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# Oxygen isotope effect on the effective mass of carriers from magnetic measurements on $La_{2-x}Sr_xCuO_4$

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Oxygen isotope effects on $T_c$ and the Meissner fraction $f$ have been investigated in fine-grained, decoupled $La_{2-x}Sr_xCuO_4$ with $x=0.105$, 0.110, and 0.115. We find that these oxygen isotope effects are related to each other: $d \ln T_c/d \ln M \approx d \ln f/d \ln M$ (where $M$ is the mass of oxygen). We also show that the trapped flux due to intergrain weak-link and intragrain flux pinning is negligible in our samples, and that the Meissner fractions for the samples with the same $^{16}O$ isotope are nearly equal The observed large oxygen isotope effects on $T_c$ and the Meissner fraction can be explained as due to the oxygen-mass dependence of $m^*$ (effective mass of carriers). The results may suggest that the conducting carriers in the cuprate superconductors are of polaronic type.

The discovery and development of the high-$T_c$ cuprate superconductors have prompted a burst of experimental and theoretical investigations on these systems. However, the microscopic pairing mechanism for high-$T_c$ superconductivity remains controversial. Opinions on the role of electron-phonon interaction vary widely.[1-3] One way to assess the importance of phonons in the pairing is the isotope effect on $T_c$. Very small oxygen isotope effect on $T_c$ was observed in the optimally doped cuprates[4-7] while large oxygen isotope effect was found in the underdoped cuprates.[8-11] The large isotope effect may point to the phonon-mediated pairing mechanism for high-$T_c$ superconductivity. However, since $T_c$ is sensitive to the hole concentration in the underdoped range, it has been suggested[12] that the observed large oxygen isotope effect could be due to a slight difference in the mobile-hole concentrations of the $^{16}O$ and $^{18}O$ samples. Therefore it is essential to address this issue before one can draw any conclusion about pairing mechanism from these isotope effect experiments.

It is important to note that the $^{16}O$-containing samples of $La_{2-x}Sr_xCuO_4$ have a local minimum in $T_c$ at $x \sim 0.110$, as shown by Takagi *et al.*[13] and Xiong *et al.*[14] One possible explanation to the local minimum in $T_c$ is that the mobile-hole concentration has a local minimum at this composition. However, several substitution experiments[15,16] indicate that the mobile-hole concentration $n$ is nearly equal to $x$ when $x<0.15$. The Hall effect measurements[15] further show that the Hall coefficient is a monotonic function of $x$. These results consistently suggest that the local minimum in $T_c$ for the $^{16}O$-containing samples occurs at the mobile-hole concentration $n \approx x \approx 0.110$. Since the $T_c$ values of the $^{16}O$-containing samples have a minimum at $n \approx x \approx 0.110$, any isotope-induced increase or decrease in the hole concentration at this composition will always raise $T_c$. Therefore, the isotope-induced decrease in $T_c$ must be caused by variables other than the change in the hole concentration.

The muon-spin-relaxation experiments[17] have shown a universal linear relationship: $T_c \propto 1/\lambda_{ab}(0)^2 \propto n/m^*$ for underdoped $p$-type cuprates, where $\lambda_{ab}(0)$ is the in-plane penetration depth at zero temperature and $m^*$ is the effective mass of carriers along $a$-$b$ plane. This result implies that the observation of oxygen isotope effect on $T_c$ must be accompanied by the observation of oxygen isotope effect on the penetration depth $\lambda_{ab}(0)$. Since the Meissner fraction $f(0)$ for a fine-grained sample is a function of grain size and penetration depth, the observation of oxygen isotope effect on $\lambda_{ab}(0)$ will be equivalent to the observation of oxygen isotope effect on $f(0)$.

Here we report the detailed results of oxygen isotope effects on $T_c$ and Meissner fraction $f$ for the fine-grained and decoupled $La_{2-x}Sr_xCuO_4$ with $x=0.105$, 0.110, and 0.115. We find that the oxygen isotope effects on $T_c$ and Meissner fraction $f$ are related to each other: $d \ln T_c/d \ln M \approx d \ln f/d \ln M$ (where $M$ is the mass of oxygen). The results can be explained as due to the oxygen-mass dependence of $m^*$.

Samples of $La_{2-x}Sr_xCuO_4$ with $x=0.100$, 0.105, 0.110, 0.115, and 0.120 were prepared by conventional solid-state reaction using $La_2O_3$ (99.99%), $SrCO_3$ (99.999%), and CuO (99.999%). The $La_2O_3$ was dried for 6 h at 900 °C prior to weighing. The powders were mixed and ground thoroughly under isopropyl alcohol, and then were pressed into pellets of 6 mm diam with $\sim 2$ ton/cm$^2$ pressure. These pellets were then fired in air at 1000 °C for $\sim 70$ h with three intermediate grindings. X-ray-diffraction (XRD) results indicate that the samples are very good single phase without any observable trace of the Sr-rich phase $La_{1.67}Sr_{0.33}Cu_2O_5$. To obtain samples with small grains and enough porosity, we reground the samples thoroughly, pressed them into pellets, and annealed them in air at 900 °C for 12 h. The cooling time to room temperature was 4 h.

Each pellet was broken in half, and the halves were then subjected to $^{16}O$ and $^{18}O$ isotope diffusion, which was conducted in two parallel quartz tubes separated by about 2 cm (see Ref. 7). The purities of the $^{16}O$ and $^{18}O$ gases used for isotope exchange are as follows: $^{16}O_2$ gas contains 99.993% $^{16}O$, 0.005% $^{17}O$, 0.002% $^{18}O$, CO < 14

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ppm, $CO_2<7$ppm, $CH_4<5$ ppm, $H<39$ ppm, $He<13$ ppm, and $N<18$ ppm; $^{18}O_2$ gas contains 96.9% $^{18}O$, 2.6% $^{16}O$, 0.5% $^{17}O$, $CO<18$ ppm, $CO_2<18$ ppm, $CH_4<7$ ppm, $N<21$ ppm, $H<18$ ppm, and $He<15$ ppm. The diffusion was carried out for 40 h at 900 °C and oxygen pressure of about 0.7 bar. The cooling time to room temperature was 4 h. The oxygen isotope enrichment was determined from the weight changes of the $^{16}O$ and $^{18}O$ samples. The $^{18}O$ samples had $\sim 85-90\%$ $^{18}O$ and $\sim 15-10\%$ $^{16}O$. Back exchange was carried out at 900 °C for 40 h in flowing $^{16}O_2$ on the samples with $x=0.115$.

The susceptibility was measured with a Quantum Design superconducting quantum interference device magnetometer. The field-cooled, measured-on-warming (FCW) susceptibility was measured in a nominal field of 5 Oe. All samples were carefully aligned in the same direction (along the axis parallel to the field) during each measurement. The samples were held at 40 K in a field of $\sim 5$ Oe for $\sim 10$ min, and then cooled directly to 5 K. The cooling rates for all measurements were similar. The data were collected upon warming. The magnetic field was kept unchanged throughout each series of measurements. The before-diffusion samples had been measured at an earlier time in the nominal field of 5 Oe while the back-exchanged samples were measured at a later time in the same nominal field. The zero-field-cooled (ZFC) susceptibility was measured in a field of 4.8 Oe after the sample was zero-field ($\sim 0.1$ Oe) cooled from normal state to 5 K, and the field-cooled (FC) susceptibility was measured in the same field as that for ZFC measurement.

In Figs. 1(a)–1(c), we show the FCW susceptibility for the $^{16}O$ and $^{18}O$ samples with $x=0.105$, 0.110, and 0.115. The nominal magnetic field for the measurement is 5 Oe. From Fig. 1, we find that the Meissner fractions for the $^{18}O$ samples are $\sim 5-8\%$ smaller than for the $^{16}O$ samples at low temperatures, in agreement with results reported by Franck *et al.*[18] The detailed isotope-effect results are summarized in Table I and Fig. 2. From Table I, one can see that the oxygen isotope effect on $T_c$ ($\alpha_O=-d\ln T_c/d\ln M$) is correlated with the oxygen isotope effect on the Meissner fraction $f$ as $d\ln T_c/d\ln M \sim d\ln f/d\ln M$ (where $M$ is the mass of oxygen).

Since the $T_c$ values of the $^{16}O$-containing samples have a local minimum at $n\approx x\approx 0.110$ (see Fig. 2), any increase or decrease in the hole concentration upon isotope substitution will raise the $T_c$ of the sample at this composition. Therefore, a lowering in $T_c$ of the $^{18}O$ sample at this composition is not possibly due to a lower or higher hole concentration in the $^{18}O$ sample. From Fig. 2, one can also see that $dT_c/dn<0$ at $n=0.105$, and $dT_c/dn>0$ at $n=0.115$. So there would be a positive oxygen isotope effect on $T_c$ at $n\approx x\approx 0.115$, and a negative oxygen isotope effect on $T_c$ at $n\approx x\approx 0.105$, if there were only a positive oxygen isotope effect on the hole concentration. The observed large positive oxygen isotope effect on $T_c$ at all the three compositions implies that the oxygen isotope effect on the hole concentration, if it exists, will be small.

The observed oxygen isotope effect on the Meissner fraction is possibly caused by the differences in grain-size, remanent magnetization (trapped flux) and demagnetization factor of the $^{16}O$ and $^{18}O$ samples. To rule out this possibility, we show, in Figs. 3(a) and 3(b), the results of FCW susceptibility (a) for $x=0.110$ before isotope exchange; (b) for $x=0.115$ after back exchange. The nominal magnetic field for the measurements is 5 Oe. It is clear that the Meissner fractions of the $^{16}O$ and $^{18}O$ samples are the same within $\pm 1.5\%$ before isotope exchange [see Fig. 3(a)]. After back exchange, the $T_c$ of the $x=0.115$ sample which previously contained $^{18}O$ is $\sim 0.2$ K lower than the original $^{16}O$ sample as shown in Fig. 3(b), possibly due to incomplete substitution of $^{16}O$ for $^{18}O$ ($\sim 6\%$ $^{18}O$ remains). The reversibility of the Meissner fraction upon isotope exchange suggests that the observed isotope effect is not due to the differences in grain size, demagnetization factor, and remanent magnetization of the $^{16}O$ and $^{18}O$ samples.

Note that the apparent differences in the absolute sus-

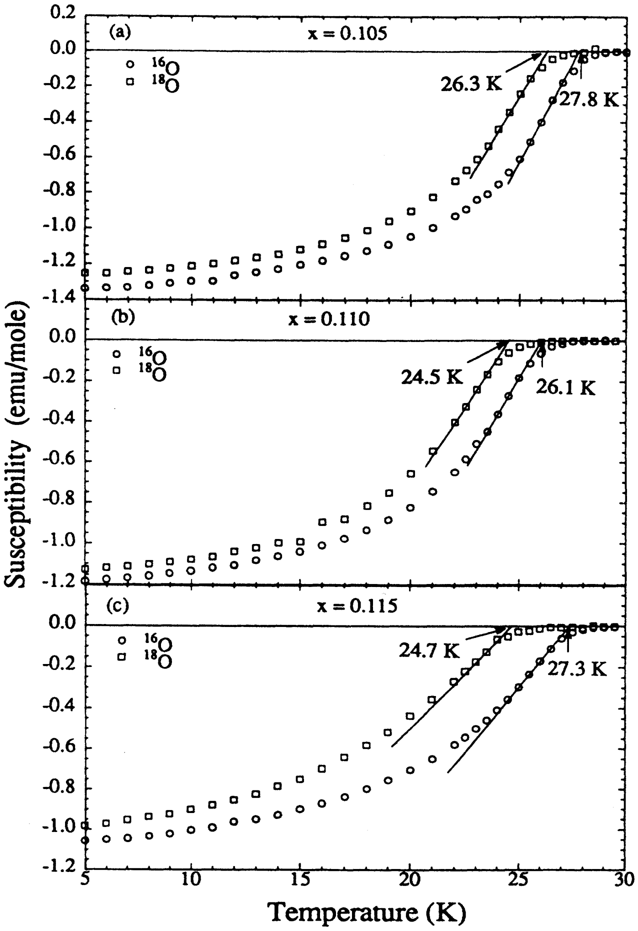

FIG. 1. The FCW susceptibility for the $^{16}O$ and $^{18}O$ samples of $La_{2-x}Sr_xCuO_4$ with (a) $x=0.105$; (b) $x=0.110$; (c) $x=0.115$. The data shown were divided by a nominal field of 5 Oe and not corrected by demagnetization factors. The real magnetic field for measurements is $5.9\pm 0.2$ Oe.

TABLE I. Oxygen isotope effects in $La_{2-x}Sr_xCuO_4$.

| $x$ | $^{18}O$ % | $T_c$ (K) | $\alpha_0$[a] | $\Delta T_c/T_c$ (%) | $f$ (%)[b] | $\Delta f/f$ (%) |
|---|---|---|---|---|---|---|
| 0.105 | 0 | 27.8 | 0.50 | −5.4 | 16.6 | −6.8 |
| 0.105 | 86 | 26.3 | | | 15.5 | |
| 0.110 | 0 | 26.1 | 0.54 | −6.1 | 14.7 | −5.0 |
| 0.110 | 90 | 24.5 | | | 14.0 | |
| 0.115 | 0 | 27.3 | 0.90 | −9.5 | 13.1 | −7.8 |
| 0.115 | 85 | 24.7 | | | 12.1 | |

[a] $\alpha_0 = -d\ln T_c/d\ln M$.

[b] $f$ is the Meissner fraction at 5 K. The data shown were divided by a real field of 5.9 Oe and corrected by a demagnetization factor of 1/3.

ceptibility of the $^{16}O$ samples as shown in Fig. 1(b) and Fig. 3(a), or in Fig. 1(c) and Fig. 3(b) are due to resetting the magnetic field in the different series of measurements which were conducted in different periods. We usually set a magnetic field in no overshoot mode after the field is reduced from − or +5.0 T to zero in oscillate mode [which leads to a remanent field of + or − (0.9±0.2) Oe]. Then the real magnitude of the field will be 4.1±0.2 or 5.9±0.2 Oe if one sets a nominal field of 5 Oe.

It was also suggested that the observed oxygen isotope effects on $T_c$ and $f$ could be explained by a picture in which the $^{18}O$ samples contain more nonsuperconducting phase ($La_{1.67}Sr_{0.33}Cu_2O_5$) than the $^{16}O$ samples.[19] However, this is not consistent with our XRD results, which do not show any evidence of a second phase (e.g., $La_{1.67}Sr_{0.33}Cu_2O_5$) in either the $^{16}O$ or the $^{18}O$ samples. In our XRD patterns (the wavelength of x ray is 1.540 60 Å), the weak peak at $2\theta = 36.277°$ for $La_{2-x}Sr_xCuO_4$ (3% of the most intense peak) can be clearly identified, but the most intense peak for $La_{1.67}Sr_{0.33}Cu_2O_5$ is not visible. This indicates that the Sr-rich phase is below 5% in our samples, and cannot account for the 5–8 % difference in the Meissner fractions of the $^{16}O$ and $^{18}O$ samples. In addition, the isotope-exchange temperature is 900 °C, so any impurity phase, once formed, would not be expected to convert back to the superconducting phase. The reversible change of the Meissner fraction upon oxygen isotope substitution further rules out this possibility.

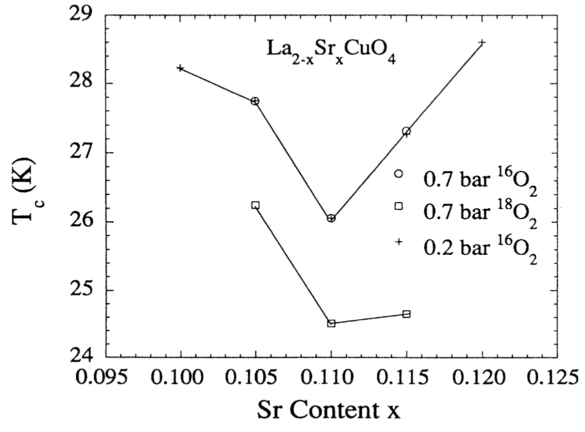

FIG. 2. The superconducting transition temperatures $T_c$ vs $x$ for the $^{16}O$ and $^{18}O$ samples of $La_{2-x}Sr_xCuO_4$. Since the $T_c$ values of the $^{16}O$-containing samples have a local minimum at $n \approx x \approx 0.110$, any increase or decrease in the hole concentration upon isotope substitution will raise the $T_c$ of the sample at this composition. Therefore, a lowering in $T_c$ of the $^{18}O$ sample at this composition is not due to a lower or higher hole concentration in the $^{18}O$ sample.

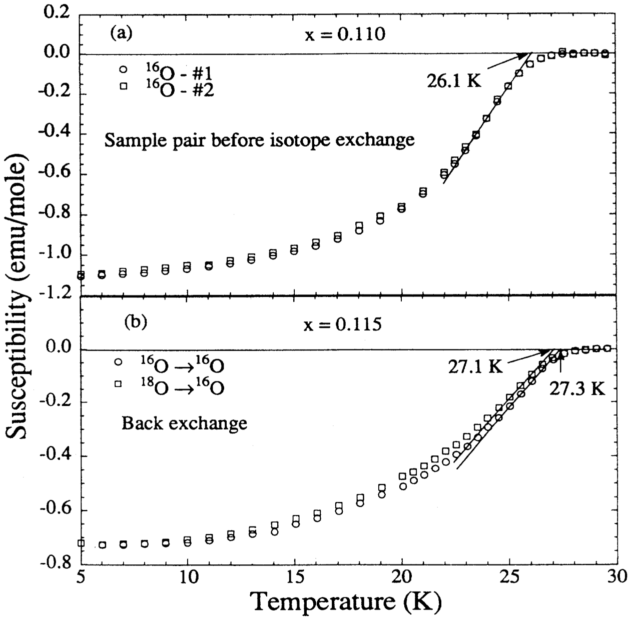

FIG. 3. The FCW susceptibility for the samples of $La_{2-x}Sr_xCuO_4$ with (a) $x = 0.110$, before isotope exchange; (b) $x = 0.115$, after back exchange. The data shown were divided by a nominal field of 5 Oe and not corrected by demagnetization factors. The real magnetic field for measurements is 5.9±0.2 Oe in (a), and 4.1±0.2 Oe in (b).

It is known that the field-cooled susceptibility (or Meissner effect) for fine-grained samples is reduced due to the penetration-depth, intergrain weak links, and intragrain flux pinning. If the intergrain link is not well established, the flux cannot be trapped in the intergrain boundary. If the samples have negligible defects, and the magnetic field is low, the flux will not be trapped inside the grain. The magnitude of the trapped flux can be obtained by the ZFC and FC measurements. The difference of ZFC and FC magnetization is the remanent magnetization due to the trapped flux.[20] In Fig. 4, we show the ZFC and FC susceptibility for $x = 0.115$ sample (after back exchange). The real magnetic field of "zero field" was checked by measuring the diamagnetic signal of Pb, and was determined to be ~0.1 Oe. From Fig. 4, one can see that the difference of the ZFC and FC signals is very small, suggesting negligible flux trapping. Further evidence for negligible flux trapping is the field independence of the FC susceptibility below 7 Oe.

Since there is negligible flux trapping in our fine-grained and decoupled samples, the Meissner fraction can

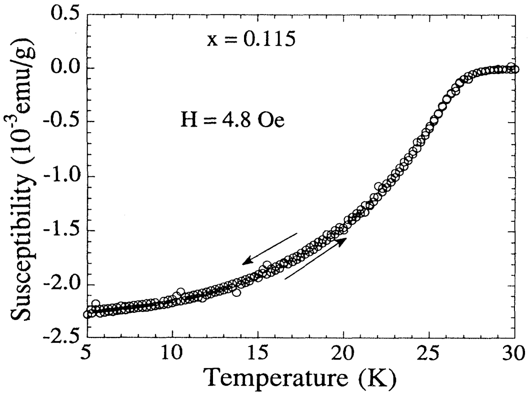

FIG. 4. The temperature dependence of ZFC and FC susceptibility for the $x=0.115$ sample. The difference of the ZFC and FC signals is small, suggesting negligible flux trapping.

be expressed as $f(0)=f(\{r\},\lambda(0))$, where $\{r\}$ is the radius distribution of grains and $\lambda(0)$ is the effective penetration depth at low temperatures. For $\Delta\lambda(0)/\lambda(0) \ll 1$, we can make a Taylor expansion for the Meissner fraction $f(0)$, leading to

$$-\Delta f(0)/f(0)=B[\Delta\lambda(0)/\lambda(0)]\,, \tag{1}$$

where $\Delta\lambda(0)$ and $\Delta f(0)$ mean isotope-induced changes of $\lambda(0)$ and $f(0)$, and $B=-[\lambda(0)/f(0)][\partial f(\{r\},\lambda(0))/\partial\lambda(0)]$. If $\lambda(0)/r \ll 1$, $f(0)\approx[1-\lambda(0)/R]^3$ (where $R$ is the average radius of grains), then $B\approx 3[1-f(0)^{1/3}]/f(0)^{1/3}$. The above relation can give a rough estimation for the coefficient $B$ [e.g., $B\sim 2$ for $f(0)\sim 20\%$].

Equation (1) indicates that the observation of oxygen isotope effect on the Meissner fraction is equivalent to the observation of oxygen isotope effect on the penetration depth. Since $\lambda \propto (m^*/n)^{1/2}$, Eq. (1) implies that the observed oxygen-mass dependence of $f(0)$ originates from the oxygen-mass dependence of $n$ and/or $m^*$. As discussed above, the results shown in Fig. 2 imply that the oxygen isotope effect on the hole concentration, if it exists, will be small. Then the observed large oxygen isotope effect on the Meissner fraction is mainly caused by the oxygen-mass dependence of $m^*$ (effective mass of carriers).

Since the hole concentration $n$ is closely related to a ratio $g=c/a$ (where $a$ and $c$ are the lattice constants along $ab$ plane and $c$-axis direction, respectively), any isotope-induced change in the hole concentration (e.g., a possible difference in the oxygen contents of the $^{16}$O and $^{18}$O samples) will lead to a change of g. Crawford *et al.*[9] have precisely determined the lattice constants for the $^{16}$O and $^{18}$O samples of $La_{2-x}Sr_xCuO_4$ from synchrotron x-ray-diffraction measurements, and found that the values of $g$ for the $^{16}$O and $^{18}$O samples are the same within $\pm 10^{-6}$ [for orthorhombic symmetry, $g$ is defined as $g=c/(ab/2)^{1/2}$]. Using a relation $\Delta n \sim 10\Delta g/g$ (Refs. 21–24), one can estimate that the hole concentrations of the $^{16}$O and $^{18}$O samples are the same within $\pm 10^{-5}$. Therefore, the observed large oxygen isotope effect on the penetration depth (or Meissner fraction) is due to the oxygen-mass dependence of $m^*$ or the density of states $N(E)$.

There are several theoretical explanations to the oxygen-mass dependence of the $N(E)$. Pickett, Cohen, and Krakauer[25] have shown that the strong anharmonicity of phonon modes will make $N(E)$ depend on the ion mass due to structure fluctuation. Alternatively, the ion-mass dependence of $N(E)$ could be due to the breakdown of Migdal adiabatic approximation. Engelesberge and Schrieffer[26] have shown that the Migdal approximation does not hold if there is a reasonably strong interaction between electrons and long wavelength optical phonons. The breakdown of the Migdal approximation will lead to the formation of polarons.[3] The interaction of the electrons with the long wavelength optical phonons (or the local phonons as in the Holstein model) narrows the electronic bandwidth and enhances the density of states by a factor $A(\omega)\exp(B/\omega)$ which is ion-mass dependent, where $A(\omega)$ has a weak dependence on $\omega$ and $B$ is a constant.[3]

In conclusion, we have observed oxygen isotope effects on $T_c$ and the Meissner fraction $f$ in the fine-grained, decoupled $La_{2-x}Sr_xCuO_4$ with $x=0.105$, 0.110, and 0.115. The observed large oxygen isotope effects on $T_c$ and the Meissner fraction can be explained as due to the oxygen-mass dependence of $m^*$ (effective mass of carriers). The present results may suggest that the conducting carriers in the cuprate superconductors are of polaronic type.

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