Giant Oxygen Isotope Effect on the Spin Glass Transition in $La_{2-x}Sr_xCu_{1-z}Mn_zO_4$ as Revealed by Muon Spin Rotation

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We have observed a huge oxygen isotope effect on the spin glass transition in $La_{2-x}Sr_xCu_{1-z}Mn_zO_4$ ($x = 0.03$ and 0.05, $z = 0.02$) using the muon-spin-rotation technique. Upon replacing ^{16}O with ^{18}O, the spin glass freezing temperature T_g in the Mn-doped samples increases by about 80% for $x = 0.03$ and 30% for $x = 0.05$. On the other hand, T_g has a small isotope shift in the Mn-free samples. These novel isotope effects clearly demonstrate a strong effect of electron-phonon interaction on magnetism which can be explained taking into account the polaronic nature of charge carriers in cuprates.

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It is well known that the parent compounds of the cuprate superconductors exhibit long-range 3D antiferromagnetic (AF) order, which is rapidly destroyed as holes are doped into the CuO_2 planes. However, short-range 2D AF correlations survive well into the superconducting region of the phase diagram. Muon-spin-rotation experiments have shown that superconductivity and magnetism can even coexist on a microscopic scale [1]. The issues of how magnetism affects superconductivity and what the nature of doping-induced charge carriers within the antiferromagnetic CuO_2 planes is remain controversial. The understanding of these fundamental issues will help to clarify the pairing mechanism of high-T_c superconductivity.

There is increasing evidence that a strong electron-phonon coupling is present in cuprates [2] which may lead to the formation of polarons (bare charge carriers accompanied by local lattice distortions) [3]. Several independent experiments have demonstrated that superconductivity and the underlying lattice vibrations are intimately linked [4]. On the other hand, little is known about the influence of the electron-phonon interaction on magnetism in cuprates. Conventional theories of magnetism neglect atomic vibrations; the atoms are generally considered as infinitely heavy and static in theoretical descriptions of magnetic phenomena, so there should be no isotope effect on magnetism. However, if charge carriers are polaronic, i.e., nuclear and electronic motions are no longer decoupled (breakdown of the Born-Oppenheimer approximation), one might expect isotope effects on magnetic properties. This is indeed the case in the ferromagnetic manganites where a giant oxygen isotope effect on the Curie temperature has been discovered [5]. The question is whether such an isotope effect also exists in the cuprate systems.

In this Letter we report studies of the oxygen-isotope effects on the low-temperature magnetism in $La_{2-x}Sr_xCu_{1-z}Mn_zO_4$ ($x = 0.03,\ 0.05;\ z = 0,\ 0.02$) using the zero-field muon-spin-rotation (μSR) technique. These samples are in the regime of a so-called cluster spin glass (CSG) [6]. We have observed a huge oxygen isotope effect on the spin glass freezing temperature T_g in the Mn-doped samples ($\alpha_{T_g} = -d\ln T_g/d\ln M = -6.0(7)$ and $-2.7(5)$ for $x = 0.03$ and 0.05, respectively), while the isotope effect is small in the Mn-free samples. The results demonstrate a strong effect of the electron-phonon interaction on the magnetism and can be explained by taking into account the polaronic nature of the charge carriers in the cuprates.

Polycrystalline $La_{2-x}Sr_xCu_{1-z}Mn_zO_4$ samples with $x = 0.03,\ 0.05$ and $z = 0,\ 0.02$ were prepared using conventional solid state reaction. We choose Mn ions to partially substitute the Cu ions in the CuO_2 planes. The isovalent Mn^{2+} substitution for Cu^{2+} does not change the total charge carrier concentration. Also, Mn^{2+} gives a strong electron paramagnetic resonance (EPR) signal [7], which allowed to perform EPR measurements in the same samples. The results of the EPR study will be published elsewhere.

The ideal isotope effect experiment requires a set of samples, which are identical in all respects except for the isotope mass. Details of the isotope exchange procedure are presented in our previous publications [8–10]. For oxygen isotope exchange, each sample was divided into two parts. Both parts were annealed in $^{16}O_2$ and $^{18}O_2$ gas atmosphere under exactly the same conditions at 800 °C for 30 h in an oxygen pressure of $\sim$1.0 bars. The difference between $^{16}O_2$ and $^{18}O_2$ partial pressures was less than 2%. Oxygen isotope enrichments of the samples were determined using thermogravimetry. The ^{18}O samples have about 85% ^{18}O and 15% ^{16}O. We determined also the oxygen content in isotope exchanged samples using high-accuracy volumetric analysis [11]. We have found that the ^{16}O and ^{18}O isotope samples have the same oxygen concentration $\delta = 4.0025$ within the experimental accuracy of ± 0.0003.

The zero-field μSR technique is especially suitable for the study of weak and short-range magnetic correlations, since the positive muon is an extremely sensitive local

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probe which is able to detect small internal magnetic fields. As a real-space probe, μSR can determine the ordered volume fraction and is particularly powerful for the study of disordered magnetic materials such as spin glasses. The μSR experiments were performed at the Paul-Scherrer-Institute in Villigen, Switzerland, using essentially 100% spin-polarized positive "surface muons." The pair of samples with different oxygen isotopes were mounted on the two sides of the sample holder. This allows one to switch between the ^{16}O and ^{18}O samples by rotating the sample holder without removing it from the cryostat, so the two isotope samples can be measured at the same experimental conditions.

At low temperatures in all studied samples we observed damped oscillations due to muon-spin precession in local magnetic fields. Figure 1(a) shows a representative zero-field (ZF)-μSR time spectrum for a $La_{1.97}Sr_{0.03}CuO_4$ sample. The time evolution of the muon-spin polarization is well described by the formula

$$A(t) = A_1 \exp(-\lambda t) + A_2 \exp(-\Delta t) \cos(\gamma_\mu B_\mu t + \Phi), \quad (1)$$

where $\gamma_\mu = 851.4$ Mrad s^{-1} T^{-1} is the gyromagnetic ratio of the positive muon, and B_μ is the average static internal magnetic field at the muon site. In the absence of an external magnetic field B_μ is determined by the local magnetic order parameter, i.e., the staggered magnetization. The two components originate from muons where B_μ is parallel or transverse to the muon-spin polarization with longitudinal (λ) and transverse (Δ) relaxation rates, respectively.

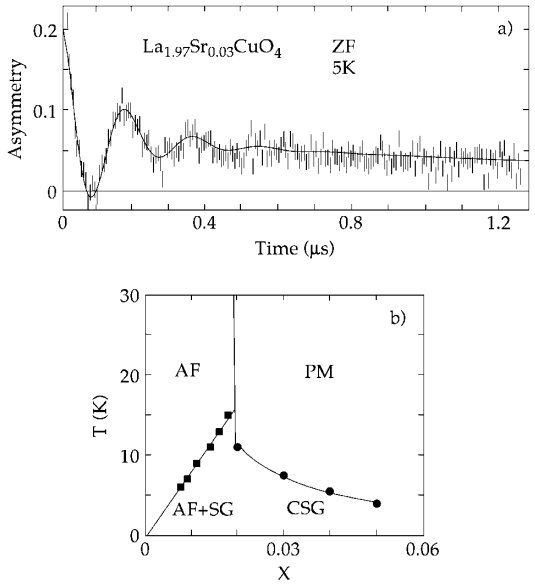

FIG. 1. (a) ZF-μSR time spectrum observed in a $La_{1.97}Sr_{0.03}CuO_4$ sample at 5 K. The solid line is a fit using Eq. (1) (see text). (b) Low-temperature magnetic phase diagram of $La_{2-x}Sr_xCuO_4$ constructed from literature data: AF, antiferromagnetic phase; SG, spin glass phase; CSG, cluster spin glass phase; PM, paramagnetic phase. After Ref. [13].

A clear oscillation observed in ZF-μSR spectra implies that muons sense a well-defined internal magnetic field, in agreement with previous μSR measurements [1]. It is well known that in $La_{2-x}Sr_xCuO_4$ long-range antiferromagnetism is destroyed at $x \approx 0.02$ and superconductivity appears at $x \approx 0.05$. A short-range ordered AF state exists at intermediate doping in the range $0.02 < x < 0.06$. Early μSR and neutron scattering experiments found that this magnetic state resembles a spin glass [12]. However, more detailed studies using ^{139}La nuclear quadrupole resonance [6] showed that the state in $La_{2-x}Sr_xCuO_4$ ($0.02 < x < 0.06$) is not a conventional spin glass, but a cluster spin glass. The coherent muon-spin precession in zero applied field confirms this picture. This is because in a conventional spin glass the muons would see a very broad distribution of local magnetic fields, leading to an incoherent precession. The CSG arises from the phase separation of doped holes which form hole-rich walls separating hole-free AF domains. The undoped mesoscopic domains with 2D magnetic correlations freeze at low temperatures due to their mutual interaction, forming a CSG [6]. The magnetic transition temperature T_g decreases with doping $T_g \propto 1/x$ [6]. Moreover, μSR studies have indicated that the CSG state persists also for $x > 0.06$ and coexists with superconductivity in the underdoped regime of $0.06 \leq x \leq 0.10$ [1]. The magnetic phase diagram of the $La_{2-x}Sr_xCuO_4$ system, constructed from literature data, is shown in Fig. 1(b) [13].

In Fig. 2 the internal magnetic fields B_μ for the two oxygen isotope (^{16}O and ^{18}O) samples ($x = 0.03$, $z = 0$) are shown as a function of temperature. One can see that B_μ in the ^{18}O sample is higher than the ^{16}O sample and this difference decreases at lower temperatures. The solid curves in Fig. 2 are the fits to the power law temperature dependence $B_\mu(T) = B_\mu(0)(1 - T/T_g)^n$. We find $B_\mu(0) = 45(1)$ mT, $n = 0.50(1)$ for both isotope samples with different spin glass freezing temperature

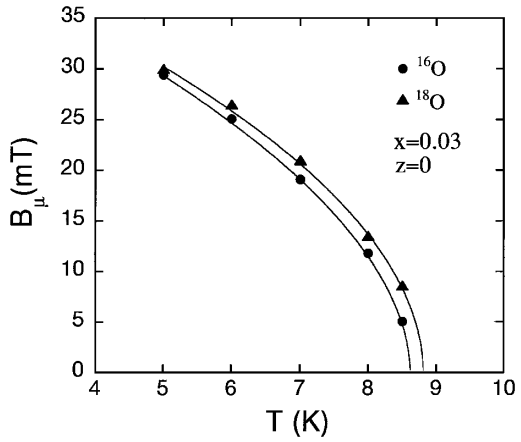

FIG. 2. Temperature dependence of the internal magnetic field at the muon site B_μ for the ^{16}O and ^{18}O samples of $La_{1.97}Sr_{0.03}CuO_4$. Solid lines represent fitted curves to the power law $B_\mu(T) = B_\mu(0)(1 - T/T_g)^n$.

$T_g = 8.60(2)$ K and 8.80(2) K for the ^{16}O and ^{18}O samples, respectively. The isotope shift of T_g is small, but observable. For $x = 0.05$, $T_g = 5.1(1)$ K in accordance with the phase diagram presented in Fig. 1(b). We found that the oxygen isotope effect on B_μ also exists in the $x = 0.05$ samples, but it is smaller compared to $x = 0.03$. In addition, the width of the magnetic field distribution significantly increases in the $x = 0.05$ samples, resulting in a strongly damped muon-spin precession. This makes it difficult to determine T_g accurately.

The oxygen isotope shift of T_g is dramatically enhanced in the Mn-doped samples as shown in Figs. 3 and 4. For $x = 0.03$ and $z = 0.02$, the T_g of the ^{18}O sample is 10 K higher than that of the ^{16}O sample. For $x = 0.05$ and $z = 0.02$ the isotope shift of T_g is about 3 K. This results in a huge value of the oxygen isotope exponent for the spin glass freezing temperature: $\alpha_{T_g} = -d\ln T_g/d\ln M = -6.0(7)$ and $-2.7(5)$ for $x = 0.03$ and 0.05, respectively. These are the largest *negative* oxygen isotope exponents ever measured for any phase transition temperature. It is essential to show that the observed isotope effects are intrinsic and not due to different oxygen content in two isotope samples. As was mentioned above, our ^{16}O and ^{18}O isotope samples have the same oxygen concentration within the experimental accuracy of ± 0.0003. Unlike the Neél temperature, the spin freezing temperature T_g is much less sensitive to the charge carrier concentration ($T_g \propto 1/x$). It is clear that the negligible oxygen content difference (less than 0.0003) cannot give a huge difference of T_g between ^{16}O and ^{18}O samples.

In order to explain the unusual increase of the spin glass freezing temperature with increasing oxygen mass, one should note that the Mn doping itself increases T_g, and this increase is strongly isotope dependent (see Table I). It is well known that doped holes strongly disturb the antiferromagnetic bonds in the CuO_2 planes [14] and intuitively one can expect that mobile holes are much more effective than static ones in destroying AF bonds. However, the detailed mechanism of the rapid suppression of T_N upon doping is poorly understood. Very recently Hücker *et al.* [15] studied experimentally the relationship between hole mobility and AF order by measuring the magnetic and electronic transport properties in $La_{2-x}Sr_xCuO_4$ doped by Zn in the AF phase ($x < 0.03$). They found a clear correlation between the degree of hole localization and the AF ordering temperature T_N. In particular, it was shown that Zn doping increases T_N due to localization of charge carriers. These results demonstrate that the charge mobility plays a crucial role in destruction of the AF order in $La_{2-x}Sr_xCuO_4$.

The same mechanism could apply to the Mn doping into $La_{2-x}Sr_xCuO_4$ in the CSG phase. The isovalent Mn^{2+} substitution for Cu^{2+} does not change the overall charge carrier concentration. However, as impurities are doped into the CuO_2 planes, they create random potentials which lead to carrier localization. A decrease of the carrier mobility due to the Mn doping can explain the increase of T_g. Now the observed oxygen isotope effect on the spin glass freezing temperature can be understood if we take into account the polaronic nature of the charge carriers. The main effect of polarons in the transport properties is to reduce the bandwidth (increase of the effective mass of carriers) by means of an exponential renormalization factor [3]

$$W_{\text{eff}} \propto W \exp(-\gamma E_b/\hbar\omega), \tag{2}$$

where W is the bare conduction bandwidth, E_b is the polaron binding energy, and ω is the characteristic frequency of the optical phonons depending on the isotope mass M ($\omega \propto M^{-1/2}$). The dimensionless parameter γ is a function of E_b/W with $0 < \gamma \leq 1$. It was shown that the effective mass of the charge carriers m^* in cuprates is strongly isotope dependent and increases with increasing

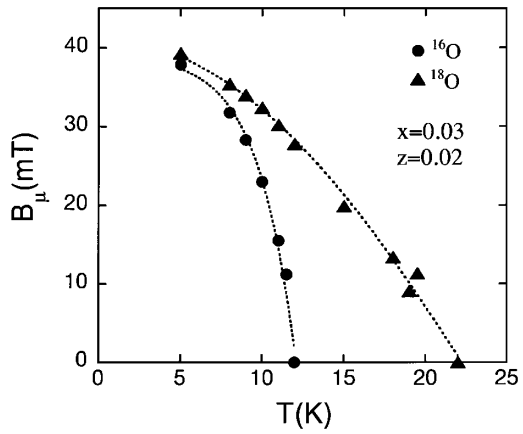

FIG. 3. Temperature dependence of the internal magnetic field at the muon site B_μ for the ^{16}O and ^{18}O samples of $La_{1.97}Sr_{0.03}Cu_{0.98}Mn_{0.02}O_4$. Dotted lines are guides to the eye.

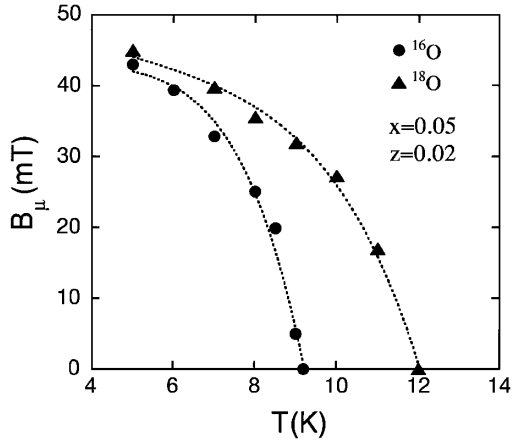

FIG. 4. Temperature dependence of the internal magnetic field at the muon site B_μ for the ^{16}O and ^{18}O samples of $La_{1.95}Sr_{0.05}Cu_{0.98}Mn_{0.02}O_4$. Dotted lines are guides to the eye.

TABLE I. The spin glass freezing temperature T_g of the oxygen-isotope exchanged samples and the corresponding isotope exponents $\alpha_{T_g} = -d\ln T_g/d\ln M$.

Sample	$T_g(^{16}\mathrm{O})$ [K]	$T_g(^{18}\mathrm{O})$ [K]	α_{T_g}
$La_{1.97}Sr_{0.03}CuO_4$	8.6 K	8.8 K	$-0.19(1)$
$La_{1.97}Sr_{0.03}Cu_{0.98}Mn_{0.02}O_4$	12 K	22 K	$-6.0(7)$
$La_{1.95}Sr_{0.05}CuO_4$	5.1 K	5.2 K	$-0.15(5)$
$La_{1.95}Sr_{0.05}Cu_{0.98}Mn_{0.02}O_4$	9 K	12 K	$-2.7(5)$

oxygen mass M, in agreement with Eq. (2) [10]. A larger m^* in ^{18}O samples will lead to a stronger localization of the charge carriers than in the ^{16}O samples. This is quite reasonable because heavier carriers are more easily localized by random impurity potentials. This can explain why T_g is higher in the ^{18}O samples than in the ^{16}O samples. For the Mn-free samples, the charge localization effect is not significant due to a weak random potential. That is why the isotope effect on the mobile carrier concentration and thus on T_g is strongly reduced in the Mn-free samples. It is interesting to note that the oxygen isotope dependent trapping of the charge carriers was recently observed in the colossal magnetoresistive manganites [16]. It was found that the density of the *mobile* polarons in the paramagnetic phase decreases with replacing ^{16}O by ^{18}O.

In summary, we have performed μSR measurements on the oxygen-isotope exchanged samples (^{16}O and ^{18}O) of the single-layer cuprates $La_{2-x}Sr_xCu_{1-z}Mn_zO_4$ ($x = 0.03, 0.05$; $z = 0, 0.02$). These samples show a transition to a cluster spin glass state at low temperatures. It was found that the spin glass freezing temperature T_g increases with the Mn doping which can be explained in terms of localization of the holes by the Mn impurities doped to the CuO_2 planes. This demonstrates the intimate relation between hole mobility and cluster spin glass magnetism in doped cuprates. More importantly, we have observed that T_g increases with the oxygen mass M and the isotope effect is very large in the Mn-doped samples where the isotope exponent $\alpha_{T_g} = -d\ln T_g/d\ln M$ reaches a huge value: $\alpha_{T_g} = -6.0(7)$ and $-2.7(5)$ for $x = 0.03$ and 0.05, respectively. To our knowledge such a huge isotope effect on the magnetism in cuprate superconductors has not been reported before. This unusual effect can be understood by taking into account the polaronic nature of the charge carriers in cuprates. The mechanism for the formation of polarons may arise from a strong Jahn-Teller effect, as is the case in doped perovskite manganites [5,17].

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