As NMR study of single crystals of the heavily overdoped pnictide superconductors
$\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x = 0.7$ and 1)

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We performed $^{75}$As NMR studies on two overdoped high-quality $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x = 0.7$ and 1) single crystals. In the normal states, we found a dramatic increase of the spin-lattice relaxation ($1/75T_1$) from the $x = 0.7$ to the $x = 1.0$ samples. In $\text{KFe}_2\text{As}_2$, the ratio of $1/75T_1TK^2_n$ where $75K_n$ is the Knight shift, increases as temperature drops. These results indicate the existence of a new type of spin fluctuations in $\text{KFe}_2\text{As}_2$ which is accustomed to being treated as a simple Fermi liquid. In the superconducting state, we observe a step-like feature in the temperature dependence of the spin-lattice relaxation of the $x = 0.7$ sample, which supports a two-gap superconductivity as the underdoped materials. However, the temperature scalings of $1/75T_1$ below $T_c$ in the overdoped samples are significantly different from those in the under or optimal doped ones. A power-law scaling behavior $1/75T_1T \sim T^{0.5}$ is observed, which indicates universal strong low energy excitations in the overdoped hole-type superconductors.

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The discovery of superconductivity at 26K in $\text{LaFeAsO}_{1-x}\text{F}_x$ and the improvement of superconducting transition temperature above 50K in other iron pnictides have caused renewed interests in high-temperature superconductivity. All iron arsenides have a layered structure, where the FeAs plane is believed to be essential to the electronic properties. The Fermi surface of the parent compounds consists of two hole-pockets around the Γ point, and one-hole pocket and two electron-pockets around the $M$ point. Upon either electron or hole doping, most compounds evolve from an antiferromagnetically ordered state to a superconducting state. The study of the interplay and the doping dependence of the band structure, the magnetism, and the pairing symmetry are crucial to understanding the mechanism of superconductivity.

The pairing symmetry of Fe-based superconductors has not been fully established. A promising candidate is the so-called $S_{\pm}$ pairing symmetry which has opposite sign on the electron and hole pockets. This pairing symmetry has been argued in both weak coupling and strong coupling theoretical models. The existence of both electron and hole pockets are critical in producing the $S_{\pm}$ pairing symmetry. In particular, the weak coupling model is entirely based on the interband interactions between the electron and hole pockets. Experimentally, one heavily studied series of materials is the hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. The ARPES study showed two isotropic s-wave superconducting gaps in the optimal-doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$. However, the relative sign between two pockets has not been measured. From NMR, the absence of a coherence peak and the power-law-like behavior of the spin-lattice relaxation rate (SLRR) below $T_c$ of the underdoped and the optimal-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ materials rules out a conventional single band s-wave, although it is still unable to differentiate the $S_{\pm}$, the d-wave or other nodal pairing symmetries.

Upon hole doping, a shrinkage of the electron-pockets is seen in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ by ARPES. In particular, in $\text{KFe}_2\text{As}_2$ ($x = 1.0$), the electron pockets disappear. The weakening of the interband interaction is expected upon heavy doping, it raises the question if the magnetism and the pairing mechanism change. Distinctive properties have also been reported in $\text{KFe}_2\text{As}_2$ comparing to low dopings. For example, $T_c$ remains finite at about 3K and the $H_{C2}$ is anisotropic rather than isotropic. Strong low energy excitations below $T_c$ is observed by NQR which supports a multiple gap superconductor. In order to understand the evolution of the normal state properties and the pairing symmetry in the overdoped side, it is essential to study the properties on high quality crystals and also with more intermediate dopings.

In this work, we performed NMR studies on high-quality overdoped $\text{Ba}_{0.3}\text{K}_{0.7}\text{Fe}_2\text{As}_2$ and $\text{KFe}_2\text{As}_2$ single
crystals. Surprisingly, we found spin fluctuations are strongly enhanced in the normal state SLRR of the heavily overdoped sample KFe$_2$As$_2$. A deviation from a simple Fermi liquid is indicated by the decrease of $1/T_1 T K_n^2$ with temperature in the normal state of KFe$_2$As$_2$, where $K_n(T)$ is the Knight shift. Below $T_C$, we found a clear step-like feature in the SLRR in Ba$_{0.3}$K$_{0.7}$Fe$_2$As$_2$, which supports a two-gap superconductivity. More importantly, the power-law behavior of the SLRR as a function of temperature, $1/T_1 \sim T^{\alpha_x}$, has a universal power law exponent $\alpha_x \sim 1.5$ below $T_C$ in the overdoped samples, in contrast to the large and non-universal power-law exponent $\alpha_o$ observed in the under- or optimally doped samples$^{15,16,17}$.

Our Ba$_{0.3}$K$_{0.7}$Fe$_2$As$_2$ and KFe$_2$As$_2$ single crystals were grown by the FeAs-flux method$^{26}$. The NMR crystals were plate-like with a surface area of 2.5mm$^2$1.2mm. We mainly perform the $^{75}$As measurements with different field strength and orientations. The SLRR is measured by the inversion-recovery method on the central transition, and the recovery curve of the SLRR is fitted with a standard double-exponential form of an S=3/2 spin, $1 - \frac{m(t)}{m(0)} = 0.9exp\left(\frac{61}{T_1}\right) + 0.1exp\left(\frac{1}{T_2}\right)$. The usage of single crystals also enables us to measure the Knight shift and the anisotropy of $1/T_1$ accurately.

In Fig. 1 inset), the magnetic susceptibility of the Ba$_{0.3}$K$_{0.7}$Fe$_2$As$_2$ single crystal is shown with a 100Oe field. From the ZFC data, the sample is 100% superconducting in volume, and bulk superconductivity starts around 19K, and the major transition completes around 15K. The $^{75}$As (S=3/2) NMR spectra of the crystal at a fixed frequency 72.9MHz with field along the crystal c-axis is shown in Fig. 1 with a center transition at $\mu_0 H \sim 10T$ and two satellites at 8.8T and 11.2T respectively. In the following, we focus on the SLRR of the central transition (spin $1/2 \rightarrow 1/2$ transition).

In Fig. 2, we show the $1/^{75}T_1$ of the Ba$_{0.3}$K$_{0.7}$Fe$_2$As$_2$ crystal at various field with two orientations (H//c and H//ab). In the normal state, $1/^{75}T_1$ can be fit by a power-law $1/^{75}T_1 \sim T^{\alpha_x}$, with $\alpha_x \approx 1.1$ from $T_C$ up to about 100K, which is close to the Fermi liquid Korringa relation. The normal-state SLRR is anisotropic with $1/T_1^{ab}$ larger than $1/T_1^c$ for two different field orientations, and the anisotropic factor, estimated to be $T_1^{c}/T_1^{ab} \approx 1.3$, holds for all temperatures above $T_C$. From 100K and above, both the transport$^{13}$ and our $1/^{75}T_1$ deviate from a simple Fermi liquid behavior. This feature has also been observed in previous NMR measurements of Ba$_{1-x}$K$_{x}$Fe$_2$As$_2$ with low different doping concentrations$^{15}$. The origin of such a deviation is not completely understood.

We took similar measurements on KFe$_2$As$_2$. The superconducting transition temperature of our sample is about 3K from resistivity, close to earlier report$^{13,22,23}$. The $^{75}$As spectrum is very narrow, with a FWHM only...
16KHz under 12T//c field at 200K, which indicates high quality of the sample. We studied the SLRR of 75As by NMR under 12T field with H//c and H//ab, as shown in Fig. 3 As both fields are much higher than the $H_{C2}^{20}$, we were able to measure the normal state SLRR down to 1.5K. The comparison between two different field orientations gives the anisotropic factor of the SLRR $T_{1}^{1}/T_{1}^{2} \approx 1.4$.

We first discuss the normal state properties of both dopings. Our low-temperature resistivity shows a $T^{2}$ dependence, or a Fermi-liquid-like behavior, for both samples, which is consistent with other reports.13 However, our NMR data also suggest the existence of strong spin fluctuations and indicates a deviation from a simple Fermi liquid behavior in $x=1.0$ within the following several aspects.

First, the temperature dependence of the SLRR in the $x=1.0$ sample deviates from the Fermi liquid behavior. The $1/T_{1}$ is fit by a power law $1/T_{1} \sim T^{\alpha}$ with the exponent $\alpha \approx 0.75$, as shown in Fig. 3 over two decades of temperature above 1.5K for both field orientations. Similar power-law behavior and power-law exponent $\alpha \approx 0.8$ were reported by a NQR measurement on KFe$_{2}$As$_{2}$ powders.22 The change of the Knight shift, as shown in Fig. 3 (inset), is negligibly small up to 200K. Taking account the power-law behavior of the SLRR, the ratio $1/T_{1}K_{\sigma}^{2}(T)$ does not follow the modified Korringa relation ($1/T_{1}K_{\sigma}^{2}(T) \sim \text{const}$). Instead, $1/T_{1}TK_{\sigma}^{2}(T) \propto T^{-0.25}$ increases as temperature drops, which is a signature of spin fluctuations.

Second, our NMR data show a prominent change of the spin dynamics with doping close to $x=1.0$. In Fig. 4 the normal-state SLRR at $T=30K$ and 200K is plotted for different dopings. Naively, a decrease of spin-lattice relaxation is expected with reduced spin fluctuation as doping increases. However, the $1/T_{1}$ is enhanced by almost a factor of three at $x=1.0$ compared to lower dopings, which is rather a surprising result. Our result can not be under-
FIG. 5: (Color Online) The power-law exponent $\alpha_x$ of $1/T_1 \sim T^{\alpha_x}$ of 1: $x=0.3$ (Ref. 25), 2: $x=0.4$ (Ref. 24), 3: $x=0.4$ (Ref. 25), 4: $x=0.7$ (current work), and 6: $x=1.0$ (NQR, Ref. 25) Ba$_{1-x}$K$_x$Fe$_2$As$_2$ samples.

...strong low-energy excitations in the overdoped samples. First, it is possible that the superconducting gap structure in the overdoped region is different from that in the underdoped region. In this case, the superconducting pairing symmetry can be changed as indicated in both strong and weak coupling theories. ARPES and other experiments below $T_c$ in the overdoped samples will be useful to address this issue in the future. Second, even if the pairing symmetry is not changed as doping increases, the effect of spin fluctuations on low energy excitations can be quite different in the overdoped region. Our normal state SLRR suggested a new type of spin fluctuations in the overdoped side. These spin fluctuations may produce $q$-dependent excitations and lead to nodal-like behavior even in the $s\pm$ pairing state. In the overdoped region, since the size of the hole pocket is rather large, such a nodal-like behavior is more likely to take place. Under such circumstances, even in the $s\pm$ pairing state, the SLRR can be described by a dirty $s$-wave or a $d$-wave superconductor.

In summary, our study of the doping and the temperature dependence of the spin-lattice relaxation rate in heavily overdoped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ suggest that a new type of spin fluctuations develops as the doping close to $x=1.0$. These results strongly suggest that system evolves towards a new magnetic quantum critical point, and rule out a simple Fermi-liquid description of the normal state. In the superconducting state, no coherence peak is seen, and a step-like behavior in the SLRR at $T_c/2$ supports the idea of a two-gap superconductivity. The SLRR below $T_c$ is characterized by a universal power-law behavior $1/T_1 \sim T^{1.5}$, which suggests strong low-energy excitations below $T_c$, in contrast to the behavior in the under- or optimally doped samples. Such low-energy excitation may be correlated with a different pairing symmetry or the new type of spin fluctuations in the overdoped side.

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1 Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
2 X. H. Chen et al., Nature 453, 761 (2008).
3 G. F. Chen et al., Phys. Rev. Lett. 100, 247002 (2008).
4 Z. A. Ren et al., Mater. Res. Inno. 12, 105 (2008).
5 S. Lebégue, Phys. Rev. B 75, 035110 (2007).
6 D. J. Singh and M. H. Du, Phys. Rev. Lett. 100, 237003 (2008).
7 G. Xu et al., Europhys. Lett. 82, 67002 (2008).
8 I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).
9 K. Seo, B. A. Bernevig, and J. Hu, Phys. Rev. Lett 101, 206404 (2008).
10 K. Kuroki et al., Phys. Rev. Lett. 101, 087004 (2008).
11 F. Wang, H. Zhai, Y. Ran, A. Vishwanath, and D. Lee, Phys. Rev. Lett. 102, 047005 (2009).
12 M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008).
13 H. Chen et al., Euro. Phys. Lett 85, 17006 (2009).
14 H. Ding et al., Euro. Phys. 3, 47001 (2008).
15 K. Matano, G. L. Sun, D. L. Sun, C. T. Lin, and G. Q. Zheng, Europhys. Lett. 87, 27012 (2009).
16 H. Fukazawa et al., J. Phys. Soc. Jpn. 78, 033704 (2009).
17 M. Yashima et al., Cond-mat/0905.1896 (2009).
18 M.-H. Julien et al., Europhys. Lett. 87, 37001 (2009).
19 Y. Nagai et al., New J. Phys. 10, 103026 (2008).
20 M. M. Parish, J. Hu, and B. A. Bernevig, Phys. Rev. B 78, 144514 (2008).
21 T. Sato et al., Phys. Rev. Lett. 103, 047002 (2009).
22 K. Sasmal et al., Phys. Rev. Lett. 101, 107007 (2008).
23 T. Terashima et al., J. Phys. Soc. Jpn. 78, 063702 (2009).
24 H. Q. Yuan, J. Singleton, F. F. Balakirev, S. A. Baily, G. F. Chen, J. L. Luo, and N. L. Wang, Nature 457, 565 (2009).
25 H. Fukazawa et al., J. Phys. Soc. Jpn. 78, 083712 (2009).
26 G. F. Chen et al., Phys. Rev. B 78, 224512 (2008).
27 F. L. Ning et al., J. Phys. Soc. Jpn. 78, 013711 (2009).
28 F. L. Ning et al., Cond-mat/0907.3875v1 (2009).
29 G. Xu, H. Zhang, X. Dai, and Z. Fang, Europhys. Lett. 84, 67015 (2008).
30 K. Selte, A. Kjekshus, and A. F. Andresen, Acta. Chem. Scand. 26, 3101 (1972).
31 S. Kawasaki, K. Shimada, G. F. Chen, J. L. Luo, N. L. Wang, and G. Zheng, Phys. Rev. B 78, 220506 (2008).
32 Y. Nakai, K. Ishida, Y. Kamihara, M. Hirano, and H. Hosono, Phys. Rev. Lett. 101, 077006 (2008).
33 Y. Bang, H. Choi, and H. Won, Phys. Rev. B 79, 054529 (2009).
34 K. Seo, C. Fang, B. A. Bernevig, and J. Hu, Phys. Rev. B 79, 235207 (2009).