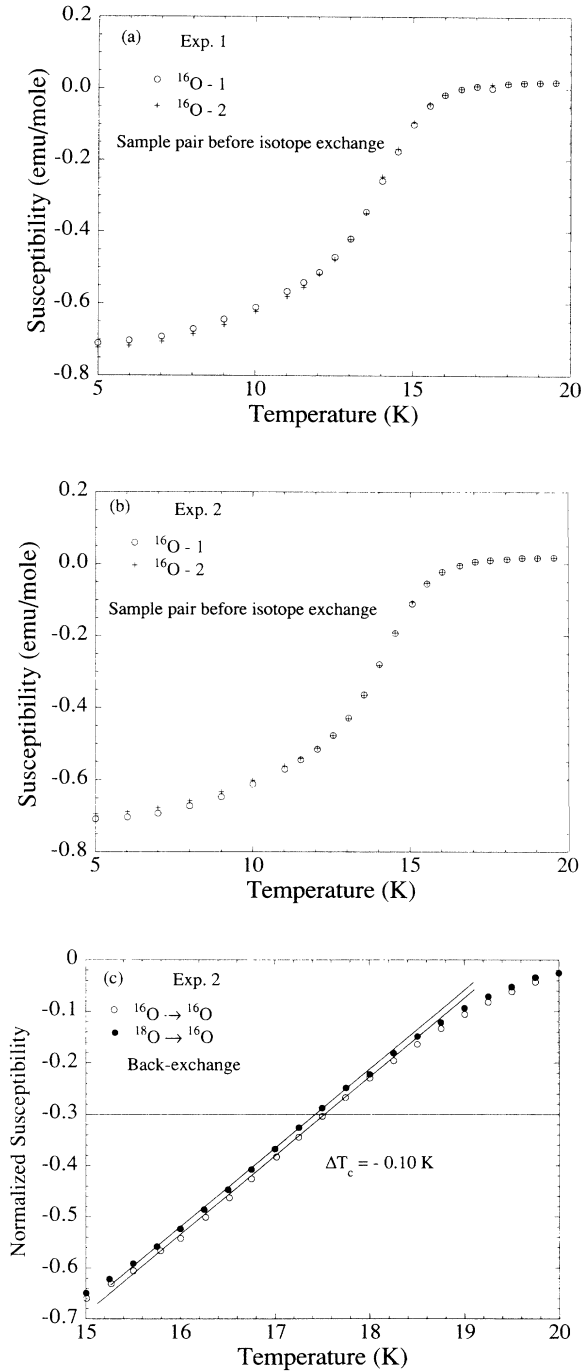


FIG. 3. The Meissner susceptibility for the samples of $\text{Pr}_{1.95}\text{Ce}_{0.15}\text{CuO}_{4-y}$ (a) before isotope exchange for experiment 1; (b) before isotope exchange for experiment 2; (c) after back exchange for experiment 2. The ^{18}O sample has $\sim 30\%$ ^{18}O and 70% ^{16}O after back exchange.

cuprates is much smaller than that of any conventional superconductor, the value of μ^* in cuprates will be larger than that of any conventional superconductor, i.e., $\mu^* > 0.2$ ($\mu^* \sim 0.20-0.22$ in V metal¹⁸). From tunneling and inelastic neutron scattering data,¹⁹⁻²⁰ we estimate that $\langle \omega \rangle \sim 500-600$ K. From the reduced gap: $2\Delta(0)/k_B T_c = 4.1$,³ one could estimate the coupling constant $\lambda \sim 1.0-1.2$. Substituting $T_c \sim 20$ K, $\langle \omega \rangle \sim 500-600$ K, $\lambda \sim 1.1$ into the McMillan's T_c formula,²¹

$$T_c = 0.83 \langle \omega \rangle \exp \left\{ -1.04(1+\lambda) / [\lambda - \mu^*(1+0.62\lambda)] \right\} \quad (1)$$

we obtain $\mu^* \sim 0.22-0.25$. Using the relation $\mu^* = \mu / [1 + \mu \ln(E_F / \langle \omega \rangle)]$ and Eq. (1), we find the total isotope exponent,

$$\alpha_t = 0.5 \left\{ \frac{1 - 1.04(1+\lambda)(1+0.62\lambda)\mu^*}{[\lambda - \mu^*(1+0.62\lambda)]^2} \right\}. \quad (2)$$

Substituting $\mu^* \sim 0.22-0.25$, $\lambda = 1.1$ into Eq. (2), one gets $\alpha_t \sim 0.25-0.30$. So the Coulomb potential effectively reduces the isotope effect in this weakly coupled superconductor. For the hole-doped cuprates, the reduced energy gap is $\sim 5.0-7.0$, and the coupling constant will be $\sim 3.0-4.0$. In this case, the reduction of isotope exponent is small even if there is a large μ^* ($\sim 0.20-0.25$).

To assess the role of electron-phonon interaction in the pairing mechanism, we need the total isotope exponent. A reliable copper isotope effect is difficult to measure for this compound, but we can estimate α_{Cu} by assuming that the observed ratio $\alpha_{\text{Cu}}/\alpha_{\text{O}} \sim 1.0-1.4$ in the hole-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (Ref. 14) will apply to this electron-doped cuprate. This assumption is justifiable because the ratio $\alpha_{\text{Cu}}/\alpha_{\text{O}}$ depends on the relative weights of oxygen and copper-dominated phonon modes (insensitive to λ and μ^*), and the relative weights will be similar in these cuprate superconductors due to similar Cu-O bonds (similar covalency). From the observed $\alpha_{\text{O}} = 0.08 \pm 0.01$, and $\alpha_{\text{Cu}}/\alpha_{\text{O}} \sim 1.0-1.4$, one obtains $\alpha_{\text{Cu}} \sim 0.08-0.11$, and $\alpha_t \sim 0.16-0.19$, in reasonable agreement with the calculated result above.

In conclusion, we observe a sizable oxygen isotope effect in the electron-doped $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. We explain the experimental results on the basis of the conventional phonon-mediated pairing mechanism, and conclude that the phonons play a significant role in the pairing mechanism for this electron-doped cuprate.

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