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Oxygen isotope effect on Néel temperature in various antiferromagnetic cuprates

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Oxygen isotope effect on Néel temperature (T_N) has been studied in the antiferromagnetic cuprates La_2CuO_4, Gd_2CuO_4, $Gd_{1.9}Ce_{0.1}CuO_4$, and CuO. For stoichiometric La_2CuO_4 with $T_N \sim 310$ K, the Néel temperature of the ^{18}O samples is ~ 1.8 K lower than the ^{16}O samples. For oxygen-annealed La_2CuO_4 samples (in 0.10 and 0.15 bar oxygen partial pressures), the Néel temperatures of the ^{18}O samples are $\sim$3.3–4.7 K lower than the ^{16}O samples. For La_2CuO_4 annealed in 0.6 bar oxygen, the Néel temperatures of the ^{16}O and ^{18}O samples are nearly equal due to segregation into oxygen-rich and oxygen-poor phases. For the other antiferromagnetic cuprates (which lack apical oxygen), we find a negligible oxygen isotope effect on T_N. We suggest that the observed oxygen isotope effect on T_N of La_2CuO_4 originates from the oxygen-mass dependences of J (in-plane antiferromagnetic exchange energy) due to the nonadiabatic motion of apical oxygen.

INTRODUCTION

The discovery[1] and development of high-T_c superconductors have led to a burst of experimental and theoretical studies on these systems. The behavior of undoped insulating compounds such as La_2CuO_4 and Gd_2CuO_4 is of interest as the starting point for discussion of the physics of superconductivity, particularly with regard to an evaluation of unusual microscopic mechanisms for superconductivity. The antiferromagnetic ordering found in parent insulating compounds such as La_2CuO_4 (Ref. 2) signals a strong electron-electron Coulomb correlation, and many unconventional pairing mechanisms[3,4] have been proposed to account for high-T_c superconductivity. On the other hand, large oxygen isotope effects on T_c found in underdoped cuprate superconductors may indicate a strong electron-phonon interaction.[5–8] It has been suggested that very strong electron-phonon interactions in cuprates may lead to the breakdown of the adiabatic approximation[9] so that electronic and lattice subsystems become strongly correlated.

Muon-spin-rotation (μSR) experiments show a universal linear relationship between T_c and n/m^* (where n is the carrier density and m^* is the effective mass of carriers) for underdoped cuprates.[10] So we speculate that large oxygen isotope effects for underdoped cuprates may arise from the oxygen-mass dependence of n and/or m^*. By carefully measuring the normal-state and Meissner susceptibility in fine-grained, decoupled ^{16}O and ^{18}O samples of $La_{2-x}Sr_xCuO_4$, we have found[11] that $\Delta T_c/T_c \approx \Delta f/f \approx -1.7\Delta\chi/\chi$ (where f is the Meissner fraction and χ is the normal-state susceptibility) upon isotope exchange. Then large oxygen isotope effects for underdoped cuprates can be only explained by the picture that m^* is oxygen-mass dependent.[11] Since the normal-state susceptibility χ in cuprates is related to the in-plane antiferromagnetic exchange J,[12] the oxygen-mass dependence of χ may imply that J is also oxygen-mass dependent. If it is true, one might observe oxygen isotope effects on J or on the Néel temperatures in antiferromagnetic cuprates. We have indeed observed an oxygen isotope effect on the Néel temperature of stoichiometric La_2CuO_4.

Here we report in detail the oxygen isotope effects on the Néel temperature (T_N) in various antiferromagnetic cuprates La_2CuO_4, Gd_2CuO_4, $Gd_{1.9}Ce_{0.1}CuO_4$, and CuO. We find that oxygen isotope effects on T_N of La_2CuO_{4+y} have a maximum at a certain hole concentration due to the competing y dependence of $\alpha(J)$ and L, where $\alpha(J)$ is the oxygen isotope effect on J and L is the extrinsic spin correlation length related to the holes. For other antiferromagnetic cuprates without apical oxygen, we find a negligible oxygen isotope effect on T_N. We suggest that the observed oxygen isotope effect on T_N of La_2CuO_4 originates from the oxygen-mass dependences of J (in-plane antiferromagnetic exchange energy) possibly due to the nonadiabatic motion of apical oxygen.

EXPERIMENTAL DETAILS

Samples of nominal composition La_2CuO_4 were prepared by the conventional solid-state reaction using La_2O_3 and CuO. Dried La_2O_3 powders were obtained by heating the original powders at 900 °C for 6 h. Well-ground mixtures of the oxides were fired to 1000 or 1100 °C in air for 12 h and cooled to room temperature in 4 h. The samples were reground, pressed into pellets, and sintered at 1000 or 1100 °C for 12 or 20 h. The details of the sample preparation conditions are given in Table I. The samples were ground again, pelletized, and annealed at 900 or 950 °C for 5 or 12 h to ensure a small grain size for rapid oxygen exchange by gas phase diffusion. Samples of Gd_2CuO_4 and $Gd_{1.9}Ce_{0.1}CuO_4$ were prepared in a similar way. These samples are single phase as checked by powder x-ray-diffraction (XRD) data.

The ^{16}O and ^{18}O samples were two pieces of the same starting sample pellet, which were then subjected to isotope diffusion. Isotopic diffusion was conducted in two parallel quartz tubes separated by about 2 cm.[7] Samples were at identical temperatures and nearly identical oxygen pressures (difference < 1%) throughout the diffusion process. The electronic pressure transducer gauges for the ^{18}O and ^{16}O sides were calibrated at the desired pressures for diffusion. For Gd_2CuO_4, $Gd_{1.9}Ce_{0.1}CuO_4$, and CuO, the oxygen isotope diffusion was done at temperatures of 900–950 °C and oxygen pressure of about 0.9 bar for 80–120 h. The cooling time from 900 °C to room temperature is 4 h. For La_2CuO_4, the oxygen isotope diffusion was first done at temperatures of 850-900 °C and oxygen pressures of ~0.6–1.0 bar for ~16–110 h. Then a final diffusion was carried out at a chosen oxygen pressure to control the oxygen content of the samples. The final diffusion conditions are shown in Table I for different sample pairs. Stoichiometric samples of La_2CuO_4 were obtained by annealing the sample pairs in vacuum (~60 mTorr) and at temperatures of 900–950 °C for ~0.5–1.5 h (see Table I). During vacuum annealing, the samples were placed in two parallel quartz tubes which were connected together and therefore had identical pressure. With continuous pumping of the system, the vacuum was nearly unchanged during the anneal. The back exchange was carried out at 900 °C for 60 h in air on the samples of experiment No. 5. The oxygen isotope enrichments were determined by weight changes of both ^{16}O and ^{18}O samples. The ^{18}O samples of La_2CuO_4 have about 85–90 % ^{18}O and 10–15 % ^{16}O. The ^{18}O samples of Gd_2CuO_4 and $Gd_{1.9}Ce_{0.1}CuO_4$ have ~95% ^{18}O and 5% ^{16}O. The ^{18}O samples of CuO have ~60–70 % ^{18}O and 30-40 % ^{16}O.

The susceptibility was measured in a commercial superconducting quantum interference device (SQUID). For La_2CuO_4, a magnetic field of 2 T was used to provide a good signal-to-noise ratio. In some cases, $B=1$ T was used (see caption of Fig. 1). The field was not changed throughout the whole series of measurements. The measurements were performed after the samples were field cooled to 200 or 260 K, at which temperature the samples were held for about 15 min to ensure thermal equilibrium. For Gd_2CuO_4, the measurements were performed after the samples were field cooled to 200 K. The measuring magnetic field was 50 Oe. The background of the empty sample holder was measured after the samples of La_2CuO_4 were removed from the sample holder. The magnitude of the background was ~5% of the signal of the La_2CuO_4 samples.

RESULTS

In Figs. 1(a)–1(e), we show the susceptibility for ^{16}O and ^{18}O sample pairs of La_2CuO_4, which had been prepared and treated under various conditions (see Table I). For experiment No. 1, the magnetic measurements were carried out after the samples were zero-field cooled at 170 K. There is no clear peak in the susceptibility, making it difficult to unambiguously specify the Néel temperatures. The absence of a clear susceptibility peak at T_N was also observed in other samples which were prepared at 1100 °C. The samples prepared at 1000 °C always have a clear susceptibility peak. In addition, the ^{18}O sample in experiment No. 1 has a lower susceptibility than the ^{16}O sample by ~20%. Whether the difference is intrinsic or caused by extrinsic factors (e.g., difference in the demagnetization factor) is not very clear since we did not measure the susceptibility of the sample pair before isotope exchange. However, our magnetic measurements on other sample pairs indicate that the susceptibility for each member of the sample pairs is nearly identical before isotope exchange. So we are sure that the differences of susceptibility above T_N for other ^{16}O and ^{18}O samples are intrinsic and caused by the differences in J.[13]

From Figs. 1(a)–1(c), one can see that the oxygen isotope effects on T_N appear to decrease as the oxygen pressures (for annealing) increase. On the other hand, oxygen isotope effects on T_N decrease when the oxygen contents are further reduced as seen from Figs. 1(d) and 1(e). These results suggest that the oxygen isotope effect on T_N may have a maximum at a certain oxygen content.

To check whether our vacuum annealing procedure can give identical oxidation conditions for both members of a sample pair, we show, in Fig. 1(f), the susceptibility results for one ^{16}O sample pair. The vacuum annealing procedure for this sample pair is the same as for those isotope-exchanged sample pairs. It is clear that the Néel temperatures for both members of the ^{16}O sample pair are nearly identical.

To check whether the observed oxygen isotope effects on T_N are reversible upon isotope exchange, we show, in Fig. 2, the susceptibility for the back-exchanged samples of experiment No. 5. The Néel temperatures for the sample pair are nearly the same after back exchange. Furthermore, the susceptibility above T_N is also the same for the sample pair (note the offset indicated by the arrow). The vacuum-annealing condition (900 °C/1 h) for the back-exchanged samples is slightly different from that for the original isotope-exchanged samples (950 °C/15 min and 400–900 °C/1.5 h). So the slight difference in T_c of the ^{16}O sample [see Figs. 1(e) and 2] is due to the slight difference in the vacuum-annealing condition.

In Fig. 3, we show the susceptibility for the ^{16}O and ^{18}O samples of Gd_2CuO_4. The susceptibility for the two isotope samples is nearly identical, indicating a negligible oxygen isotope effect on T_N in this T'-phase compound without apical oxygen. The oxygen isotope results for another T'-phase antiferromagnetic compound $Gd_{1.9}Ce_{0.1}CuO_4$ are plotted in Fig. 4. We also find a negligible oxygen isotope effect on T_N in this compound. This result is important. It implies that the oxygen contents for the two isotope samples must be identical since the T_N is sensitive to the carrier density in this composition. This result provides independent proof that our procedures for oxygen isotope exchange can ensure identical oxygen contents for the two isotope samples.

The results of oxygen isotope effects on T_N of CuO are shown in Fig. 5. The kink temperature (~230 K) as shown in the figure is the same as the Néel temperature (231±2 K) determined by neutron-scattering experiments.[13] It is very difficult to obtain oxygen exchange in CuO, possibly because it is very stable and has strong bonding. Thus, the ^{18}O substitution we obtained is only 60–70 %. From Fig. 5, one can see that the Néel temperatures for the two isotope samples are identical within ±0.2 K.

DISCUSSION

It is, of course, essential that we exclude external experimental effects which could mimic a real isotope shift of the Néel temperature of La_2CuO_4. One possible experimental effect could be a shift due to a smaller oxygen content of the ^{16}O sample than the ^{18}O sample. This possibility has been partially ruled out by the results shown

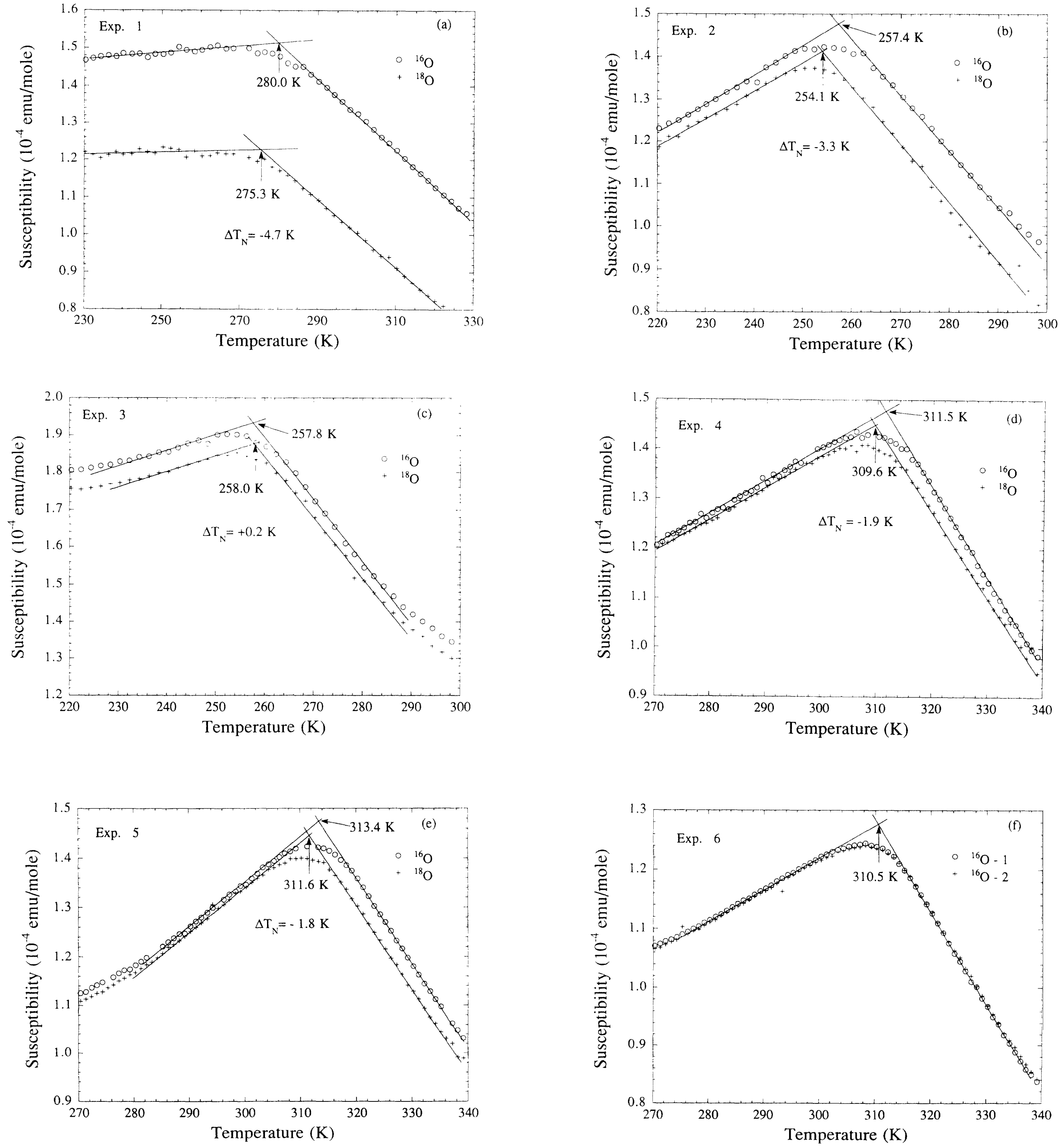

FIG. 1. Susceptibility curves for the ^{16}O and ^{18}O samples of La_2CuO_4: (a) for experiment No. 1, (b) for experiment No. 2, (c) for experiment No. 3, (d) for experiment No. 4, (e) for experiment No. 5, and (f) for experiment No. 6. The measuring magnetic fields are 1 T for experiment No. 1 and 2 T for experiment Nos. 2–6. The data were not corrected for demagnetization factors. The background of the empty sample holder was subtracted from the data. At 260 K, the susceptibility for the members of each sample pair is nearly identical within ±2% for experiment Nos. 4–6.

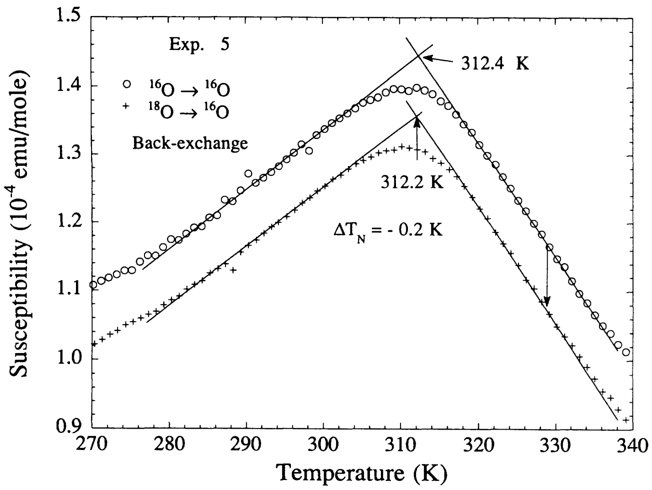

FIG. 2. Susceptibility curves for the back-exchanged samples of experiment No. 5. Note that the offset indicated by the arrow is added for clarity. The susceptibility above T_N for the sample pair is the same.

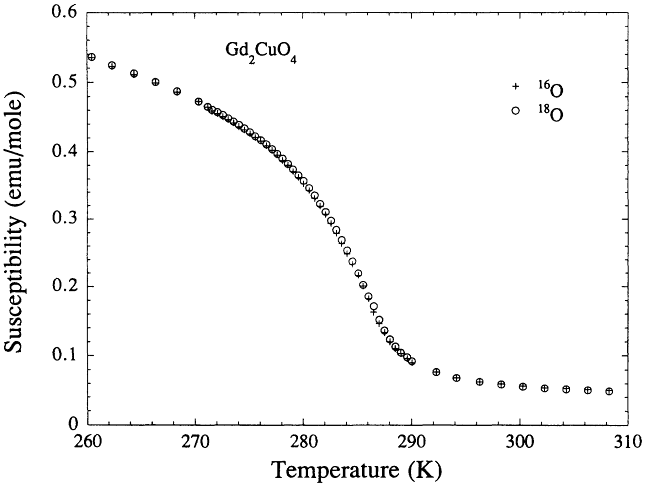

FIG. 3. Susceptibility curves for the ^{16}O and ^{18}O samples of Gd_2CuO_4. The measuring magnetic field is 50 Oe. The data were not corrected for demagnetization factors.

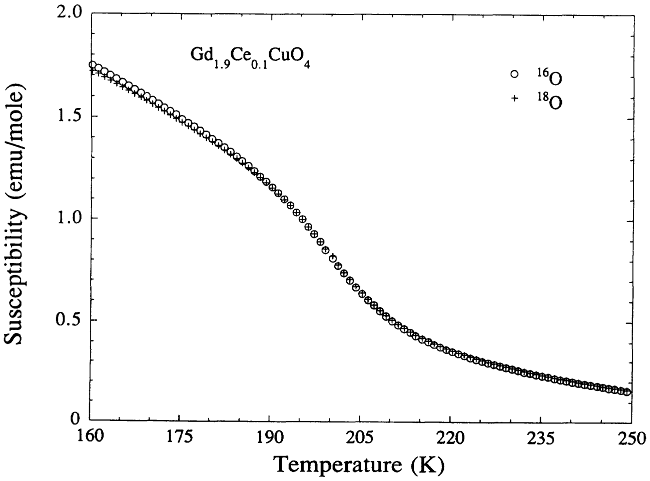

FIG. 4. Susceptibility curves for the ^{16}O and ^{18}O samples of $Gd_{1.9}Ce_{0.1}CuO_4$. The measuring magnetic field is 10 Oe. The data were not corrected for demagnetization factors.

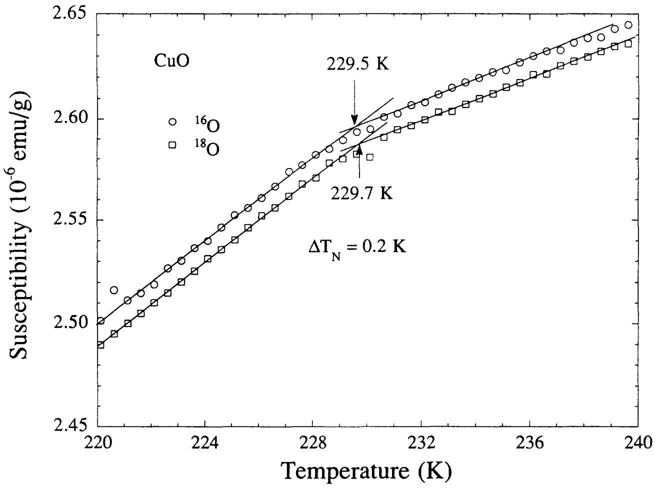

FIG. 5. Susceptibility curves for the ^{16}O and ^{18}O samples of CuO. The measuring magnetic field is 2 T. The data were not corrected for demagnetization factors.

in Figs. 1(f) and 2. Now we show our XRD results for experiment No. 4 to further exclude this possibility. On the basis of the D values of (200), (020), and (006) reflections as summarized in Table II, we find that the ratios $c/(ab)^{1/2}$ (where a, b, and c are lattice constants) for the ^{16}O and ^{18}O samples are identical within $(\pm 2\times 10^{-3})\%$. Although the absolute values of the lattice constants for the ^{16}O and ^{18}O samples are reproducible to $\sim 10^{-2}\%$ in our measurements, the ratio $c/(ab)^{1/2}$ measured from the three close-by reflections has a better reproducibility ($\sim 10^{-3}\%$) due to cancellation of several systematic errors. Since the ratios $c/(ab)^{1/2}$ have a relation with the oxygen contents as

$$\Delta y[c/(ab)^{1/2}]/\Delta[c/(ab)^{1/2}] \sim 5$$

in La_2CuO_{4+y},[14] our XRD result indicates that the ^{16}O and ^{18}O samples have identical y's within ±0.0001. More accurate XRD results for $La_{1.88}Sr_{0.12}CuO_4$ have also been obtained by Crawford *et al.*[6] They showed that the ratios $c/(ab)^{1/2}$ for the ^{16}O and ^{18}O samples are identical within $(\pm 1\times 10^{-4})\%$,[6] which is one order better than our results.

It is known that the antiferromagnetism in La_2CuO_{4+y} can be well described by mean-field theory, which leads to a T_N formula[15]

$$k_B T_N = J'[\xi(T_N)/a]^2 , \qquad (1)$$

where J' is the interlayer coupling energy and $\xi(T_N)$ is the in-plane correlation length at T_N and is given by[16]

$$\xi(T_N) = \xi_0(T_N)L(y)/[\xi_0(T_N)+L(y)] , \qquad (2)$$

where $\xi_0(T_N)$ is the in-plane correlation length when $y\sim 0$ and is given by

$$\xi_0(T_N) \sim \exp(J/T_N) . \qquad (3)$$

TABLE I. Sample preparation and annealing conditions for La_2CuO_{4+y}.

Experiment No.	Preparation conditions	Annealing conditions[a]
1	1100 °C/12 h and 1100 °C/12 h	0.10 bar/950 °C/10 h
2	970 °C/12 h and 1000 °C/20 h	0.15 bar/950 °C/16 h
3	970 °C/12 h and 1000 °C/20 h	0.60 bar/900 °C/36 h
4	1000 °C/12 h and 1000 °C/20 h[b]	vacuum/950 °C/60 min
5	970 °C/12 h and 1000 °C/20 h	vacuum/950 °C/15 min and 400–900 °C/1.5 h
6	1000 °C/12 h and 1000 °C/20 h[b]	vacuum/900 °C/60 min

[a] The vacuum-annealed samples were furnace cooled to room temperature. The oxygen-annealed samples were cooled to room temperature in 4 h.

[b] Dried La_2O_3 powders were used.

$L(y)$ arises from holes and tends to reduce the total correlation length. For $y=0$, $L(0)=\infty$. As y increases, $L(y)$ decreases.

From Eqs. (1)–(3), we find

$$\Delta T_N/T_N=\Delta J'/J'(1+B)+\Delta JB/J(1+B)\ , \tag{4}$$

where

$$B=2JL(y)/T_N[\xi_0(T_N)+L(y)]\ . \tag{5}$$

Equation (4) implies that the oxygen isotope effect on T_N is caused by the oxygen-mass dependences of J' and/or J. Since the interlayer coupling J' is proportional to the orthorhombicity in La_2CuO_4, a larger orthorhombicity means a larger interlayer coupling.[15] From Table II, we can see that the orthorhombicity of the ^{18}O sample is $\sim 7\%$ larger than the ^{16}O sample. The larger orthorhombicity for the ^{18}O sample was also observed by Crawford *et al.*[6] For $La_{1.88}Sr_{0.12}CuO_4$, they found that the orthorhombicity of the ^{18}O sample is $\sim 2\%$ larger than the ^{16}O sample.[6] Since the accuracy of the XRD results reported by Crawford *et al.* is high, we adopt the results of Crawford *et al.* and suggest $\Delta J'/J' \sim 2\%$.

For our vacuum-annealed samples where $y \sim 0$, $L(0)=\infty$. Substituting $\Delta J'/J' \sim 2\%$, $\Delta T_N/T_N \sim -0.6\%$, $T_N \sim 310$ K, and $J=1500$ K into Eqs. (4) and (5), we obtain $\Delta J/J \sim -0.8\%$. Considering $\Delta M/M \sim 11\%$ in our experiments, one finds the exponents of the oxygen isotope effects on J to be $\alpha(J)=-d\ln J/d\ln M=+0.07$.

As the hole concentration y increases, $L(y)$ decreases and the first term in the right side of Eq. (4) increases, while the second term decreases. As a result, the value of $-\Delta T_N/T_N$ will become smaller and smaller, and eventually change sign because of the different signs of the $\Delta J'/J'$ and $\Delta J/J$ terms. This is what we have observed [see Figs. 1(a)–1(c)]. For experiment No. 3 where the samples were annealed in 0.6 bar oxygen, the value of y may be large enough to drive phase segregation. If we take $\Delta T_N/T_N \sim 0$, $\Delta J/J=-0.8\%$, $\Delta J'/J'=+2\%$, $J=1500$ K, and $T_N=260$ K, we obtain $\xi_0(T_N) \sim 4L(y)$ or $\xi(T_N) \sim L(y)$ for experiment No. 3. This implies that phase segregation occurs when the spin correlation length $\xi(T_N)$ is approximately equal to the domain size $L(y)$ and that $T_N \sim J'(L/a)^2$, nearly independent of J, in agreement with the results of Cho, Chou, and Johnston.[17]

TABLE II. XRD results for the ^{16}O and ^{18}O samples of La_2CuO_4.

	Best D values (^{16}O)	Best D values (^{18}O)
(0 2 0)	2.701 46	2.703 32
(2 0 0)	2.675 89	2.675 72
(0 0 6)	2.188 40	2.189 13

We have shown in Ref. 11 that oxygen isotope effects on T_c and χ for underdoped $La_{2-x}Sr_{1-x}CuO_4$ are related as $\Delta T_c/T_c=-1.7\Delta\chi/\chi$. If we assume $\chi \sim 1/J$,[12] then $\Delta T_c/T_c \approx 1.7\Delta J/J$. Using this relation and the measured exponents of oxygen isotope effects on T_c (see Ref. 5), we find that the exponents of oxygen isotope effects on J [denoted by $\alpha(J)$] are 0.24 and 0.35, respectively, for $x=0.075$ and 0.113. The dependence of $\alpha(J)$ on the hole concentration is plotted in Fig. 6. It is evident that the oxygen isotope effect on J increases with increasing hole concentration. So the oxygen isotope effect on T_N will increase with increasing oxygen content if $L(y)$ does not change with y, which is not the case. The competing y dependence of L (decreasing with increasing y) and $\alpha(J)$ (increasing with increasing y) will lead to a maximum isotope effect on T_N at certain values of y, in agreement with the experimental results.

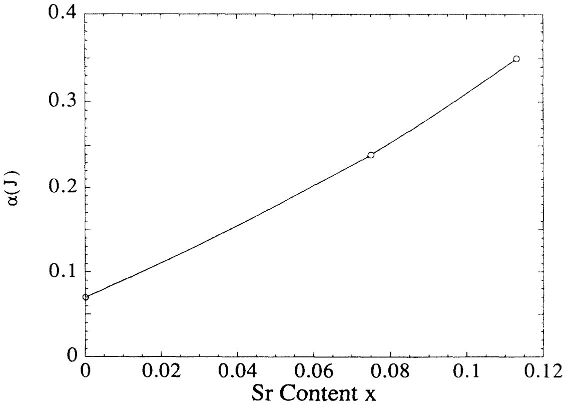

FIG. 6. The hole-concentration dependence of oxygen isotope effects on J in $La_{2-x}Sr_xCuO_4$.

The absence of oxygen isotope effects on J in T'-phase compounds and CuO indicates that apical oxygen in La_2CuO_4 is responsible for the observed oxygen isotope effects on T_N and thus J. The oxygen-mass dependence of J might be explained by the zero-point motion of in-plane oxygen due to anharmonic effects. The XRD results[6] for $La_{1.88}Sr_{0.12}CuO_4$ showed that both in-plane and out-of-plane Cu-O bond lengths for the ^{18}O sample are $\sim 0.001\%$ smaller than that for the ^{16}O sample. From the relation $J \propto d^{-4.6}$ (where d is the Cu-O bond length),[18] one obtains $\Delta J/J \sim +0.005\%$, which is too small to account for the observed results. Alternatively, we suggest that the sizable oxygen-mass dependence of J may originate from the nonadiabatic motion of apical oxygen. The double-well structure of apical oxygen possibly due to the anti–Jahn-Teller effect may be the origin of the nonadiabaticity.[19] The decreasing oxygen isotope effect on J with decreasing hole concentration may be connected with the increasing electron-electron Coulomb correlation or with the decreasing oxygen component in conduction bands.

CONCLUSIONS

In summary, we have studied oxygen isotope effects on Néel temperatures (T_N) in the antiferromagnetic cuprates La_2CuO_4, Gd_2CuO_4, $Gd_{1.9}Ce_{0.1}CuO_4$, and CuO. For stoichiometric La_2CuO_4 with $T_N \sim 310$ K, the Néel temperatures of the ^{18}O samples are ~ 1.8 K lower than the ^{16}O samples. For the oxygen-annealed La_2CuO_4 samples (in 0.10 and 0.15 bar oxygen partial pressures), the Néel temperatures of the ^{18}O samples are ~ 3.3–4.7 K lower than the ^{16}O samples. For the La_2CuO_4 samples annealed in 0.6 bar oxygen, the Néel temperatures of the ^{16}O and ^{18}O samples are nearly identical due to phase segregation. For other antiferromagnetic cuprates (which do not have apical oxygen), we find a negligible oxygen isotope effect on T_N. Our results indicate that both in-plane antiferromagnetic exchange energy J and interlayer coupling J' in La_2CuO_4 have rather strong oxygen-mass dependence, while the J of Gd_2CuO_4 has a negligible oxygen-mass dependence. The oxygen-mass dependences of J and J' may originate from the nonadiabatic motion of apical oxygen due to strong electron-phonon interaction. High-T_c superconductivity may be closely related to apical oxygen.

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