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Observation of magnetic order in the double-layer system $La_2MCu_2O_{6+\delta}$ (M = Ca,Sr)

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Measurements of the spin rotation and depolarization of implanted positive muons have revealed that $La_2SrCu_2O_{6+\delta}$, $La_2CaCu_2O_{6+\delta}$, and $La_{1.9}Y_{0.1}CaCu_2O_{6+\delta}$, members of the double-layer perovskite family $La_2MCu_2O_{6+\delta}$ (M=Ca,Sr), display magnetic ordering similar to that of $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_x$. Their magnetic order parameters are remarkably close to those of the other layered cuprates. A superconducting minority phase has been detected in $La_2CaCu_2O_{6+\delta}$ ($\delta \geq 0.02$), with onset at ~45 K and accompanied by a change in the muon-spin-precession signals from the majority antiferromagnetic phase, phenomena absent in $La_2SrCu_2O_{6+\delta}$. This behavior was attributed to mobility and local clustering of intercalated oxygen excess in the layer between the CuO_2 planes.

The study of $La_2MCu_2O_{6+\delta}$ (M=Ca,Sr) is very appealing because they provide, in principle, a simpler family of layered cuprates in which to compare the physical properties of superconducting and nonsuperconducting members of the family. Although superconductivity was reported recently in Sr-substituted $La_{2-x}Sr_xCaCu_2O_6$ (x=0.25–0.45) and $La_2CaCu_2O_{6.037}$,[1,2] the results obtained so far still appear somewhat controversial. Previous work has shown that hole-doped $La_2SrCu_2O_{6+\delta}$ is metallic but not superconducting,[3–5] and samples of nominal composition $La_{1.6}Sr_{0.4}CaCu_2O_y$ prepared at an O_2 pressure of 1 atm failed to show bulk superconductivity, i.e., the oxygen stoichiometry is particularly important.[6] In the present work, we show that samples at low hole concentration, for which the oxygen excess is well known, do order magnetically, thus clarifying the other aspect of the puzzle these structures posed previously in not displaying either superconductivity or clear magnetic-ordering phenomena. In addition, we have confirmed that a fraction of $La_2CaCu_2O_{6+\delta}$ is superconducting with onset $\simeq$45 K.[2]

Muon spin rotation-relaxation, μ^+SR, is a very sensitive microscopic probe of magnetic order,[7] especially when short ranged or in the presence of nonmagnetic phases. The technique has been used extensively in studies of the interplay between superconductive and magnetic ordering in $La_2CuO_{4+\delta}$, $La_{2-x}Sr_xCuO_{4-y}$, $YBa_2Cu_3O_x$,[8–16] and the electron-doped copper oxides.[17] The present experiments were carried out at the μSR facilities at the TRIUMF cyclotron, as part of our systematic study of magnetic ordering in oxides related to high-T_c superconductors. The results showed that antiferromagnetic order does indeed exist in both members of the $La_2MCu_2O_{6+\delta}$ (M=Ca,Sr) family, albeit of a more complex nature than for one-layer cases. Using neutron diffraction we determined that one $La_2SrCu_2O_{6+\delta}$ sample (prepared in air, herewith called the "oxygenated sample") had a nominal oxygen excess $\delta=0.2$, while $\delta\leq 0.06$ was obtained both for a $La_{1.9}Y_{0.1}CaCu_2O_{6+\delta}$ and for a second $La_2SrCu_2O_{6+\delta}$ sample prepared in a reducing atmosphere ("reduced sample"). We also studied a $La_2CaCu_2O_{6+\delta}$ sample prepared under identical conditions as the $La_2CaCu_2O_{6.037}$ sample of Ref. 2, where susceptibility and structural data are discussed in detail. The yttrium substitution in $La_{1.9}Y_{0.1}CaCu_2O_{6+\delta}$ was carried out to decrease the oxygen content since a reduction of the ionic ratio should lead to lower oxygen coordination for the nominally eightfold coordinated site. Other oxides were present below the 1% level. Neutron diffraction also showed that the Ca ions in $La_2CaCu_2O_{6+\delta}$ are mainly located at the eightfold coordinated sites stacked between the double CuO_2 layers (75% occupancy).[2] By contrast, a nearly random distribution of Sr ions among the eightfold and ninefold coordinated sites of the structure is found in $La_2SrCu_2O_{6+\delta}$.[4–6] This different cationic distribution and the size difference between Sr^{2+} and Ca^{2+} lead to changes in the Cu-O distances of the pyramid,[2,6] and, as shown by Adachi *et al.*, to remarkable changes in resistivity for nonsuperconducting substitution-doped samples,[6] which suggests that these structural features are also important in determining the physical properties of $La_2MCu_2O_{6+\delta}$ (M=Ca,Sr), especially the superconductive behavior, as shown below.

The simplest way to search for static magnetic order by μ^+SR is to detect the precession of the muon spin in zero applied field, which is due to the internal fields at the muon interstitial locations. The depolarization envelope of the precessing signal furthermore gives a measure of the rms width of the internal field distribution. The muon spin, responding to a few shells of neighbors with atomic moments as low as $0.1\mu_B$, is able to detect ordering with short correlation lengths, and possible nonmagnetic phases appear as nonoscillating backgrounds. An example of the data is shown in Fig. 1 for reduced $La_2SrCu_2O_{6+\delta}$. Two damped oscillating signals, corresponding to about 65% of the full signal, are clearly seen. The main signal, with a 4.8-MHz extrapolated ($T\rightarrow 0$) precession frequency, corresponds to an effective ordered field of ~360 Oe, with a 7% spread in magnitude. The magnitude of the internal field is similar, but its width is larger than for La_2CuO_{4-y}, indicating shorter magnetic correlation lengths. This signal then corresponds to muons bound to apical oxygens as in La_2CuO_{4-y}.[10,12] The second signal, at 18 MHz, can be identified with muons located at or near the CuO_2 planes.[13,17] The temperature dependence of the measured frequencies, shown in Fig. 2 and the depolarization rate (not displayed), indicate a spin-freezing temperature T_N of over 300 K. Figure 3 displays frequency and depolarization rates for oxygenated $La_2SrCu_2O_{6+\delta}$, to illustrate how both quantities signal the onset of magnetic order; also, the larger oxygen excess δ results in a decrease in the freezing temperature when compared to the reduced sample.

Significantly different results were obtained for $La_2CaCu_2O_{6+\delta}$. As shown in Fig. 4, the frequencies and T_N of the two main signals are lower than for reduced $La_2SrCu_2O_{6+\delta}$, but increase below ~35 K to 5.8 and 18 MHz. Such signals account for about 60% of the full signal. The remaining fraction of the signal corresponds to muons stopping in nonmagnetic environments, such as sample backing and cryostat materials, together with a paramagnetic contribution due to the superconducting phase. Although not clearly identified, such background signals are nonoscillating and show a low relaxation rate,

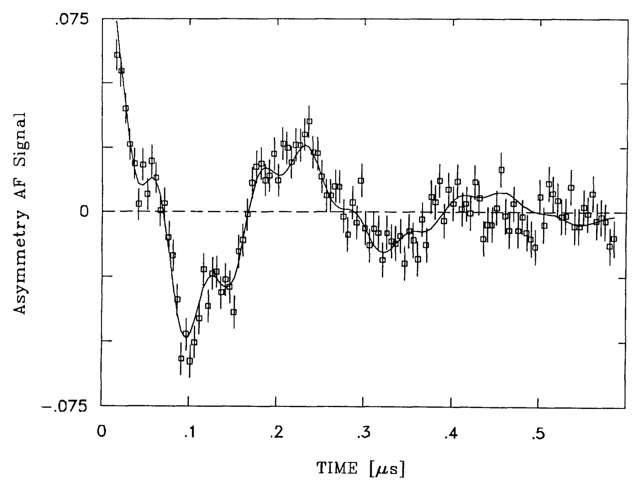

FIG. 1. Muon-spin-precession signal for reduced $La_2SrCu_2O_{6+\delta}$ at 20 K, in zero external field. The oscillating signals (4.8 and 18 MHz), due to the ordered moments, are superimposed on a slowly-depolarized nonoscillating background signal due to muons decaying in a nonmagnetic environment (cryostat walls, sample backing), which has been subtracted.

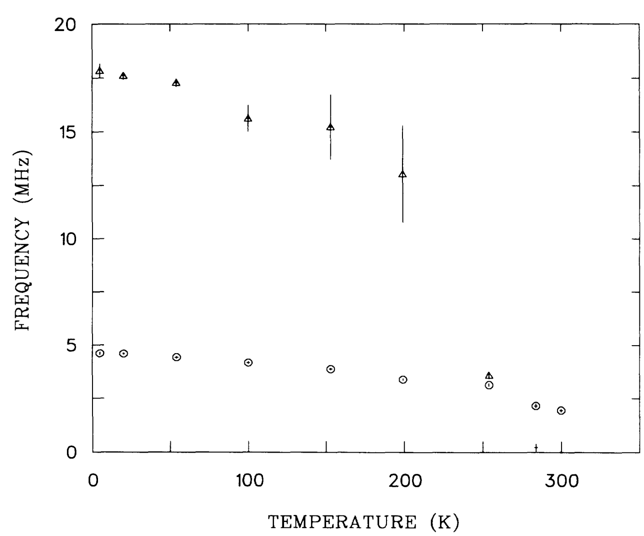

FIG. 2. Temperature dependence of the frequencies of the main signals in reduced $La_2SrCu_2O_{6+\delta}$. The 18-MHz (small amplitude, triangles) signal could not be followed at temperatures over 200 K, due to its increasing relaxation rate. The freezing temperature T_N is above 300 K. This is strikingly similar to the $YBa_2Cu_3O_x$ case, where 4- and 18-MHz signals appear, with a $T_N\sim 400$ K.

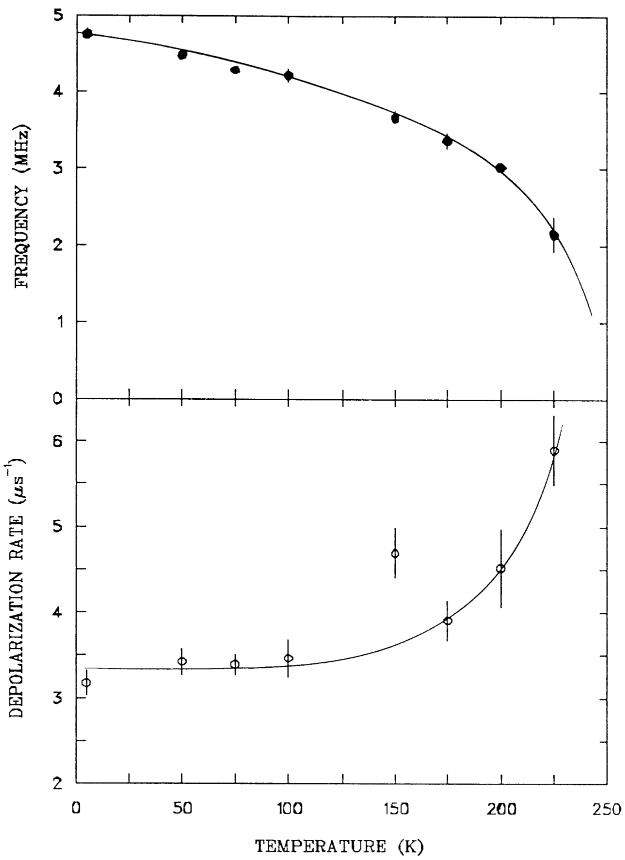

FIG. 3. Frequency (top panel) and depolarization rate (lower panel) for oxygenated $La_2SrCu_2O_{6+\delta}$ (main signal). This illustrates how both quantities signal the onset of spin-freezing, and shows that oxygenation reduces the magnetic correlation length.

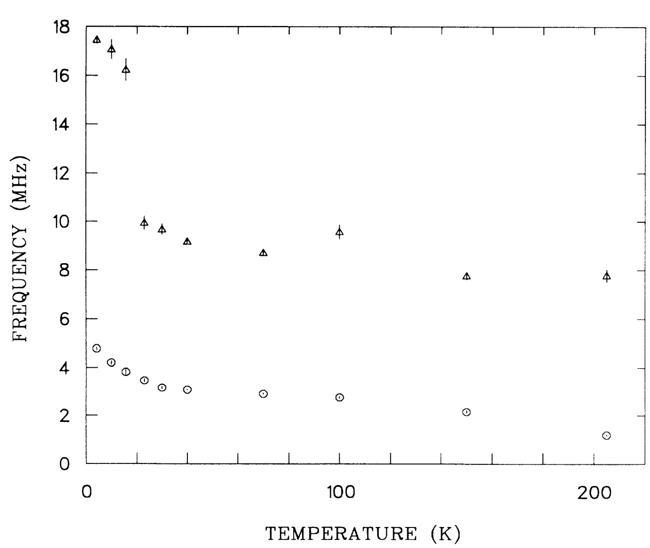

FIG. 4. Similar to Fig. 2, but for the $La_2CaCu_2O_{6+\delta}$ sample. Notice that the frequencies become close (5.8 and 18 MHz) to those of $La_2SrCu_2O_{6+\delta}$ only below 10 K. Both from the decrease of the frequencies and increase of the relaxation rate (not shown), $T_N \sim 250$ K in this case.

and thus do not affect the determination of frequencies and relaxation rates for the main oscillatory signals. Their strength is temperature independent in the zero-field measurements. The lattice constants do not change much from 1.5 to 295 K[2], so that the low temperature change is not due to a structural transition. The transition is unlikely to be due to the muons changing sites in an unchanged structure, since the onset of hoping in the oxides is at higher temperature, and the signals of Figs. 2–4 show no indication of diffusion up to 250 K. A possible mechanism is an actual spin-reorientation transition in the ordered spin structure, resembling the known transition in Nd_2CuO_4, for which a similar (but sharper) change in the frequency for the apical oxygen-bound muons was found.[17] This is unlikely, however, since the 18-MHz signal shows the same change, but originates from a crystallographically different site. We attribute this change to the onset of superconductivity, due to mobility and segregation of the excess oxygen intercalated in the Ca(La) planes between the CuO_2 layers—the open part of the structure where the O(3) vacancies reside. If randomly distributed throughout the lattice, the hole concentration due to the oxygen excess may be enough to decrease the ordered moment by a frustration mechanism. As the temperature is lowered, the labile oxygens may cluster into domains having a local hole concentration high enough to generate locally a segregated superconducting phase, while the rest of the sample volume recovers magnetic moment and order identical to that of reduced $La_2SrCu_2O_{6+\delta}$. This is confirmed by examination of Fig. 5, which shows that the amplitudes of these signals decrease at low temperature, indicating a reduction of the magnetic phase volume as the superconducting phase forms. The relaxation rate $1/T_2$ for $\sim 15\%$ of the muons in a 100-Oe field applied transverse to the muon polarization shows an increase below 45 K (see Fig.

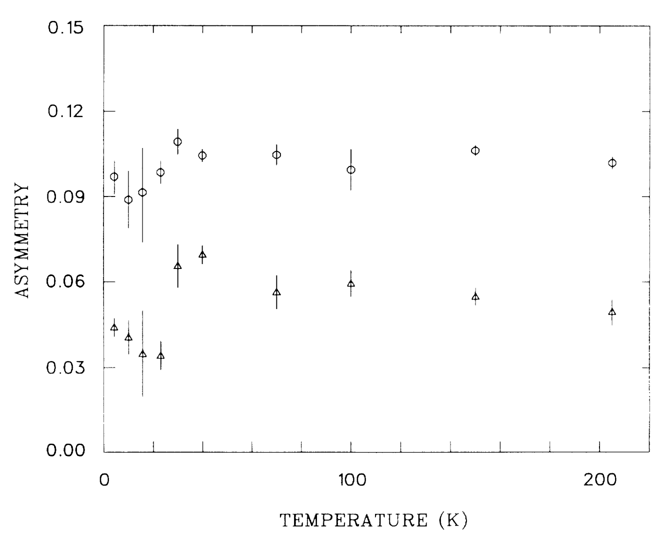

FIG. 5. Amplitudes (asymmetry) for the signals of Fig. 4. There is a significant decrease at low temperatures, consistent with the segregation of a minority superconducting phase. Notice that here and in Fig. 2 the 18-MHz signal (triangles) displays higher sensitivity to the mobility effects, since it is due to muons associated with oxygens in the conducting plane.

6). This is typical for the onset of superconductivity, confirming that this is indeed the superconducting fraction of Ref. 2, not present in $La_2SrCu_2O_{6+\delta}$. Muons in the ordered phase are quickly depolarized in the internal field, and do not affect the transverse field depolarization rate for this fraction, which is determined by the data at later times.[8,11] It should be noted that, although not displaying a superconductive fraction, the (oxygenated) $La_2SrCu_2O_{6+\delta}$ specimen prepared in air also showed some evidence for frustration, with a lower frequency for the main signal and $T_N \sim 230$ K (Fig. 3). The $La_{1.9}Y_{0.1}CaCu_2O_{6+\delta}$ sample displayed an intermediate behavior, with a $T_N \sim 250$ K and a main signal frequency changing from 4 MHz at 50 K to 5.8 MHz below 10 K. Because of the small sample size, the measurement was not sensitive enough to detect the superconducting fraction directly. The yttrium substitution therefore did not completely eliminate the frustration–phase-segregation effect discussed above.

In conclusion, we have shown that the title family extends the striking feature of all lamellar CuO_2 antiferromagnets, in that the freezing temperatures and size of the atomic moments are quite similar, regardless of differences in structure. There are, however, important structural differences between the two members of the family,[2] which are reflected in the differences in the μ^+SR results obtained. Stoichiometric $La_2SrCu_2O_{6+\delta}$ (reduced sample) displays a more persistent magnetic ordering, with a comparatively high T_N and smooth temperature dependence of the muon-precession frequencies, while $La_2CaCu_2O_{6+\delta}$ is more tantalizing since superconductivity could be induced by excess oxygen and there is a change in the magnetic muon signals at temperatures similar to those for the superconducting ordering. Such change is most likely due to the excess oxygen clustering that also gives rise to the superconductivity. From this point of view, it is $La_2SrCu_2O_{6+\delta}$ that is puzzling because it fails to display superconductivity, i.e., oxygenated and reduced samples show only magnetic ordering. In a picture in which the observed effects are due to mobile excess oxygen in the Ca(La) layer in between the CuO_2 planes that cluster to form islands of high hole concentration, it may simply be that such clustering is inhibited in the $La_2SrCu_2O_{6+\delta}$ structure. The ionic radius of La^{3+} (1.14 Å) is larger than for Ca^{2+} (0.99 Å), but similar to Sr^{2+} (1.12 Å). The (25% occupancy) La^{3+} ions in between the CuO_2 planes may actually enhance the clustering in $La_2CaCu_2O_{6+\delta}$, especially if they are ordered, compared to $La_2SrCu_2O_{6+\delta}$ where the La and Sr ions are more randomly distributed overall, in addition to the direct inhibiting effect of oxygen vacancies in the CuO_2 planes discussed in Ref. 18. As noted in Ref. 2, clustering in the present context means that, starting with one extra oxygen every 14 unit cells present on average, hole-rich superconducting regions require a redistribution to roughly one extra oxygen every five unit cells—not a massive change. Note that, in this scenario, the actual critical temperature for the superconducting fraction could be higher than the 45-K onset temperature seen here and in Ref. 2. Finally, it should be remarked that complex changes in the precession frequencies of the two main signals were also seen in careful studies of oxygen-deficient $YBa_2Cu_3O_x$ (for $6.0 \le x \le 6.4$),[13] and that frustration effects for in-plane muon locations are posited for $La_{2-x}Sr_xCuO_{4-y}$.[12] The phase separation in $La_2CaCu_2O_{6+\delta}$ is analogous to the one for $La_2CuO_{4+\delta}$,[8,19] where the segregation occurs at higher temperatures.

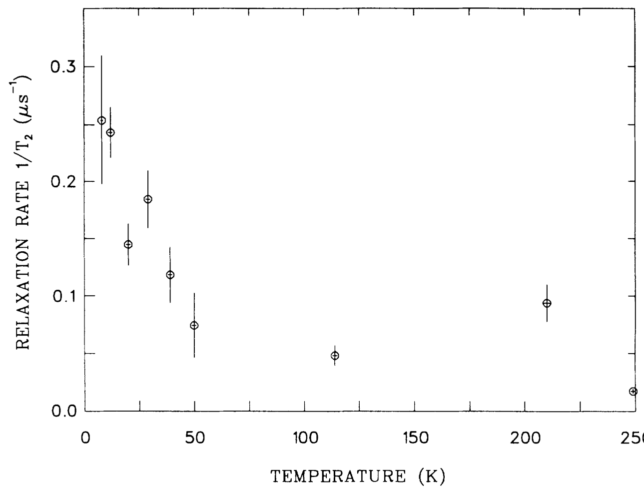

FIG. 6. Muon spin relaxation rate in a 100-Oe applied field for the superconducting phase of $La_2CaCu_2O_{6+\delta}$. The increase below 50 K is due to the field inhomogeneity of the vortex lattice in the mixed state (Ref. 8). The actual critical temperature T_c may be higher if the transition is due to the effect of oxygen clustering discussed in the text. The 100-Oe field is too low to allow the reliable extraction of the magnetic penetration depth from the relaxation rate.

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