μSR studies of Li-doped La_2CuO_4

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Magnetic properties of the Li-doped cuprates $La_2Cu_{1-x}Li_xO_4$ (where $x = 0.01$, 0.05, 0.10, 0.45, and 0.50) have been studied by μSR. For low Li concentrations ($x \leqslant 0.10$) we find a rapid suppression of T_N as x increases, but little change in the magnitude and temperature dependence of the AFM order parameter. This indicates that Li doping effectively destroys AFM (similar to Sr doping, but different from Zn doping) without strongly affecting the onsite Cu moments and the shape of the spinwave excitation spectrum. For high Li concentrations we find magnetic clusters in about 15% of the sample volume; the remaining volume is non-magnetic, suggesting possible singlet-state formation.

1. Introduction

The interplay between magnetism and superconductivity in the cuprate superconductors continues to be a subject of primary interest. Recently, the effects of substituting Li for Cu have been investigated [1]. Naively, the addition of a Li atom is roughly equivalent to adding both a Sr and a Zn atom, in the sense that Li both removes a Cu moment (as does Zn) and adds a hole (as does Sr). One key difference between Sr- and Li-doping, however, is that the Sr-added holes are very mobile, while the Li holes are not [2]. For $x = 0.5$ this compound forms an ordered sublattice of Cu and Li, and the onsite Cu moments disappear [3]. The object of our investigation is to use μSR as a microscopic probe of the Li concentration dependence of both the loss of magnetic order and the onset of the non-magnetic state (perhaps like a Zhang–Rice singlet [4]). We find that small amounts of Li doping will strongly suppress the AFM ordering temperature without significantly affecting either the onsite Cu moments or the temperature dependence of the sublattice magnetization. Additional Li doping leads to an inhomogeneous magnetic phase with low ordering temperature ($x = 0.05$–0.10), and eventually destroys the Cu moments for x near 0.5.

2. Experiment

The μSR measurements were carried out at TRIUMF, Vancouver, Canada, using the M15 and M20 surface muon channels. Polycrystalline samples of $La_2Cu_{1-x}Li_xO_4$ were prepared by standard solid state reaction techniques at Florida State University. The samples were carefully annealed so that they contained no oxygen deficiency, pressed to pellets and then mounted in a He gas-flow cryostat.

3. Results and discussions

For the lightly-doped systems spontaneous muon spin precession is observed in zero applied field, indicating the onset of magnetic ordering. (The precession frequency ν is proportional to the sublattice magnetization M.) Figure 1(a) shows the temperature dependence of ν for $x = 0$, 0.01, 0.05 and 0.10. The rapid suppression of T_N is evident. However, one sees that despite the reduction of T_N by a factor of 60 (from 300 K to 5 K for $x = 0$ and $x = 0.10$, respectively), the zero-temperature frequency declines only by 1/3 (from 5.8 MHz to about 4 MHz). This indicates that the Li doping efficiently breaks down the strength of the magnetic correlations, but only weakly reduces the onsite Cu moments. As seen in other μSR experiments, this also occurs with different dopants, such as with excess oxygen [5], doping Sr on the La site [6] and Zn on the Cu site [8].

In fig. 1(b) we show the normalized linewidth $\delta\nu/\nu$ vs. temperature for various Li concentrations. We see that the spread in local fields becomes larger as the Li concentration is increased, indicating increasing microscopic inhomogeneity. The observed linewidth and change in zero-temperature frequency could be due either to a dilution of the Cu moments or to a spread in the magnitude of the Cu moments. The differ-

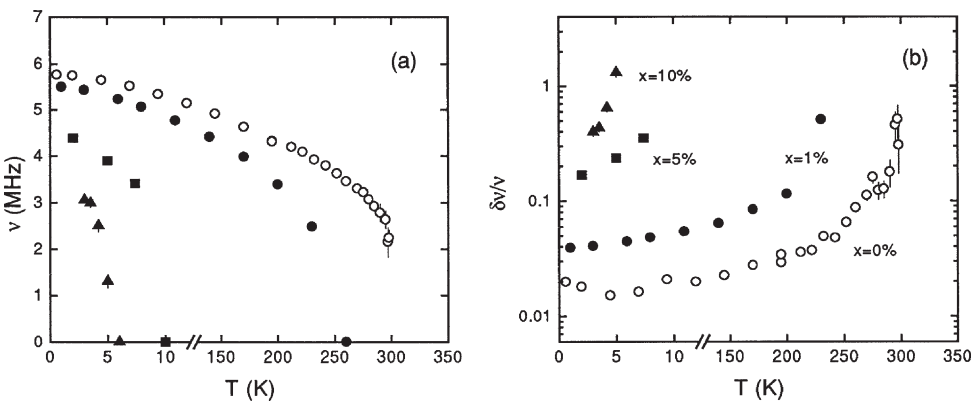

Fig. 1. Temperature dependence of ZF-μSR (a) precession frequency and (b) normalized linewidth observed in $La_2Cu_{1-x}Li_xO_4$, with $x = 0$ (taken from [5]), 0.01, 0.05 and 0.10. Note the different temperature scales for $x \leqslant 0.01$ and $x \geqslant 0.05$.

ence between these two scenarios can be studied by simulating the field distribution sensed by the muon. For a dilute spin system with a small number of non-magnetic sites, we find a small low-frequency peak in the field distribution, which corresponds to a missing Cu spin nearest the muon site. The dominant peak is unshifted with respect to the undoped system, however. For the 10%-diluted system the large peak has a roughly Lorentzian lineshape with a normalized linewidth of 0.06. This number is significantly smaller than the measured values 0.15 and 0.3 for the 5% and 10% Li-doped systems, respectively. Thus, Li doping must decrease the average onsite moments and broaden the linewidth, though these effects are much weaker than the reduction of $T_N(x)$ with x.

Figure 2 shows a comparison of the magnetic phase diagrams in $La_2Cu_{1-x}Li_xO_4$, $La_2Cu_{1-x}Zn_xO_4$ and $La_{2-x}Sr_xCuO_4$. We see that Li doping strongly depresses the antiferromagnetic order, similar to Sr doping. If we fit the small-x Li data phenomenologically to $T_N(x)/T_N(0) = 1-(x/x_c)^2$, we obtain a critical value $x_c = 0.03$, slightly larger than 0.02 for Sr doping, but much smaller than 0.12 for Zn doping [10]. The difference between Sr, Li and Zn doping is that Zn doping only removes spins from the Cu sites, so that the remaining spins are still well coupled magnetically if the doping concentration is not large. On the other hand, both Sr and Li create holes in the CuO_2 planes which frustrate the AFM coupling between the neighboring spins. Thus the presence of holes in the CuO_2 planes is much more effective in destroying the AFM order than simple dilution of the Cu moments.

There are differences between Sr and Li doping, however. First, Li doping removes a Cu spin while Sr doping does not. As shown above, this has only a weak effect

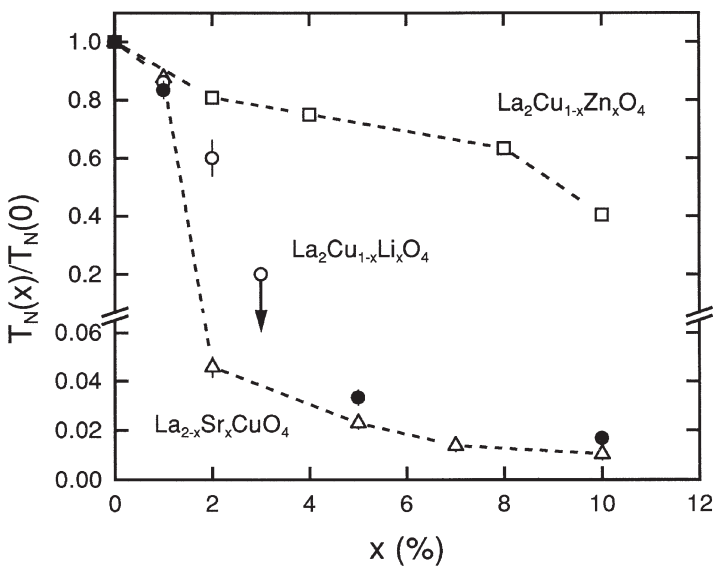

Fig. 2. Magnetic ordering temperature as a function of doping concentration in $La_2Cu_{1-x}Li_xO_4$ (open circles from [7]), $La_2Cu_{1-x}Zn_xO_4$ [8], and $La_{2-x}Sr_xCuO_4$ [9].

on $T_N(x)$. Second, Li doping creates a more localized hole than Sr doping. This conclusion is mainly derived from the behavior in the heavily doped compounds; namely, Sr doping leads to superconductivity, while Li doping leads to insulating diamagnetism at $x = 0.50$. However, in the low Li-doping range the high-temperature resistivity actually becomes smaller with increasing Li concentration and reaches a minimum near $x \approx 0.10$ [2]. Similarly, the residual susceptibility χ_0 initially increases with increasing x and reaches a maximum also near $x \approx 0.10$ [7]. These results indicate that as long as x is small, Li doping introduces somewhat delocalized holes in the CuO_2 planes, similar to Sr doping. This is consistent with our observation that Sr doping is only marginally more effective than Li doping in destroying the AFM coupling.

As shown in fig. 2, $T_N(x)$ changes behavior for $x \geqslant 0.03$ in both the Sr- and Li-doped systems, namely, T_N is small but persists to a rather high concentration, of the order of 10%. To investigate the nature of this magnetic state, we conducted longitudinal field measurements. We find that the oscillation is decoupled completely in 1 kG (about 4 times the internal field), indicating the presence of static magnetic correlations. We note that the magnetic correlations for $x \geqslant 0.03$ Li doping have not been seen in neutron scattering measurements [11]. The absence of magnetic Bragg peaks implies the formation of either short-range magnetic correlations or possibly an incommensurate magnetic structure. The relatively narrow linewidth (about 0.15 for the 5%-Li system) rules out a spin-glass state.

One of the interesting observations in our experiments is the universal scaling of the temperature dependence of the frequency for $0 \leqslant x \leqslant 0.10$, as shown in fig. 3. This

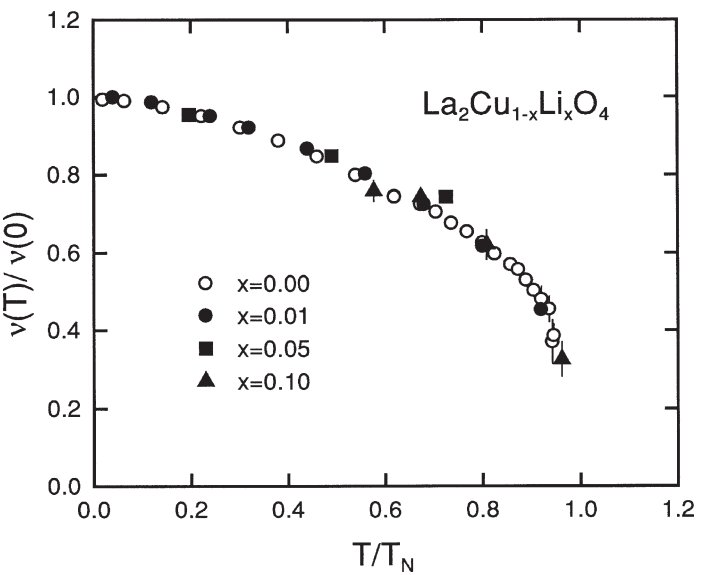

Fig. 3. Reduced frequency vs. reduced temperature in $La_2Cu_{1-x}Li_xO_4$. A universal temperature dependence is seen for $x = 0$, 0.01, 0.05 and 0.10.

scaling behavior is remarkable because it holds over a wide range of T_N, including a possible change in the magnetic structure, as discussed above. A possible explanation for this scaling behavior is that both the intraplane and interplane exchange coupling between the Cu moments ($J_{\|}$ and $J_{\perp}$, respectively) decrease proportionately (as $T_N(x)$) as a result of Li doping. To see this, we note that $J_{\perp}$ is primarily due to the orthorhombic distortion of the CuO_2 lattice, which lifts the frustration of the body-centered Cu spin. In the Li-doped system the orthorhombic strain decreases with increasing x and disappears above $x = 0.10$ at room temperature [1,7]. Consequently, the shape of magnon spectrum remains largely unchanged, with its characteristic energy scaled by T_N. This leads to the universal scaling of $M(T/T_N)/M(0)$.

Finally, we discuss our results obtained in the high Li concentration regime ($x = 0.45$ and 0.50). We find that the ZF-μSR spectra at high temperatures are well described by a Kubo–Toyabe relaxation function due to nuclear dipoles. Below about 200 K, however, a fast relaxing component is observed which grows both in amplitude and relaxation rate as the temperature is reduced. At the lowest measured temperature, this component corresponds to about 15% of the sample volume with a static magnetic field of 260 G. Both the magnitude of the internal field and the onset temperature are comparable to those obtained in the lightly-doped systems. Thus, the formation of the fast-relaxing signal is most likely due to magnetic clusters with partially frozen Cu moments. Such uncompensated moments could also give rise to the Curie tails seen in the susceptibility measurements [1,7]. The remaining slow component (about 85% of the sample volume) is essentially the same as that found at high temperatures. We estimate the upper limit of the magnetic field from the electron moments is about 1 G, which corresponds to a frozen moment of $10^{-3}\mu_B$ per Cu ion. This is consistent with a spin-singlet state in the 50% doped system.

4. Conclusions

We have performed μSR measurements on Li-doped La_2CuO_4. We obtained the magnetic phase diagram for doping concentrations varying from $x = 0$ to 0.5. In the low doping range ($x \leqslant 0.03$) a rapid suppression of T_N is seen, similar to Sr doping, but different from Zn doping, indicating that the presence of holes in the CuO_2 planes is much more effective in destroying antiferromagnetic correlations than simple dilution of the Cu moments. In the intermediate doping range ($x = 0.05$–0.10), we find that the magnetic correlations persist, but with increasing inhomogeneity. Up to $x = 0.10$ we found little change in the onsite Cu moments and the temperature dependence of the magnetic order parameter, despite the fact that T_N declines by a factor of 60. As the doping concentration increases further, we find no evidence of magnetic relaxation in the majority of the sample volume, consistent with the formation of the singlet ground state for $x = 0.45$–0.50.

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