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Phys. Rev. B **94**, 134407 — Published 7 October 2016

DOI: [10.1103/PhysRevB.94.134407](https://doi.org/10.1103/PhysRevB.94.134407)

Coupling of Magnetic Orders in $\text{La}_2\text{CuO}_{4+x}$

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(Dated: 15 August 2016)

High transverse magnetic field and zero field muon spin rotation and relaxation measurements have been carried out in a lightly oxygen-doped high- T_c parent compound La_2CuO_4 in a temperature range from 2 K to 300 K. As in the stoichiometric compound, muon spin rotation spectra reveal, along with the antiferromagnetic local field, the presence of an additional source of magnetic field at the muon. The results indicate that this second magnetic order is driven by the antiferromagnetism at low temperature but the two magnetic orders decouple at higher temperature. The ability of $\mu^+\text{SR}$ to detect this additional magnetism deteriorates with doping, thus rendering the technique impotent to reveal time-reversal symmetry breaking in superconductors.

Superconducting (SC) cuprates exhibit a pseudogap (PG) state with anomalous transport, magnetic, optical and thermodynamic properties [1, 2]. This enigmatic state is believed to hold the key to the mechanism of high-temperature SC (HTSC) but its nature is still a major unsolved problem in condensed matter physics. Some theories suggest that the PG is a disordered precursor to the SC phase lacking phase coherence among preformed pairs [3, 4]. However, mounting experimental evidence associates the PG with a broken symmetry state accompanied by onset of charge density wave, nematic or magnetic orders [5–10].

In particular, the magnetic order causes time-reversal symmetry breaking (TRSB). Angle-resolved photoemission spectra of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ demonstrate spontaneous dichroism, an indication of a TRSB ordered state [11]. Polarized neutron scattering (NS) experiments in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [5], $\text{HgBa}_2\text{CuO}_{4+x}$ [12], $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [13] and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ [14] reveal an intra-unit-cell magnetic order. Its onset coincides with the known PG boundary T^* [15]. The electronic state identified in those experiments is qualitatively consistent with the model of orbital current loops for the PG state [16, 17], gaining further support from weak magnetic excitations detected in cuprates [18, 19]. The puzzling part is the observation of large in-plane components of magnetic moments. Possible explanations include a spin component due to spin-orbit coupling [20], a quantum superposition of loop currents [21], or a contribution from apical oxygen atoms [22]. A recent study [23] suggests that T^* corresponds only to the onset of the in-plane component.

Additional evidence for broken symmetry in the PG region comes from high-precision polar Kerr effect (PKE) measurements of cuprates [6, 24, 25]. The effect signals TRSB but demonstrates unusual characteristics ascribed to a chiral order [25]. The relation between the PKE and NS observations is unclear: The characteristic PKE-detected moments are tiny, about 4 orders of magnitude

smaller than those revealed in the NS experiments. The onset of PKE occurs at a temperature which is noticeably lower than T^* but is close to that of charge ordering, prompting proposals in which fluctuating charge- [26] or pair-density-wave [27] states induce spontaneous currents with broken mirror symmetries.

Somewhat surprisingly, the magnetic order eludes detection with local magnetic probe techniques, thus arousing legitimate doubts on its intrinsic and universal nature. The failure of nuclear magnetic resonance (NMR) [10, 28] is certainly conspicuous — upper bounds on static fields at oxygen sites are two orders of magnitude smaller than estimates for the current-loop order [10]. Similarly unsuccessful is the search for orbital currents with the Zeeman-perturbed nuclear quadrupole technique [29]. It can be explained by a fluctuating character of the magnetic order, possibly induced by defects [17], and a large difference in the characteristic correlation times accessible by NMR and NS: the fluctuations may be too fast for NMR causing dynamical narrowing but fall within the time window of the NS technique.

In terms of the characteristic correlation times, muon spin relaxation ($\mu^+\text{SR}$) techniques bridge the gap between NMR and NS, thus seeding expectations that the magnetic order observed with NS may leave pronounced fingerprints in $\mu^+\text{SR}$ spectra. However, $\mu^+\text{SR}$ experiments in highly doped HTSC cuprates [30, 31] have not detected the expected magnetic order. Among the explanations put forward are again the defect-driven fluctuating character of the order [17] but also screening of the charge density in the vicinity of the muon [32]. Both problems are absent in the insulating parent compounds while the ordering may well be present should it be an intimate feature of chemical bonding in CuO_2 planes. Indeed, orbital currents have been observed in the antiferromagnetic (AFM) phase of insulator CuO [33]. Following this strategy we recently carried out $\mu^+\text{SR}$ measurements on single crystals of another parent compound, stoichio-

metric La_2CuO_4 [34]. The transverse-field measurements show characteristic splittings in the spectra indicating the presence of a source of magnetic field *additional to AFM*. The estimated magnitude and tilting of the local moments are found to match those detected in the NS experiments [34]. The main interest, however, concerns doped cuprates which exhibit or approach the PG state.

In this Letter we present the results of $\mu^+\text{SR}$ studies of doped samples, namely $\text{La}_2\text{CuO}_{4+x}$. We follow the evolution of the spectra with doping (x), temperature and external magnetic field and demonstrate that the local muon probe does detect a magnetic order distinct from AFM in doped cuprates. The results also set limitations on the applicability of $\mu^+\text{SR}$ spectroscopy to such problems.

The current $\mu^+\text{SR}$ studies employ stoichiometric La_2CuO_4 and oxygen-doped $\text{La}_2\text{CuO}_{4+x}$ with $x=0.0075$ and $x=0.0085$. Higher doping sets an insurmountable hurdle for the $\mu^+\text{SR}$ technique (see below). Single crystals of $\text{La}_2\text{CuO}_{4+x}$ are grown from CuO flux. The crystal orientation, lattice parameters, and mosaicity (not exceeding 0.05° along the \hat{c} axis) are determined with x-ray diffractometry. To produce stoichiometric samples, the surplus oxygen is removed by annealing in vacuum for 168 h at 700°C . The samples with $x=0.0075$ come from annealing in air for 6 h at 900°C , while $x=0.0085$ is reached by similar annealing in oxygen ($p=1$ atm). The oxygen concentration is determined from the lattice parameter c of orthorhombic $\text{La}_2\text{CuO}_{4+x}$ using Vegard's law [35]. Time-differential $\mu^+\text{SR}$ experiments, employing 100% spin-polarized positive muons, were carried out on the M15 surface muon channel at TRIUMF using the *HiTime* spectrometer.

The AFM behavior of the samples is well characterized by zero field (ZF) $\mu^+\text{SR}$ spectroscopy. Positive muons, being a local microscopic magnetic probe, have proved to be remarkably sensitive to any kind of magnetic order. In La_2CuO_4 the muon stopping site is at a bonding distance from an apical oxygen on the plane bisecting an O-Cu-O angle of the copper-oxygen plaquette [34]. Figure 1 demonstrates the temperature dependence of the ZF muon spin precession frequency in all three samples. In the case of stoichiometric La_2CuO_4 , ZF- $\mu^+\text{SR}$ spectra at low temperature contain an additional small-amplitude component associated with a second muon site [34]. Such spectra are fitted by a 2-component spin polarization function with exponential relaxation and common phase. The second signal disappears below the background at higher temperature in La_2CuO_4 (as in Figure 1) and is not detected at all in the doped samples. The Néel temperatures determined from the temperature dependence of the muon frequencies are 325 ± 5 K, 225 ± 5 K and 170 ± 5 K for La_2CuO_4 , $\text{La}_2\text{CuO}_{4.0075}$ and $\text{La}_2\text{CuO}_{4.0085}$, respectively. These values are in full agreement with magnetization measurements: the inset of Figure 1 shows the Néel temperatures of all 3 samples determined with

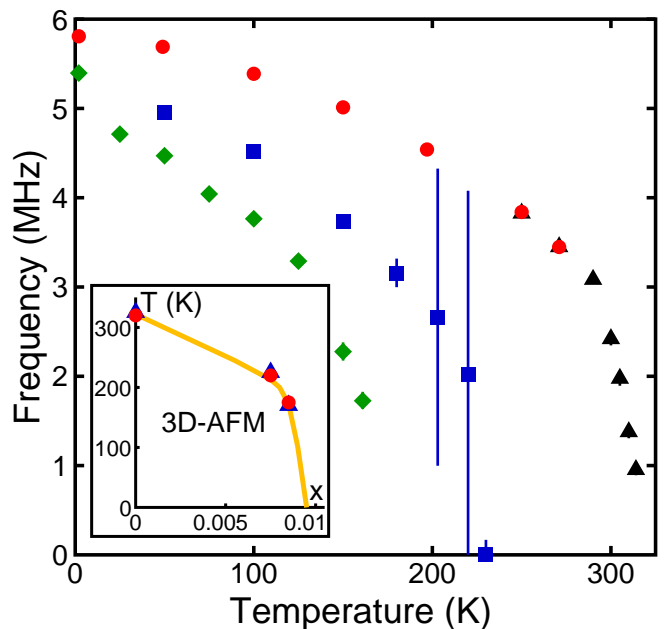


FIG. 1: Temperature dependence of the muon spin precession frequency in ZF in La_2CuO_4 (red circles for 2-component fit and black triangles for 1-component fit), $\text{La}_2\text{CuO}_{4.0075}$ (blue squares) and $\text{La}_2\text{CuO}_{4.0085}$ (green diamonds). Inset: Néel temperatures determined for the samples with SQUID (red circles) and ZF- $\mu^+\text{SR}$ (blue triangles) plotted against the boundary line for the 3D-AFM state of $\text{La}_2\text{CuO}_{4+x}$.

SQUID and ZF- $\mu^+\text{SR}$ superimposed on the phase diagram of $\text{La}_2\text{CuO}_{4+x}$ [35].

The difference between the samples is not limited to signal frequencies and their temperature dependences — the envelope of spectra also changes. Figure 2 shows the evolution of ZF- $\mu^+\text{SR}$ spectra at 50 K with oxygen doping, in both time and frequency domains. One can see that even small doping results in significant broadening of the spectra. Probably inhomogeneities in the oxygen distribution cause magnetic field inhomogeneities, increasing the linewidth of the $\mu^+\text{SR}$ signal. Such $\mu^+\text{SR}$ line broadening may prevent detection of magnetic order, especially in heavily doped cuprates.

Like the NMR studies, broad ZF- $\mu^+\text{SR}$ spectra do not reveal any additional magnetism (AM). However, in order to reconcile the experimental facts accumulated so far, one has to appreciate peculiarities of the techniques. Indeed, comparatively long characteristic times may excuse NMR, but the $\mu^+\text{SR}$ technique should be able to do the job when the sample is close to be insulating so that the charge screening effect does not apply. In fact, $\mu^+\text{SR}$ is expected to be better suited for the task than neutrons as it “measures” in real space and “sees” roughly only the first coordination sphere around the muon, while NS is essentially a k -space technique requiring a substantial correlation length for the neutron to be effective as a magnetic probe.

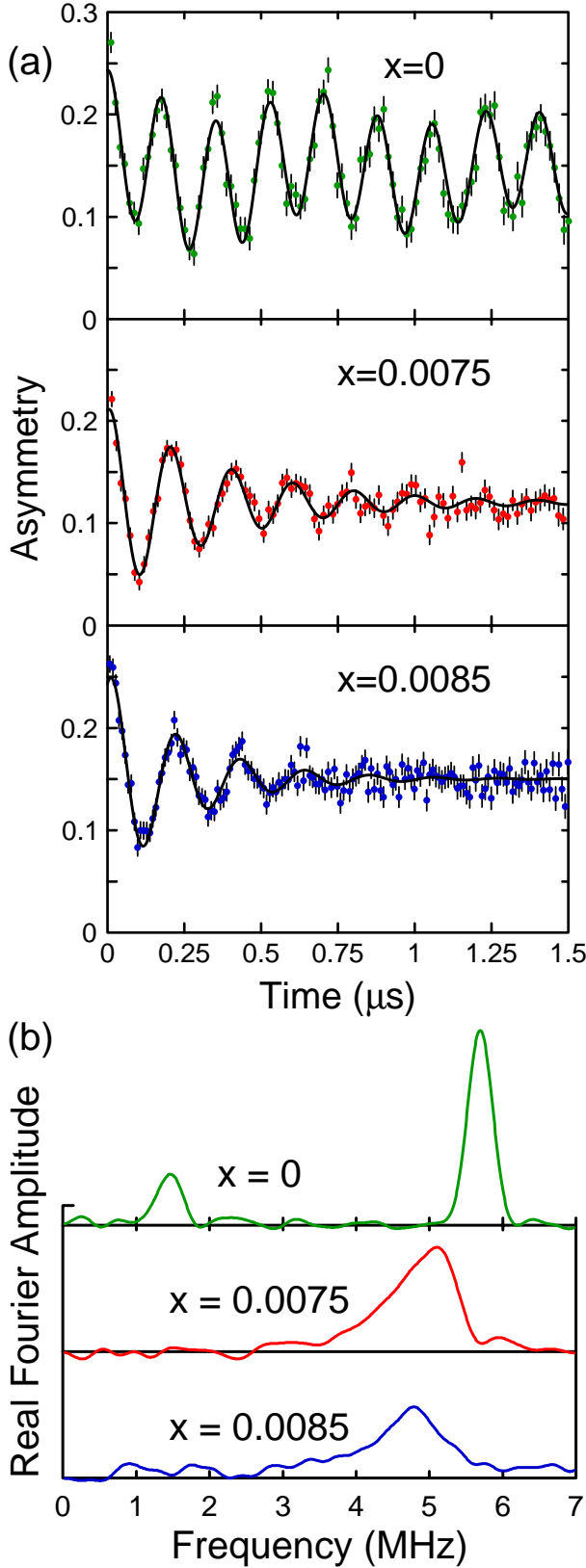


FIG. 2: (a) Time-domain spectra of muon spin precession in ZF at 50 K in La_2CuO_4 (green line), $\text{La}_2\text{CuO}_{4.0075}$ (red line), and $\text{La}_2\text{CuO}_{4.0085}$ (blue line); (b) Fourier transforms of the same spectra.

For detection of AM we resort to transverse field (TF) μ^+ SR studies, which are often helpful in revealing differences in local magnetic fields that are hidden from ZF- μ^+ SR spectra. Figure 3 presents μ^+ SR spectra for the doped samples in a transverse magnetic field of 1 T at different temperatures. The corresponding spectra for the stoichiometric La_2CuO_4 are given in Ref. [34]. The central line at about 135.6 MHz comes from muons that miss the sample and stop in a nonmagnetic environment. In the case of AFM there should be only two signals besides the central one. Additional peaks indicate the presence of AM. Namely, each of the two AFM signals on both sides of the central line is further split into two. In fact, the spectra are those expected for a combination of the AFM order and the AM detected by NS in highly doped cuprates. Such form of spectra is also the one expected for the model of orbital current loops in cuprates [16, 17, 34]. As in the ZF spectra, doping leads to broadening of the signals and the extra (additional to AFM) splitting becomes smeared. The study of signal splittings in La_2CuO_4 for different directions of the external magnetic field [34] allowed us to determine the magnetic field vector at the muon. This information is sufficient to rule out some of the proposed models for AM in cuprates [34]. However, all those conclusions are valid only if the splitting is indeed caused by AM. One can imagine that the splitting pattern comes not from an independent magnetism but from the same AFM moments acting upon muons in two different structural positions — arising, for example, from two different tiltings of CuO_6 octahedra [36]. The absence of any signal splittings above the Néel temperature certainly adds credibility to this alternative. Although the observed splitting is too large for such an explanation [34], further studies are necessary to exclude such a possibility.

The hypotheses of AM *vs.* two inequivalent sites can be verified by combined analysis of the temperature dependence of the splittings, especially in the vicinity of the Néel temperature. TF- μ^+ SR time-domain spectra are typically modeled as

$$P(t) = \sum_n A_n G_n(t) \cos(\omega_n t + \phi_n), \quad (1)$$

where index n counts states of μ^+ with amplitudes A_n , relaxation functions $G_n(t)$, Larmor frequencies ω_n and phases ϕ_n . We fitted the spectra in the time-domain by $n = 5$ oscillating components with exponential relaxation and common phase. One (central) component corresponds to μ^+ in a non-magnetic environment (for those muons which miss the sample) while the other 4 components characterize the material: the magnetic field B on the muon is determined from $\omega = \gamma_\mu B$, where $\gamma_\mu = 2\pi \times 135.53879 \text{ MHz/T}$. Since $B = \sqrt{(B_\parallel + B_{\text{ext}})^2 + B_\perp^2}$, the component of the local magnetic field on the muon B_\parallel along the external magnetic field B_{ext} can be evaluated

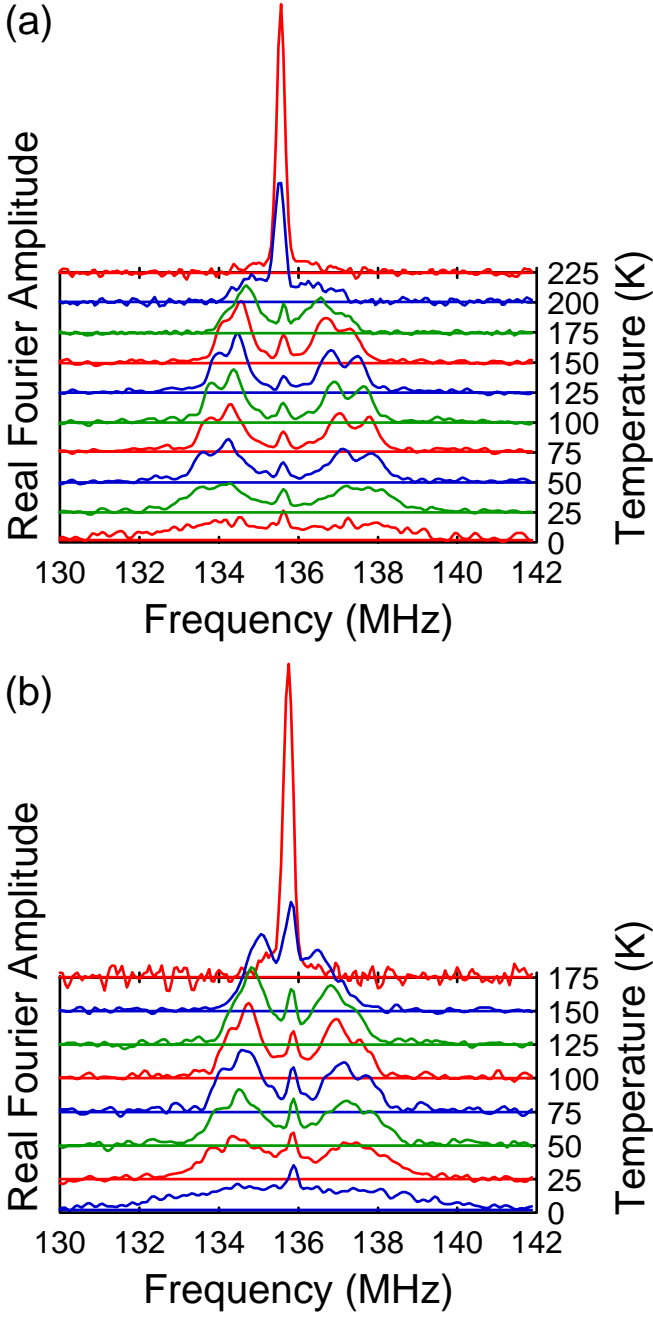


FIG. 3: Fourier transforms of the muon spin precession signal in (a) $\text{La}_2\text{CuO}_{4.0075}$ and (b) $\text{La}_2\text{CuO}_{4.0085}$ in an external magnetic field of 1 T directed along the \hat{c} axis of the crystal at different temperatures.

as $(B^2 - B_0^2 - B_{\text{ext}}^2)/2B_{\text{ext}}$, where B_0 is the modulus of the local magnetic field as given by ZF- μ^+ SR. To characterize the magnetic structure we analyze the 4 signals coming from AFM and (supposedly) AM in the TF- μ^+ SR spectra fits. Namely, 4 magnetic field projections B_{\parallel}^I , B_{\parallel}^{II} , B_{\parallel}^{III} and B_{\parallel}^{IV} (in ascending order) are computed and the average splittings associated with the AFM and AM magnetic orders are defined as $(B_{\parallel}^{IV} + B_{\parallel}^{III} - B_{\parallel}^{II} - B_{\parallel}^I)/2$

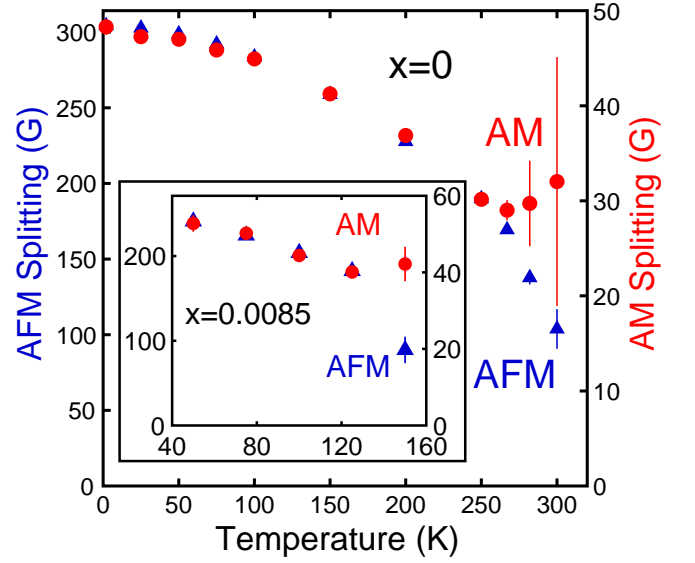


FIG. 4: Temperature dependence of the splittings in TF- μ^+ SR spectra of La_2CuO_4 caused by AFM (blue triangles) and AM (red circles) orders. Inset: the same dependences for $\text{La}_2\text{CuO}_{4.0085}$.

and $(B_{\parallel}^{IV} - B_{\parallel}^{III} + B_{\parallel}^{II} - B_{\parallel}^I)/2$, respectively.

Figure 4 shows the temperature dependence of the two splittings for stoichiometric La_2CuO_4 . The behavior is quite peculiar. One can distinguish two regions: below 250 K the splittings are proportional to each other but above 250 K there is a sharp divergence of the trends. The behavior within the higher temperature region probably rules out the hypothesis of two structural muon positions and a single AFM order. It means that the muon local probe indeed detects some AM which is quite similar to the intra-unit-cell magnetic order observed in the NS experiments for highly doped cuprates [5, 12–14]. As shown in Ref. [34] by analysis of The local magnetic field on the muon (in the dipole approximation) in conjunction with different models of the magnetic order suggests the magnitude of the local moments producing AM to be $0.04 \mu_B$. This value agrees well with estimates around $0.05 \div 0.1 \mu_B$ coming from both the NS experiments [5] and the orbital current loop model [20]. Furthermore, both NS and TF- μ^+ SR experiments determine the magnetic moments to be significantly tilted (around 50°) [5, 34]. Similar temperature dependences of the splittings are observed for the doped samples — the inset of Figure 4 shows it for $\text{La}_2\text{CuO}_{4.0085}$. The coupling of the two magnetic orders seems to be largely determined by the strength of the AFM order: at lower temperature the AM is driven by AFM but in the region close to the Néel temperature, the AFM order is rapidly dying out and the AM order decouples from the AFM order. The AM splitting even *increases* when the Néel temperature is approached. However, the AM order is not observed above the Néel temperature. This does not necessarily

mean that it is absent, only that μ^+ SR techniques are not capable to detect any AM. It is reasonable to suppose that AFM affects the fluctuation time of the AM order: without the AFM order the characteristic fluctuation times of AM are too small for this magnetism to be detected directly with μ^+ SR (in contrast to neutrons). Regrettably, it also means that μ^+ SR techniques stand no chance in finding this AM in heavily doped cuprates.

In summary, we studied local magnetic fields in lightly oxygen-doped as well as stoichiometric La_2CuO_4 with ZF- and TF- μ^+ SR spectroscopy. Both techniques demonstrate that doping leads to an increase in magnetic field inhomogeneity that hinders detection of magnetic ordering. TF- μ^+ SR experiments show a characteristic pattern based on 5 signals: a central line from muons that missed the sample and 4 signals corresponding to AFM superimposed with some additional magnetic order. The temperature dependence of the spectral lines reveals that the two magnetic orders are strongly coupled at low temperature. However, when the AFM order is weakened at higher temperature, the second magnetic order gains strength. Thus, we assert the existence of an additional magnetic order stemming from the AFM phase. The result is especially important since recent Hall coefficient measurements establish that the pseudogap in cuprates is a separate phenomenon from the charge order but strongly linked with the AFM Mott insulator [37]. Our results also explain the failure of previous attempts to detect the magnetic order in doped cuprates with μ^+ SR: the technique is capable of its detection only when the doping level is relatively small.

This work was partially supported by the Kurchatov Institute, the Russian Science Foundation (Grant 14-19-00662), the Russian Foundation for Basic Research (Grants 16-07-00204 and 16-29-03027), NSERC of Canada and the U.S. DOE, Basic Energy Sciences (Grant DE-SC0001769).

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- [1] T. Timusk and B. Statt, *Rep Prog. Phys.* **62**, 61 (1999).
- [2] M. R. Norman, D. Pines, and C. Kallin, *Adv. Phys.* **54**, 715 (2005).
- [3] V. J. Emery and S. A. Kivelson, *Nature* **374**, 434 (1995).
- [4] P. A. Lee, N. Nagaosa, and X.-G. Wen, *Rev. Mod. Phys.* **78**, 17 (2006).
- [5] B. Fauqué, Y. Sidis, V. Hinkov, S. Pailhès, C. T. Lin, X. Chaud, and P. Bourges, *Phys. Rev. Lett.* **96**, 197001 (2006).
- [6] J. Xia *et al.*, *Phys. Rev. Lett.* **100**, 127002 (2008).
- [7] R. Daou *et al.*, *Nature* **463**, 519 (2010).
- [8] E. H. da Silva Neto *et al.*, *Science* **343**, 393 (2014).
- [9] R. Comin *et al.*, *Nature Mat.* **14**, 796 (2015).
- [10] T. Wu, H. Mayaffre, S. Krämer, M. Horvatić, C. Berthier, W. N. Hardy, R. Liang, D. A. Bonn, and M.-H. Julien, *Nature Comm.* **6**, 6438 (2015).
- [11] A. Kaminski *et al.*, *Nature* **416**, 610 (2002).
- [12] Y. Li, V. Balédent, N. Barišić, Y. Cho, B. Fauqué, Y. Sidis, G. Yu, X. Zhao, P. Bourges, and M. Greven, *Nature* **455**, 372 (2008).
- [13] V. Balédent, B. Fauqué, Y. Sidis, N. B. Christensen, S. Pailhès, K. Conder, E. Pomjakushina, J. Mesot, and P. Bourges, *Phys. Rev. Lett.* **105**, 027004 (2010).
- [14] S. De Almeida-Didry, Y. Sidis, V. Balédent, F. Giovannelli, I. Monot-Laffez, and P. Bourges, *Phys. Rev. B* **86**, 020504(R) (2012).
- [15] A. Shekhter, B. J. Ramshaw, R. Liang, W. N. Hardy, D. A. Bonn, F. F. Balakirev, R. D. McDonald, J. B. Betts, S. C. Riggs, and A. Migliori, *Nature* **498**, 75 (2013).
- [16] C. M. Varma, *Phys. Rev. B* **73**, 155113 (2006).
- [17] C. M. Varma, *J. Phys.: Cond. Matter* **26**, 505701 (2014).
- [18] Y. Li *et al.*, *Nature* **468**, 283 (2010).
- [19] Y. Li *et al.*, *Nature Phys.* **8**, 404 (2012).
- [20] V. Aji and C. M. Varma, *Phys. Rev. B* **75**, 224511 (2007).
- [21] Y. He and C. M. Varma, *Phys. Rev. B* **86**, 035124 (2012).
- [22] C. Weber, A. Läuchli, F. Mila, and Th. Giamarchi, *Phys. Rev. Lett.* **102**, 017005 (2009).
- [23] L. Mangin-Thro, Y. Sidis, A. Wildes, and P. Bourges, *Nature Comm.* **6**, 7705 (2015).
- [24] R.-H. He *et al.*, *Science* **331**, 1579 (2011).
- [25] H. Karapetyan, J. Xia, M. Hücker, G. D. Gu, J. M. Tranquada, M. M. Fejer, and A. Kapitulnik, *Phys. Rev. Lett.* **112**, 047003 (2014).
- [26] Y. Wang, A. Chubukov, and R. Nandkishore, *Phys. Rev. B* **90**, 205130 (2014).
- [27] D. F. Agterberg, D. S. Melchert, and M. K. Kashyap, *Phys. Rev. B* **91**, 054502 (2015).
- [28] A. M. Mounce *et al.*, *Phys. Rev. Lett.* **111**, 187003 (2013).
- [29] S. Strässle, B. Graneli, M. Mali, J. Roos, and H. Keller, *Phys. Rev. Lett.* **106**, 097003 (2011).
- [30] G. J. MacDougall, A. A. Aczel, J. P. Carlo, T. Ito, J. Rodriguez, P. L. Russo, Y. J. Uemura, S. Wakimoto, and G. M. Luke, *Phys. Rev. Lett.* **101**, 017001 (2008).
- [31] J. E. Sonier, V. Pacradouni, S. A. Sabok-Sayr, W. N. Hardy, D. A. Bonn, R. Liang, and H. A. Mook, *Phys. Rev. Lett.* **103**, 167002 (2009).
- [32] A. Shekhter, L. Shu, V. Aji, D. E. MacLaughlin, and C. M. Varma, *Phys. Rev. Lett.* **101**, 227004 (2008).
- [33] V. Scagnoli, U. Staub, Y. Bodenthin, R. A. de Souza, M. Garcia-Fernández, M. Garganourakis, A. T. Boothroyd, D. Prabhakaran, S. W. Lovesey, *Science* **332**, 696 (2011).
- [34] V. G. Storchak, J. H. Brewer, D. G. Eshchenko, P. W. Mengyan, O. E. Parfenov, A. M. Tokmachev, P. Dosanjh, and S. N. Barilo, *Phys. Rev. B* **91**, 205122 (2015).
- [35] A. A. Nikonov and O. E. Parfenov, *JETP Letters* **72**, 550 (2000).
- [36] M. Reehuis, C. Ulrich, K. Prokeš, A. Gozar, G. Blumberg, S. Komiya, Y. Ando, P. Pattison, and B. Keimer, *Phys. Rev. B* **73**, 144513 (2006).
- [37] S. Badoux *et al.*, *Nature* **531**, 210 (2016).