Magnetic behavior in Li-doped La_2CuO_4

L. P. Le and R. H. Heffner
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

D. E. MacLaughlin
Department of Physics, University of California, Riverside, California 92521

K. Kojima, G. M. Luke, B. Nachumi, and Y. J. Uemura
Department of Physics, Columbia University, New York, New York 10027

J. L. Sarrao and Z. Fisk
Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306

(Received 3 May 1996)

We report muon-spin-relaxation studies in the Li-doped cuprates $La_2Cu_{1-x}Li_xO_4$ for $x=0.01$, 0.05, 0.10, 0.45, and 0.50. 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 antiferromagnetic order parameter. This indicates that Li doping effectively destroys antiferromagnetism (similar to Sr doping, but different from Zn doping) without strongly affecting either the on-site Cu moments or the shape of the spin-wave excitation spectrum. For high Li concentrations we find that the majority of the sample volume is nonmagnetic, suggesting possible singlet-state formation. [S0163-1829(96)01538-X]

The interplay between magnetism and superconductivity in the cuprate superconductors continues to be a subject of considerable interest. The parent compound La_2CuO_4 is an antiferrmagnetic (AFM) insulator ($T_N \approx 325$ K) with a perovskite structure. When an out-of-plane dopant, such as Sr or Ba, is substituted for La, holes are doped into the CuO_2 planes and the AFM order is destroyed. Increased doping leads to superconductivity. Doping into the CuO_2 plane itself destroys both superconductivity and magnetic order. Generally, the in-plane dopants, such as Zn or Mg substituted for Cu, rapidly depress T_c,[1] but only modestly depress T_N.[2]

Recently, the effects of substituting Li for Cu have begun to be investigated.[3] 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. This is evident because $La_2Cu_{1-x}Li_xO_4$ remains an insulator for $0 \leqslant x \leqslant 0.5$.[4] For $x=0.5$ the Li sublattice is ordered, and the bulk magnetic susceptibility is negative (due to core diamagnetism).[5]

In this paper we use muon spin relaxation (μSR) as a microscopic probe of the Li concentration dependence of both the loss of magnetic order and the onset of a nonmagnetic state. Because μSR is extremely sensitive to very small magnetic moments and is easily carried out in zero applied field, the technique is well suited to such a study. We find that a small amount of Li doping ($\leqslant 10\%$) will strongly suppress the AFM ordering temperature without drastically reducing the on-site Cu moments. The temperature dependence of the sublattice magnetization is essentially unchanged. Furthermore, there is an inhomogeneous magnetic phase which forms for $x=0.05-0.10$ and has a low ordering temperature. Eventually the Cu moments are destroyed completely for x near 0.5; we set an upper limit of $10^{-3}\mu_B$ for the size of any residual copper moment for $x=0.5$.

The μSR measurements were carried out at TRIUMF, 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 about 25 mm in diameter and 3 mm thick, and then mounted in a He-gas-flow cryostat.

For the lightly doped systems a spontaneous muon spin precession is observed at low temperatures in zero applied field, indicating the onset of magnetic ordering. The spectra below T_N can be fit by the function

$$G(t)=\tfrac{2}{3}\cos(2\pi\nu_\mu t+\phi)\exp(-\lambda t)+\tfrac{1}{3}\exp(-\lambda' t), \quad (1)$$

where the frequency ν_μ is a measure of the sublattice magnetization M, and the spectral weights for the oscillating and nonoscillating signals (2:1) are due to the powder average for a single muon lattice site. The temperature dependence of ν_μ for $x=0$ (taken from Ref. 6), 0.01, 0.05, and 0.10 is given in Fig. 1(a). 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 on-site Cu moments. (The cause of the decrease in M will be examined below.) Other μSR experiments with different dopants, excess oxygen,[6] doping Sr on the La site,[7] and Zn on the Cu site,[8] also show a much larger reduction in T_N compared to the on-site moments.

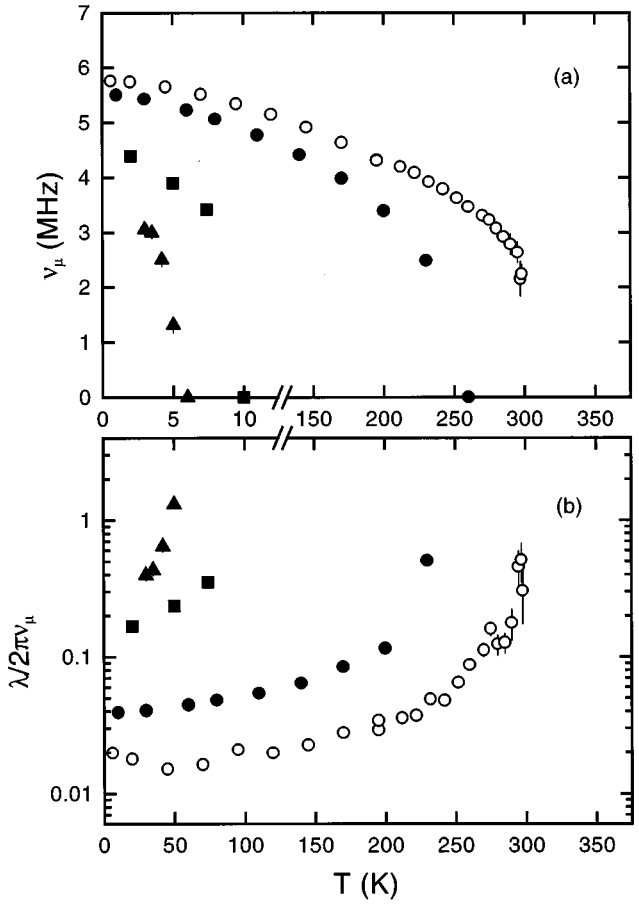

FIG. 1. (a) Temperature dependence of ZF-μSR frequency and (b) normalized linewidth observed in $La_2Cu_{1-x}Li_xO_4$, with $x=0$ (open circles, Ref. 6), 0.01 (solid circles), 0.05 (solid squares), and 0.10 (solid triangles). Note the different temperature scales for $x\leqslant 0.01$ and $x\geqslant 0.05$; the breaks apply to $x\geqslant 0.05$ only.

Figure 1(b) shows the normalized linewidth $\lambda/2\pi\nu_\mu$ 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 in $La_2Cu_{1-x}Li_xO_4$ could be due either to a dilution of the Cu moments or to a spread in the magnitude of the Cu moments. To differentiate between these two scenarios, we have computed the field distribution for a dilute spin system, using the La_2CuO_4-type magnetic structure with a frozen moment of $0.5\mu_B$.[6] We also assume a random distribution of nonmagnetic sites and a muon lattice site of (0.253, 0, 0.162) in the tetragonal notation,[9] with respect to a Cu site at the origin. Figure 2 shows the field distribution $\rho(B)$ for a 10%-spin-diluted system. The small peak near 80 G has a spectral weight of 10% and corresponds to a missing Cu spin at the origin. Compared to the internal field in the undoped system (a single line indicated by the arrow in Fig. 2), the large peak shows some broadening, but no frequency shift. Except for the small tails, the line shape of this peak can be reasonably described by a Lorentzian distribution with a normalized linewidth of 0.06 (the dashed line in Fig. 2). Because Li doping removes one spin from the Cu site and also creates a hole, x Li atoms will create at most $2x$ nonmagnetic sites. Since for

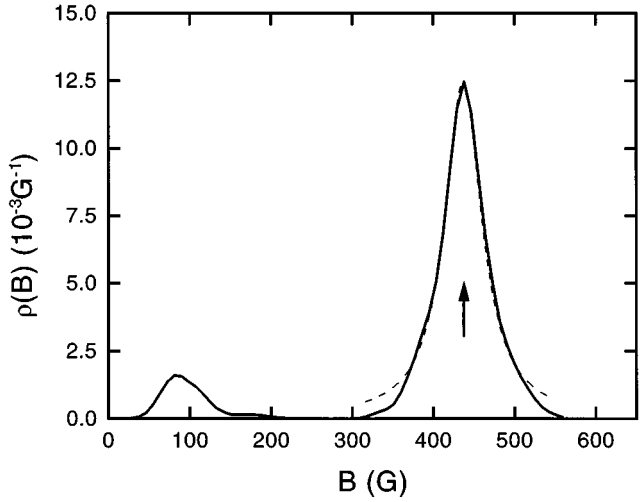

FIG. 2. Calculated field distribution in a 10%-diluted spin system, for the La_2CuO_4-type magnetic structure. The arrow indicates the single-line position for the undoped spin system.

$x=0.05$–0.10 neither the decrease in ν_μ (20–30%) nor the broader linewidth (0.15–0.30) is explained by spin dilution alone, Li doping must decrease the average on-site moments and broaden the moment distribution. These effects, however, are much weaker than the reduction of $T_N(x)$ with x.

We now examine the effects of Li doping on the magnetic transition temperature. Figure 3 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 AFM order, similar to Sr doping. If we fit the small-x_{Li} data to $T_N(x)/T_N(0)=1-(x/x_c)^2$ phenomenologically,[10] 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.[2] The difference between Sr or Li and Zn is that Zn only removes spins from the Cu sites, so that the remaining spins are still magnetically coupled if the doping concentration is not large. Although $x_c=0.12$ for Zn doping is smaller than the percolation threshold of 0.41 expected for

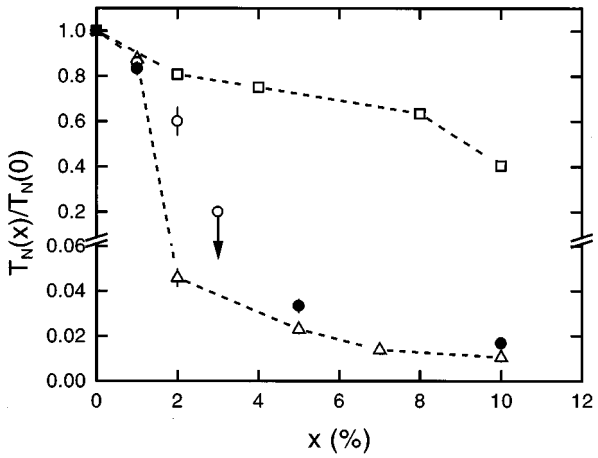

FIG. 3. Magnetic ordering temperature as a function of doping concentration in $La_2Cu_{1-x}Li_xO_4$ from Ref. 10 (open circles) and this work (solid circles), $La_2Cu_{1-x}Zn_xO_4$ (open squares, Ref. 8), and $La_{2-x}Sr_xCuO_4$ (open triangles, Ref. 11).

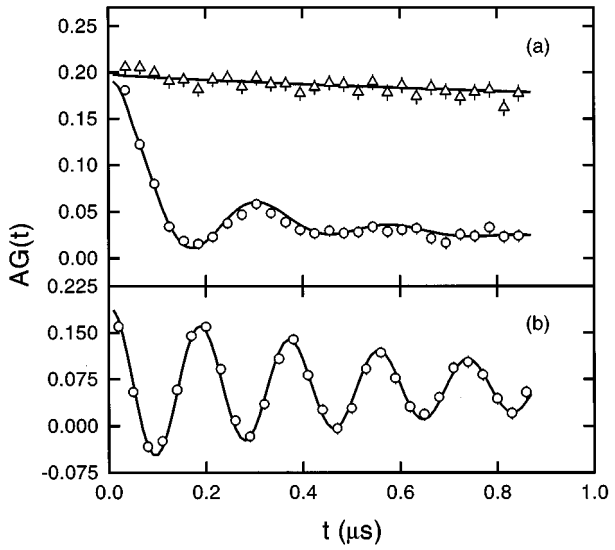

FIG. 4. (a) μSR time spectra observed in $La_2Cu_{0.9}Li_{0.1}O_4$ at 3 K, in zero applied field (open circles) and a longitudinal field of 1 kG (open triangles), (b) ZF spectrum in $La_2Cu_{0.99}Li_{0.01}O_4$ at 10 K.

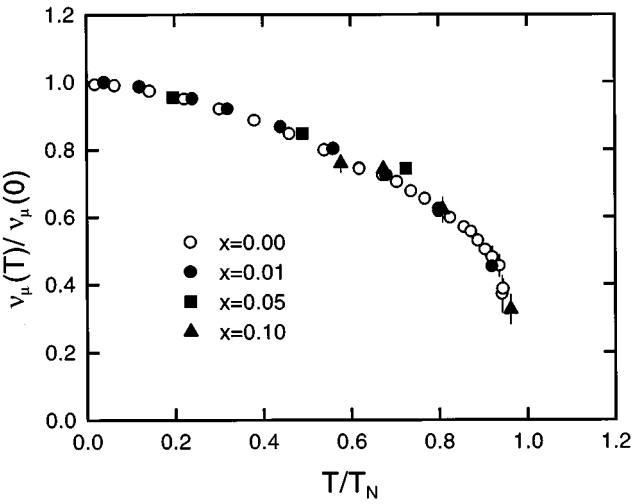

FIG. 5. Reduced frequency vs reduced temperature in $La_2Cu_{1-x}Li_xO_4$. A universal temperature dependence is seen for $x=0$, 0.01, 0.05, and 0.10.

a two-dimensional (2D) Heisenberg square lattice,[12] the magnetic order does survive up to a relatively high doping concentration compared to Sr or Li. On the other hand, both Sr and Li create holes in the CuO_2 planes which frustrate the antiferromagnetic 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 discussed above for the case of Zn, this has only a weak effect on $T_N(x)$. Of greater importance is that 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 $x=0.5$. However, in the low Li-doping range the high-temperature resistivity actually becomes smaller with increasing Li concentration and reaches a minimum near $x\approx 0.10$.[4] Similarly, the residual susceptibility χ_0 initially increases with increasing x and reaches a maximum also near $x\approx 0.10$.[10] These results indicate that as long as x is small, which is the range of importance for magnetism, Li doping may introduce somewhat delocalized holes in the CuO_2 plane, 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. 3, $T_N(x)$ changes behavior for $x\geqslant 0.03$ in both the Sr- and Li-doped systems; namely, the magnetic ordering temperature is small but persists to a rather high concentration, of the order of 10%. To investigate the nature of this intermediate magnetic state, we conducted zero (ZF) and longitudinal (LF) field measurements. The μSR time spectra observed at 3K in the 10% Li-doped system are shown in Fig. 4(a). We see that the ZF spectrum clearly shows oscillations, accompanied by strong damping [comparing with the 1% system, as shown in Fig. 4(b)]. The frequency is 3.1 MHz, corresponding to a muon local field of 230 G. When a longitudinal field of 1 kG is applied, the oscillation is decoupled completely, indicating a static local field, at least during the muon lifetime. (The upper limit on the spin fluctuation rate is about 10^6 s^{-1}.)

We note that magnetic correlations for $x_{Li}\geqslant 0.03$ [Fig. 4(a)] have not been observed in susceptibility or neutron scattering measurements. In the former case, we find a Curie-like upturn in χ around 50 K, which would hide any AFM signature at low temperatures. For neutron studies, a short-ranged spin correlation ($\xi\approx 40$ Å) is found below room temperature, but no 3D magnetic ordering is observed down to 5 K in the $x=0.05$ system.[13] The absence of magnetic Bragg peaks together with our μSR observations implies either short-range magnetic correlations or possibly an incommensurate magnetic structure.

Features similar to those seen in Fig. 4(a) are also found with μSR in the Sr-doped compounds.[11] The observation of magnetic correlations, particularly in the superconducting region ($x_{Sr}\approx 0.10$), has led to much debate on whether magnetism coexists with superconductivity[14] or whether the observed correlations are due to magnetic impurities.[15] Unfortunately, it is not clear at this point whether the correlations seen in Sr-doped La_2CuO_4 are static, because no longitudinal field measurements have been conducted. For lower Sr concentration, a more careful measurement combining both μSR and neutron studies on a sample with $x_{Sr}=0.06$ (Ref. 16) showed the formation of a spin glass-like state below 6 K. Our μSR data for a sample with $x_{Li}=0.05$–0.10 show similar results, although the field distribution in our samples seems more consistent with either a broad width around a finite mean value or an incommensurate magnetic structure, rather than a spin glass state. This is particularly true for the sample with $x_{Li}=0.05$, where the normalized linewidth is about 0.15, much smaller than 0.42 expected for a spin glass (assuming a Gaussian line shape).

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. 5. This scaling behavior is remarkable because it holds over a wide range of T_N, which includes a possible change in the magnetic struc-

ture, as discussed above. Note that this result does not hold for all other dopants. For example, doping with excess oxygen stiffens the magnon excitations, leading to a flattening of $M(T)$ at low temperatures.[17]

The parent La_2CuO_4 compound can be viewed as a 2D Heisenberg antiferromagnet, with a small interplane coupling $J_\perp$ and a small XY anisotropy J_{XY}.[17] $J_\perp$ is primarily due to the orthorhombic distortion of the CuO_2 lattice, which lifts the frustration of the body-centered Cu spin. When doping with Li or Zn, the Cu sites are no longer completely filled with spins. Nevertheless, if x is small, the $M(T)$ data may still be explained by considering an effective intraplane coupling $J_\parallel$, as well as $J_\perp$ and J_{XY}. The observed scaling behavior for $M(T)$ implies that all three exchange constants decrease proportionally as x_{Li} increases, so that $T_N(x) \propto J_\parallel(x)$ and $M(T/T_N,x)$ is independent of x.[18] This result agrees qualitatively with a decrease in the orthorhombic strain (and hence $J_\perp$) with increasing x_{Li}.[3,10]

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[19] due to nuclear dipoles alone. 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 and a muon static magnetic field of 260 G. Both the magnitude of the muon static 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; these clusters are inhomogeneously distributed throughout the sample volume. The remaining slow relaxation component (about 85% of the sample volume) is essentially the same as that found at temperatures above 200 K. We estimated that the zero-field relaxation rate due to the electronic magnetism is less than 0.08 μs^{-1}, which corresponds to an upper limit for the residual Cu moment of $10^{-3}\mu_B$, a reduction by more than three orders of magnitude. This is consistent with a spin-singlet state in the 50% doped system.

In conclusion, we have performed μSR measurements on the Li-doped cuprates La_2CuO_4. We obtained the magnetic phase diagram for doping concentrations which vary from $x=0$ to $x=0.5$. 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 found that the magnetic correlations persist, but with increasing inhomogeneity. A change of T_N vs x behavior near $x\approx 0.03$ may indicate a possible change in the nature of the magnetic state of $La_2Cu_{1-x}Li_xO_4$. This is also suggested by the form of the relaxation function (Fig. 4). For $x\leqslant 0.10$ we found a modest 20–30 % change in the magnitude of the on-site Cu moments and no change in the temperature dependence of the magnetic order parameter, despite the fact that T_N declines by a factor of 60. This suggests that both the interplane and intraplane coupling constants scale with T_N. 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.

The authors thank D. Scalapino, Y. Yoshinari, and S. Trugman for helpful discussions. Work at Los Alamos was performed under the auspices of the U.S. DOE. Work at UC Riverside and Columbia was supported in part by the U.S. NSF (Grants Nos. DMR-94-18991 and DMR-95-10454, respectively). Work at NHMFL was supported in part by the NSF and the state of Florida through cooperative agreement No. DMR-90-16241.

[1] G. Xiao *et al.*, Phys. Rev. B **42**, 8752 (1990).
[2] M. Corti *et al.*, J. Appl. Phys. **75**, 7143 (1994).
[3] J. L. Sarrao *et al.*, Phys. Rev. B (to be published).
[4] M. A. Kastner *et al.*, Phys. Rev. B **37**, 111 (1988).
[5] G. Demazeau *et al.*, Mater. Res. Bull. **7**, 913 (1972); J. P. Attfield and G. Ferey, J. Solid State Chem. **80**, 112 (1989).
[6] Y. J. Uemura, J. Appl. Phys. **64**, 6087 (1988); Y. J. Uemura *et al.*, Phys. Rev. Lett. **59**, 1045 (1987).
[7] D. R. Harshman *et al.*, Phys. Rev. B **38**, 852 (1988).
[8] R. L. Lichti *et al.*, Physica C **180**, 358 (1991).
[9] M. J. Stott and E. Zaremba, Phys. Rev. B **22**, 1564 (1980); M. Decroux *et al.*, Europhys. Lett. **3**, 1035 (1987).
[10] A. I. Rykov *et al.*, Physica C **247**, 327 (1995).
[11] A. Weidinger *et al.*, Phys. Rev. Lett. **62**, 102 (1989).
[12] A. R. McGurn, J. Phys. C **12**, 3523 (1979).
[13] Y. Endoh *et al.*, Phys. Rev. B **37**, 7443 (1988).
[14] D. R. Harshman *et al.*, Phys. Rev. Lett. **63**, 1187 (1989).
[15] R. H. Heffner and D. L. Cox, Phys. Rev. Lett. **63**, 2538 (1989); R. F. Kiefl *et al.*, *ibid.* **63**, 2136 (1989).
[16] B. J. Sternlieb *et al.*, Phys. Rev. B **41**, 8866 (1990).
[17] B. Keimer *et al.*, Phys. Rev. B **45**, 7430 (1992); **46**, 14 034 (1992).
[18] These results can be seen using the spin-wave approximation [A. Singh *et al.*, Phys. Rev. Lett. **64**, 2571 (1990)] $T_N \propto J_\parallel/\ln(J_\parallel/J_\perp)$ and $-\Delta M(T)\propto(T/J_\parallel)\ln[T/(2J_\parallel J_\perp)^{1/2}]$, where the first equation holds for $T\gg 2(J_\parallel J_\perp)^{1/2}\sim 0.02J_\parallel$.
[19] R. S. Hayano *et al.*, Phys. Rev. B **20**, 850 (1979).