Correlations between charge ordering and local magnetic fields in overdoped $YBa_2Cu_3O_{6+x}$

J. E. Sonier,[1,3] J. H. Brewer,[2,3] R. F. Kiefl,[2,3] R. H. Heffner,[4] K. F. Poon,[1] S. L. Stubbs,[5] G. D. Morris,[4] R. I. Miller,[2,3] W. N. Hardy,[2] R. Liang,[2] D. A. Bonn,[2] J. S. Gardner,[6] C. E. Stronach,[7] and N. J. Curro[4]

[1]*Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*

[2]*Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*

[3]*TRIUMF, Vancouver, British Columbia, Canada V6T 2A3*

[4]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

[5]*Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2J1*

[6]*National Research Council, Chalk River, Ontario, Canada K0J 1P0*

[7]*Department of Physics, Virginia State University, Petersburg, Virginia 23806*

(Received 15 March 2002; published 3 October 2002)

Zero-field muon spin-relaxation (ZF-μSR) measurements were undertaken on under- and overdoped samples of superconducting $YBa_2Cu_3O_{6+x}$ to determine the origin of the weak static magnetism recently reported in this system. The temperature dependence of the muon spin-relaxation rate in overdoped crystals displays an unusual behavior in the superconducting state. A comparison to the results of NQR and lattice structure experiments on highly doped samples provides compelling evidence for strong coupling of charge, spin, and structural inhomogeneities.

DOI: 10.1103/PhysRevB.66.134501 PACS number(s): 74.25.Nf, 74.72.Bk, 76.75.+i

There is growing evidence that phase segregation of doped charges may be an intrinsic property of high-T_c superconductors. While the static spin/charge stripes[1] observed in the marginal superconductor $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ (Ref. 2) are expected to be incompatible with the metallic behavior of the CuO_2 layers,[3] there is evidence from neutron-scattering measurements that a stripe phase that is short range and dynamic may exist in several high-T_c systems.[4–6] At low temperatures muon spin-relaxation (μSR) experiments indicate a freezing of the Cu spins.[7–10] Local static magnetic order observed in highly underdoped samples is gradually destroyed with increased hole concentration, giving rise to a spin-glass-like state. Niedermayer *et al.* found that the transition temperature for spin freezing in the $La_{2-x}Sr_xCuO_4$ and $Y_{1-x}Ca_xBa_2Cu_3O_6$ systems shows a similar reduction with increased hole doping.[9] Above the spin freezing temperature Panagopoulos *et al.* observed slow spin fluctuations that persist slightly above optimal doping.[10] Recently, Pan *et al.* observed nanoscale spatial variations in the electronic state at the surface of optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ using scanning tunneling microscopy (STM).[11] Together these observations are consistent with nanoscale phase segregation into antiferromagnetic (AF) hole-poor clusters surrounded by nonmagnetic hole-rich regions.

In the $YBa_2Cu_3O_{6+x}$ (Y123) system there is the added complication of charge ordering in the CuO chains. Nuclear quadrupole resonance (NQR),[12–15] STM,[16] and neutron[17] measurements on *highly doped* Y123 are compatible with the formation of a charge-density-wave (CDW) state in the CuO chains. The NQR studies provide strong evidence that the CDW chain state induces a charge-density modulation in the CuO_2 planes.[15]

While early ZF-μSR studies found no evidence for electronic moments in Y123 for $x \geqslant 6.54$,[8,18] recently we reported detection of weak static magnetism of unknown origin in $x = 0.67$ and $x = 0.95$ single crystals.[19] While these findings were discussed primarily in the context of orbital current models for the pseudogap phase,[20] we also noted that these ZF-μSR measurements may be characteristic of a dilute spin system, and thus incompatible with such theories. In an attempt to identify the source of the weak magnetism detected by μSR, we have performed additional measurements of under- and overdoped Y123 crystals using an improved experimental arrangement. Interesting features that are clearly observed in the overdoped sample suggest that the temperature dependence of the local magnetic-field distribution sensed by the muon results from a redistribution of the doped charge carriers—rather than the onset of spontaneous circulating electronic currents. The effects of charge ordering on the ZF-μSR spectrum become less pronounced with decreasing x and are not clearly recognizable in the data of Ref. 19. We suggest that the redistribution of holes that takes place near 60 K in Y123 is related to local structural changes that have been reported by some groups.

Small single crystals of $YBa_2Cu_3O_{6+x}$ [$x = 0.80$, 0.92, 0.985 with $T_c = 85(1.2)$ K, 93.0(0.3) K, and 90.2(0.8) K, respectively] ~100 μm thick were grown in $BaZrO_3$ crucibles. The $x = 0.80$ and $x = 0.985$ crystals were mechanically detwinned. The μSR measurements were carried out on the M20B surface muon beam line at TRIUMF with the initial muon spin polarization $\mathbf{P}_\mu(0)$ perpendicular to the $\hat{c}$ axis of the crystals. The LAMPF spectrometer was used with a side-axis low background insert (rather than the axial configuration of Ref. 19), resulting in a marked improvement in the quality of the time spectra. While the μ^+ stopping sites in Y123 have never been firmly established, we show that correlations with Cu(2) NQR linewidth measurements in fully doped Y123 imply that the μ^+ is sensitive to magnetism in the CuO_2 planes.

Figure 1 shows the time evolution of the muon spin polarization in overdoped $x = 0.985$ crystals in zero external field. As a spin-1/2 particle, the muon is directly sensitive only to changes in its magnetic environment. Thus the in-

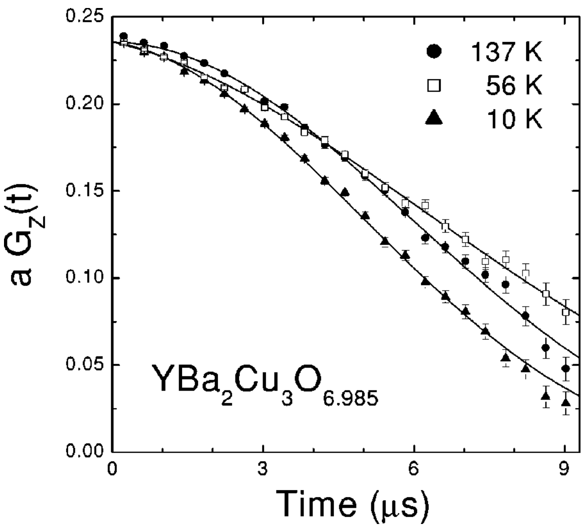

FIG. 1. The time evolution of the muon spin polarization in $YBa_2Cu_3O_{6.985}$ in zero external field at $T=10$, 56 and 137 K. The signal at 10 K relaxes faster than at 137 K. At 56 K the signal at early times relaxes faster than at 137 K, but exhibits a slower relaxation beyond 5 μs.

creased signal relaxation between 137 and 10 K indicates a growth in the size of the local magnetic fields at the μ^+ stopping sites. In addition to this, we observe a striking change in the shape of the relaxation function near 55 K, with the signal displaying a slower relaxation at later times. This behavior was not identified in our study of lower x samples.[19] We find that a longitudinal field (LF) of 100 Oe is sufficient to completely decouple the muon spin from the local internal field distribution over the entire temperature range. This implies that the magnetism sensed by the μ^+ fluctuates at a rate slower than 10 MHz.

To identify gross features the ZF time spectra can be fit to a ''stretched exponential'' relaxation function $G_z(t)=\exp[(-\Lambda t)^p]$. Figures 2 and 3 show the temperature dependence of the relaxation rate Λ and the power p, respectively. Included in these figures are similar fits to the $x=0.67$ and $x=0.95$ data of Ref. 19. The $x=0.95$ sample was prepared in yttria-stabilized zirconia crucibles and was not detwinned. For $x=0.985$, Λ and p display an anomalous minimum near 55 K. Below 35 K, the increase of Λ with decreasing T indicates an increase in the width of the local-field distribution. These features become less pronounced with decreasing x, and are not observed for $x=0.67$. The absence of an obvious minimum in p near 55 K for $x=0.95$ reflects the reduced accuracy of our original measurements.

The relaxation of the muon spin by the randomly oriented weak dipolar fields of the host nuclei is conventionally described by a static Gaussian Kubo-Toyabe (KT) function,

$$G_z^{\mathrm{KT}}=\frac{1}{3}+\frac{2}{3}(1-\Delta^2t^2)\exp\left(-\frac{1}{2}\Delta^2t^2\right), \tag{1}$$

where Δ is the width of the field distribution. For $\Delta t\ll 1$, this reduces to $G_z^{\mathrm{KT}}\approx\exp[(-\Delta t)^2]$. In Fig. 3, $p\approx 2$ at high temperatures, but decreases to a smaller value below the 55-K dip. This indicates the presence of more than one muon spin

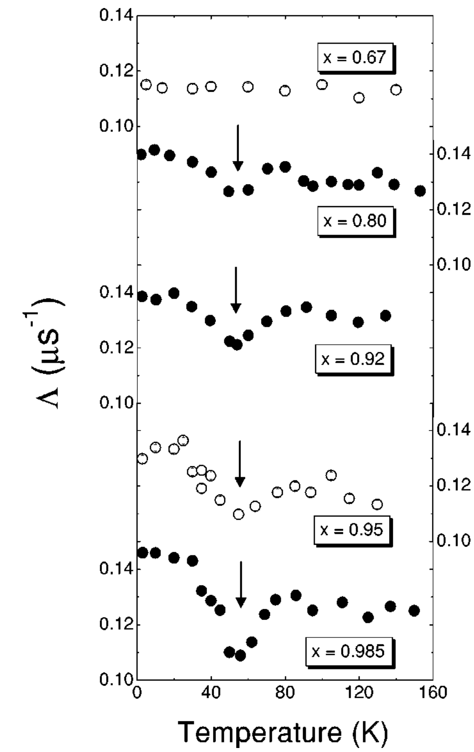

FIG. 2. Temperature dependence of the relaxation rate Λ. Open circles are from fits to the data of Ref. 19.

relaxation rate. As in Ref. 19 we find that the ZF-μSR time spectra are well fit to the product

$$G_z(t)=G_z^{\mathrm{KT}}\exp(-\lambda t). \tag{2}$$

For the case of static fields, an exponential relaxation is expected from a dilute random distribution of magnetic moments. In Ref. 19 we made the reasonable assumption that Δ was independent of T. However, to obtain good fits to data in the vicinity of 55 K, it was necessary to allow Δ to vary freely with temperature. We note that from a careful analysis of ZF-μSR spectra at high temperatures, we have determined that the muon ''hops'' at temperatures above 175 K. A fast moving μ^+ averages over the fields it sees during its lifetime, thus experiencing a narrower field distribution from the nuclear dipoles. Figure 4 shows the results of a separate analysis of ZF-μSR signals in the $x=0.67$ sample of Ref. 19 above 100 K, whereby a *dynamic* Gaussian KT function G_z^{dKT} was used in place of the static function G_z^{KT} of Eq. (1). The relaxation function G_z^{dKT}, which is determined by numerical calculation,[22] is characterized by a hopping rate ν that reflects the changing local field experienced by the mobile muon. As shown in the plot of Fig. 4, the temperature dependence of ν is well described by an Arrhenius relation $\nu=\nu_0\exp(-E_a/kT)$, characteristic of a thermally activated process. Previously, muon diffusion was clearly identified in Y123 above 200 K.[23]

Figure 5 shows the temperature dependence of Δ and λ in the overdoped sample. Below $\sim$130 K, λ increases with decreasing T. This behavior appears to coincide with the gradual increase of the Cu(2) NQR linewidth $\delta^{63}\nu_Q(2)$ [see

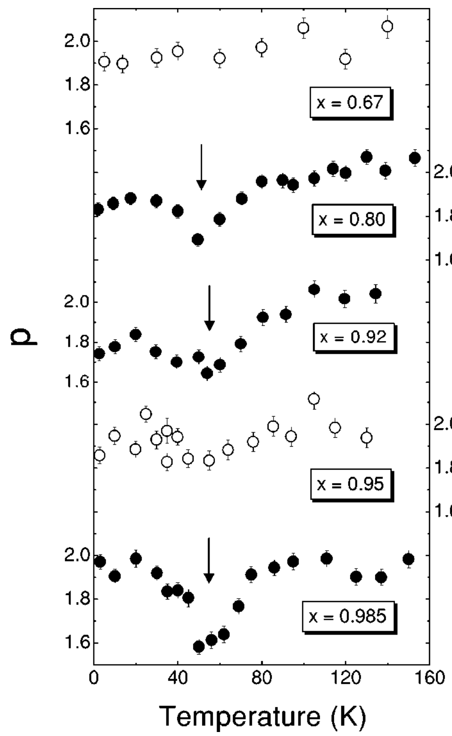

FIG. 3. Temperature dependence of the power p. Open circles are from fits to the data of Ref. 19.

Fig. 5(a)] observed by Grévin *et al.* in a fully doped ($x=1.0$) Y123 powder.[13,15] In Ref. 15 the increase in $\delta^{63}\nu_Q(2)$ was attributed to the formation of charge correlations in the CuO_2 planes that are induced by a CDW transition in the CuO chains. A similar finding was reported in an NQR study of $PrBa_2Cu_3O_7$.[21] The finite value of λ below ~130 K indicates that charge ordering is accompanied by the onset of local magnetic fields at the muon site(s). Because charge ordering is expected to give rise to strong local Cu spin correlations in the hole depleted regions of the sample (due to the tendency toward AF order in the underdoped system) we hypothesize that the fields are associated with these Cu moments.

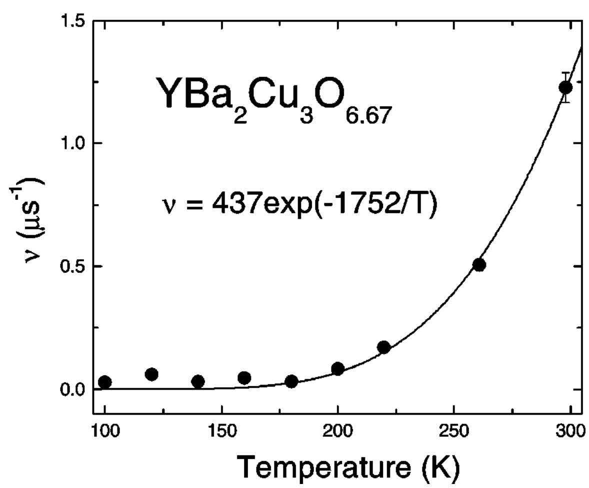

FIG. 4. Plot of the temperature dependence of the μ^+ hop rate in $YBa_2Cu_3O_{6.67}$.

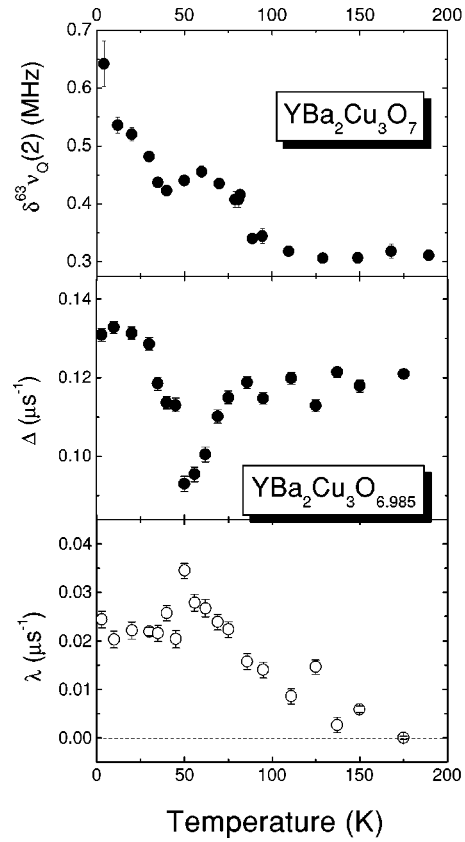

FIG. 5. Temperature dependence of (a) $\delta^{63}\nu_Q(2)$ in an $x=1.0$ powdered sample (from Ref. 15) and of (b) Δ and (c) λ from fits of the ZF-μSR time spectra in $x=0.985$ crystals to Eq. (2).

Between 75 and 175 K, Δ is independent of T. Fits of the time spectra to a dynamic Gaussian KT function G_z^{dKT} in place of the static function G_z^{KT} of Eq. (2), yielded $\nu\approx 0$ at all temperatures below 175 K, where ν reflects time-dependent local fields experienced by the μ^+. Thus the change in Δ beginning below 75 K [see Fig. 5(b)] is not due to a dynamical relaxation mechanism—a conclusion which is supported by the LF measurements. The minimum at 55 K and the increase in Δ below 35 K coincide with features observed in the temperature dependence of $\delta^{63}\nu_Q(2)$ [see Fig. 5(a)]. The Cu(2) NQR linewidth displays a maximum near 60 K,[13,15] a minimum at 35 K, and increases monotonically below 35 K with decreasing temperature.[12–15] In slightly underdoped Y123 the peak in $\delta^{63}\nu_Q(2)$ near 60 K is not observed.[12,14] The weakening of the 55 K feature in the μSR data with decreasing x (see Figs. 2 and 3) may be due to an emptying of the CuO chains and/or a decreased coupling with the CuO_2 planes. It may also reflect a change in the population of the muon stopping site(s). We elaborate on this latter possibility below.

Grévin *et al.*[15] argued that the 60 K peak in $\delta^{63}\nu_Q(2)$ arises from a transition between short- and long-range charge ordering. The transition is accompanied by electric-field gradient (EFG) and/or magnetic-field fluctuations perpendicular to the CuO_2 planes—as evidenced by a broad peak in the transverse relaxation rate $1/T_2$ of the Cu(2) nuclei near 55 K,[24,25] and also at 35 K.[12,24–26] Local EFG fluctuations may arise from doped charges that are dynamic. Although the μ^+ is sensitive to the effects of EFG fluctuations on the nuclear dipole fields, the absence of dynamical relaxation of the muon spin polarization is understandable given that the T_2 minima measured with NQR are about an order of magnitude longer than the μSR time scale. High-resolution dilatometry,[27] x-ray scattering[28] and microwave[29] measurements suggest that the redistribution of charge may be intimately related to local lattice distortions. Below $\sim$60 K (75 K) the $\hat{b}$ axis increases with decreasing T,[27,28] whereas the $\hat{a}$ axis expands below 35 K.[28] One interpretation of these structural anomalies is that they correspond to an unbuckling of the CuO_2 layers.[28] It is noteworthy that the microwave measurements of Ref. 29 were performed on the parent compound $YBa_2Cu_3O_{6.0}$. This suggests that in highly doped samples the lattice distortion taking place near 60 K induces the redistribution of holes.

The unusual T dependence of Δ below 75 K indicates a change in the distribution of Cu nuclear dipole moments sensed by the μ^+. In general, the second moment of this distribution will depend on the relative angles between $\mathbf{P}_\mu(0)$, the direction of the EFG at the nuclear site and the orientation of the position vector connecting the nucleus and the μ^+, as well as the distances between the μ^+ and the host nuclei.[22] The small change in the tilt angle of the CuO_5 pyramid that accompanies the unbending of the Cu-O-Cu bonds does not produce a large enough modification of the nuclear dipole interaction with the μ^+ to account for the observed behavior. Furthermore, the change in the EFG distribution at the Cu sites due to the redistribution of charge is too small to produce such a large change in Δ.

One possible explanation for the T dependence of Δ is that it reflects a change in the Coulomb repulsion between the μ^+ and the positive charged holes that are hopping on and off the copper sites. In particular, any change in the time averaged local hole distribution should alter the mean distance between the μ^+ and the Cu nuclear moments, and modify the resulting muon-nuclear dipolar linewidth parameter Δ. It is also possible that the relative population of the muon stopping sites changes slightly at temperatures below 75 K. Pinkpank *et al.*[30] have suggested that for $0<x<1$, a fraction of the implanted muons stop near the O(1) oxygen site in the CuO chains, while the rest stop near the O(4) bridging oxygen site. Given the close proximity of the O(1) and O(4) sites, it is conceivable that a local lattice distortion could trigger tunneling of the muon between these sites and thereby alter Δ. Both of these suggested effects are difficult to model, considering the lack of a general consensus on the muon stopping site(s). For example there is also evidence that in highly doped Y123 the μ^+ prefers to stop near an oxygen ion located in a CuO_2 plane[31]—rather than near a chain oxygen. Thus while it is difficult to make a precise statement about the exact origin of the change in Δ below 75 K, it is at least plausible that it is driven by subtle changes in the local lattice structure and charge redistribution detected by other techniques.

A variable Δ confounds the quantitative evaluation of the "extra" magnetism characterized by λ. Although λ is certainly nonzero, the increase in relaxation below 35 K, previously reported for $x=0.95$,[19] was at least partly due to an increase in Δ. The weak magnetism likely originates from dilute (quasi)static electronic moments and not from a dense pattern of orbital currents spontaneously forming below the pseudogap crossover line $T^*(x)$. While some theories[32] suggest a close connection between the onset of charge ordering and $T^*(x)$, we cannot assign an unambiguous "onset" temperature T^* due to the rich relaxation phenomenology and the gradual decrease of λ with increasing temperature.

From a comparison with NQR measurements on fully doped Y123, we have determined that the weak local magnetism sensed by the muon is strongly influenced by the evolution of spatial charge inhomogeneities. The agreement between separate μSR, NQR, and lattice structure experiments suggests that spatial inhomogeneity is an intrinsic property of the Y123 system that arises independent of the sample preparation details.

This work was supported in part by the Natural Sciences and Engineering Research Council of Canada, the Canadian Institute for Advanced Research, the National Science Foundation, the U.S. Air Force Office of Scientific Research, and at Los Alamos by the U.S. Department of Energy. We thank W.A. MacFarlane and Z. Yamani for fruitful discussions. We are especially grateful to Syd Kreitzman, Mel Good, Donald Arseneau, and Bassam Hitti for technical assistance.

[1] J. Zaanen and O. Gunnarsson, Phys. Rev. B **40**, 7391 (1989); D. Poilblanc and T.M. Rice, *ibid.* **39**, 9749 (1989); K. Machida, Physica C **158**, 192 (1989); M. Kato, K. Machida, H. Nakanishi, and M. Fujita, J. Phys. Soc. Jpn. **59**, 1047 (1990); H.J. Schulz, Phys. Rev. Lett. **64**, 1445 (1990).

[2] J.M. Tranquada, B.J. Sternlieb, J.D. Axe, Y. Nakamura, and S. Uchida, Nature (London) **375**, 561 (1995).

[3] S.A. Kivelson, E. Fradkin, and V.J. Emery, Nature (London) **393**, 550 (1998).

[4] R.J. McQueeney, Y. Petrov, T. Egami, M. Yethiraj, G. Shirane, and Y. Endoh, Phys. Rev. Lett. **82**, 628 (1999).

[5] K. Yamada, C.H. Lee, K. Kurahashi, J. Wada, S. Wakimoto, S. Ueki, H. Kimura, Y. Endoh, S. Hosoya, G. Shirane, R.J. Birgeneau, M. Greven, M.A. Kastner, and Y.J. Kim, Phys. Rev. B **57**, 6165 (1998); H.A. Mook and F. Doğan, Nature (London) **401**, 145 (1999); M. Arai, T. Nishijima, Y. Endoh, T. Egami, S. Tajima, K. Tomimoto, Y. Shiohara, M. Takahashi, A. Garrett, and S.M. Bennington, Phys. Rev. Lett. **83**, 608 (1999); H.A. Mook, P. Dai, F. Doğan, and R.D. Hunt, Nature (London) **404**, 729 (2000).

[6] Y. Petrov, T. Egami, R.J. McQueeney, M. Yethiraj, H.A. Mook, and F. Dogan, cond-mat/0003414 (unpublished).

[7] A. Weidinger, Ch. Niedermayer, A. Golnik, R. Simon, E. Recknagel, J.I. Budnick, B. Chamberland, and C. Baines, Phys. Rev. Lett. **62**, 102 (1989).

[8] R.F. Kiefl, J.H. Brewer, J. Carolan, P. Dosanjh, W.N. Hardy, R.

Kadono, J.R. Kempton, R. Krahn, P. Schleger, B.X. Yang, Hu Zhou, G.M. Luke, B. Sternlieb, Y.J. Uemura, W.J. Kossler, X.H. Yu, E.J. Ansaldo, H. Takagi, S. Uchida, and C.L. Seaman, Phys. Rev. Lett. **63**, 2136 (1989).

[9] Ch. Niedermayer, C. Bernhard, T. Blasius, A. Golnik, A. Moodenbaugh, and J.I. Budnick, Phys. Rev. Lett. **80**, 3843 (1998).

[10] C. Panagopoulos, B.D. Rainford, J.R. Cooper, and C.A. Scott, Physica C **341-348**, 843 (2000).

[11] S.H. Pan, J.P. O'Neal, R.L. Badzey, C. Chamon, H. Ding, J.R. Engelbrecht, Z. Wang, H. Eisaki, S. Uchida, A.K. Gupta, K.-W. Ng, E.W. Hudson, K.M. Lang, and J.C. Davis, Nature (London) **413**, 282 (2001).

[12] S. Krämer and M. Mehring, Phys. Rev. Lett. **83**, 396 (1999).

[13] B. Grévin, Y. Berthier, and G. Collin, Phys. Rev. Lett. **84**, 1636 (2000).

[14] S. Krämer and M. Mehring, Phys. Rev. Lett. **84**, 1637 (2000).

[15] B. Grévin, Y. Berthier, and G. Collin, Phys. Rev. Lett. **85**, 1310 (2000).

[16] H.L. Edwards, D.J. Derro, A.L. Barr, J.T. Markert, and A.L. de Lozanne, Phys. Rev. Lett. **75**, 1387 (1995).

[17] H.A. Mook, P. Dai, K. Salama, D. Lee, F. Dogan, G. Aeppli, A.T. Boothroyd, and M.E. Mostoller, Phys. Rev. Lett. **77**, 370 (1996).

[18] R.F. Kiefl, J.H. Brewer, I. Affleck, J.F. Carolan, P. Dosanjh, W.N. Hardy, T. Hsu, R. Kadono, J.R. Kempton, S.R. Kreitzman, Q. Li, A.H. O'Reilly, T.M. Riseman, P. Schleger, P.C.E. Stamp, H. Zhou, L.P. Le, G.M. Luke, B. Sternlieb, Y.J. Uemura, H.R. Hart, and K.W. Lay, Phys. Rev. Lett. **64**, 2082 (1990).

[19] J.E. Sonier, J.H. Brewer, R.F. Kiefl, R.I. Miller, G.D. Morris, C.E. Stronach, J.S. Gardner, S.R. Dunsiger, D.A. Bonn, W.N. Hardy, R. Liang, and R.H. Heffner, Science **292**, 1692 (2001).

[20] C.M. Varma, Phys. Rev. B **55**, 14 554 (1997); S. Chakravarty, R.B. Laughlin, D.K. Morr, and C. Nayak, *ibid.* **63**, 094503 (2001).

[21] B. Grévin, Y. Berthier, G. Collin, and P. Mendels, Phys. Rev. Lett. **80**, 2405 (1999).

[22] A. Schenck, *Muon Spin Rotation Spectroscopy: Principles and Applications in Solid State Physics* (Adam Hilger, Bristol, England, 1985), pp. 83–87.

[23] N. Nishida and H. Miyatake, Hyperfine Interact. **63**, 183 (1990).

[24] Y. Itoh, H. Yasuoka, and Y. Ueda, J. Phys. Soc. Jpn. **59**, 3463 (1990).

[25] M.V. Eremin, Yu.A. Sakhratov, A.V. Savinkov, A.V. Dooglav, I.R. Mukhamedshin, and A.V. Egorov, JETP Lett. **73**, 540 (2001).

[26] O.N. Bakharev, R.Sh. Zhdanaov, A.V. Egorov, M.V. Eremin, V.V. Naletov, M.S. Tagirov, and M.A. Teplov, JETP Lett. **47**, 458 (1988); A.V. Bondar, S.M. Ryabchenko, Yu.V. Fedotov, and A.A. Motuz, *ibid.* **50**, 146 (1989); N. Tei, H. Takai, K. Mizoguchi, and K. Kume, Solid State Commun. **74**, 1117 (1990); K.-i. Kumagai, Y. Nakamichi, Y. Nakamura, T. Takatsuka, and H. Nakajima, J. Phys. Soc. Jpn. **59**, 2336 (1990).

[27] C. Meingast, O. Kraut, T. Wolf, H. Wühl, A. Erb, and G. Müller-Vogt, Phys. Rev. Lett. **67**, 1634 (1991).

[28] H. You, U. Welp, and Y. Fang, Phys. Rev. B **43**, 3660 (1991).

[29] Z. Zhai, P.V. Parimi, J.B. Sokoloff, S. Sridhar, and A. Erb, Phys. Rev. B **63**, 092508 (2001).

[30] M. Pinkpank, A. Amato, D. Andreica, F.N. Gygax, H.R. Ott, and A. Schenck, Physica C **317-318**, 299 (1999).

[31] J.H. Brewer, R.F. Kiefl, J.F. Carolan, P. Dosanjh, W.N. Hardy, S.R. Kreitzman, Q. Li, T.M. Riseman, P. Schleger, H. Zhou, E.J. Ansaldo, D.R. Noakes, L.P. Le, G.M. Luke, Y.J. Uemura, K. Hepburn-Wiley, and C.E. Stronach, Hyperfine Interact. **63**, 177 (1990).

[32] See references within S. Andergassen, S. Caprara, C. Di Castro, and M. Grilli, Phys. Rev. Lett. **87**, 056401 (2001).