

^{75}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 1.0) single crystals. In the normal states, we found a dramatic increase in the spin-lattice relaxation ($1/T_1$) from the $x=0.7$ to the $x=1.0$ samples. In KFe_2As_2 , the ratio of $1/T_1TK_n^2$, where $^{75}\text{K}_n$ is the Knight shift, increases as temperature drops. These results indicate the existence of another type of spin fluctuations in KFe_2As_2 which is accustomed to being treated as a simple Fermi liquid. In the superconducting state, the temperature scalings of $1/T_1$ below T_c in the overdoped samples are significantly different from those in the under or optimally doped ones. A power-law scaling behavior $1/T_1T \sim T^{0.5}$ is observed, which indicates universal strong low-energy excitations in the overdoped hole-type superconductors.

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The discovery of superconductivity at 26 K in $\text{LaFeAsO}_{1-x}\text{F}_x$ (Ref. 1) and the improvement of superconducting transition temperature above 50 K in other iron pnictides²⁻⁴ 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.⁵⁻⁷ Upon either electron or hole doping, most compounds evolve from an antiferromagnetically ordered state to a superconducting state.³ 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.⁸⁻¹² 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 $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$.^{13,14} An angle-resolved photoemission spectroscopy (ARPES) study showed two isotropic s -wave superconducting gaps in the optimally doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$.¹⁵ However, the relative sign between two pockets has not been measured. From NMR, the absence of a coherence peak and the power-lawlike behavior of the spin-lattice relaxation rate (SLRR) below T_c of the underdoped and the optimally doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ materials¹⁶⁻¹⁹ are evidences against a conventional single band s wave although it is still unable to differentiate the s_{\pm} , the d -wave or other nodal pairing symmetries.^{16-18,20,21}

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.^{15,22} In particular, in

KFe_2As_2 ($x=1.0$), the electron pockets disappear completely.²² Since 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 KFe_2As_2 comparing to low dopings. For example, T_c remains finite at about 3 K (Refs. 14, 23, and 24) and the H_{c2} is anisotropic²⁴ rather than isotropic.²⁵ Strong low-energy excitations below T_c are observed by nuclear quadrupole resonance (NQR) which is consistent with a multiple-gap superconductor.²⁶ 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 Brief Report, we performed NMR studies on high-quality overdoped $\text{Ba}_{0.3}\text{K}_{0.7}\text{Fe}_2\text{As}_2$ and KFe_2As_2 single crystals. Surprisingly, we found spin fluctuations are strongly enhanced in the normal-state SLRR of the heavily overdoped sample KFe_2As_2 . A deviation from a simple Fermi liquid is indicated by the decrease of $1/T_1TK_n^2$ with temperature in the normal state of KFe_2As_2 , where $K_n(T)$ is the Knight shift. Below T_c , we found a clear steplike feature in the SLRR in $\text{Ba}_{0.3}\text{K}_{0.7}\text{Fe}_2\text{As}_2$, which is consistent with two-gap superconductivity. Importantly, the power-law behavior of the SLRR as a function of temperature, $1/T_1 \sim T^{\alpha_s}$, has a universal power-law exponent $\alpha_s \sim 1.5$ below T_c in the overdoped samples, in contrast to the large and nonuniversal power-law exponent α_s observed in the underdoped or optimally doped samples.¹⁶⁻¹⁸

Our $\text{Ba}_{0.3}\text{K}_{0.7}\text{Fe}_2\text{As}_2$ and KFe_2As_2 single crystals were grown by the FeAs-flux method.²⁷ The NMR crystals were platelike with a surface area of $2.5 \text{ mm} \times 1.2 \text{ mm}$. We mainly performed ^{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 for an $S=3/2$ spin, $1 - \frac{m(t)}{m(0)} = 0.9 \exp(-\frac{6t}{T_1}) + 0.1 \exp(-\frac{t}{T_1})$. The usage of single crystals also enables us to

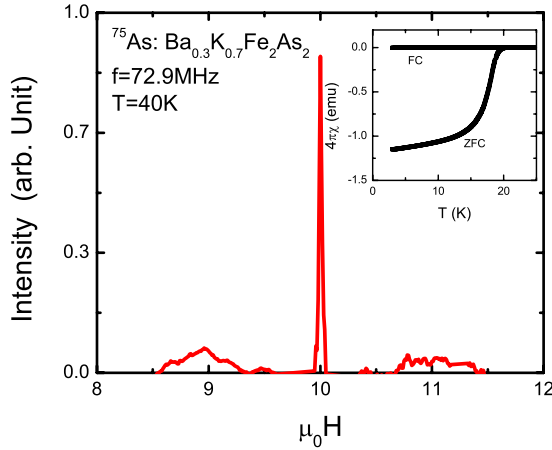


FIG. 1. (Color online) The ^{75}As NMR spectrum of the $\text{Ba}_{0.3}\text{K}_{0.7}\text{Fe}_2\text{As}_2$ single crystal at a fixed frequency 72.9 MHz. Inset: the dc susceptibility of the crystal under field cooling and ZFC with a 100 Oe field.

measure the Knight shift and the anisotropy of $1/T_1$ accurately.

In Fig. 1 (inset), the magnetic susceptibility of the $\text{Ba}_{0.3}\text{K}_{0.7}\text{Fe}_2\text{As}_2$ single crystal is shown with a 100 Oe field. From the zero-field cooling (ZFC) data, the sample is 100% superconducting in volume, and bulk superconductivity starts around 19 K, and the major transition completes around 15 K. The ^{75}As ($S=3/2$) NMR spectra of the crystal at a fixed frequency 72.9 MHz with field along the crystal c axis is shown in Fig. 1 with a center transition at $\mu_0 H \sim 10$ T and two satellites at 8.8 and 11.2 T, 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 $1/^{75}\text{T}_1$ of the $\text{Ba}_{0.3}\text{K}_{0.7}\text{Fe}_2\text{As}_2$ crystal with various fields for two orientations ($H\parallel c$ and $H\parallel ab$). In the normal state, $1/^{75}\text{T}_1$ can be fit by a power law $1/^{75}\text{T}_1 \sim T^{\alpha_n}$ with $\alpha_n \approx 1.1$ from T_C up to about 100 K, 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 anisotropy factor, es-

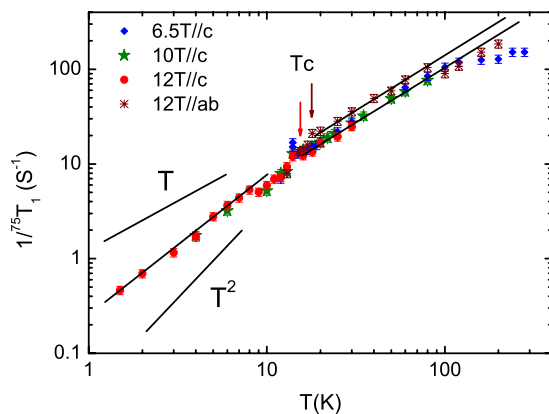


FIG. 2. (Color online) The temperature dependence of ^{75}As spin-lattice relaxation rate of the $\text{Ba}_{0.3}\text{K}_{0.7}\text{Fe}_2\text{As}_2$ single crystal measured at four different fields, 12 T $\parallel c$, 10 T $\parallel c$, 6.5 T $\parallel c$, and 12 T $\parallel ab$.

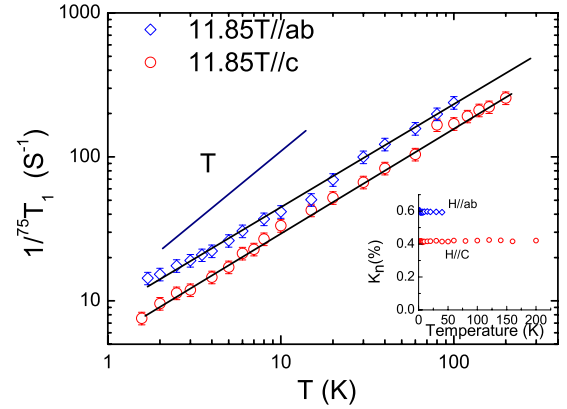


FIG. 3. (Color online) The spin-lattice relaxation rate $1/^{75}\text{T}_1$ of the KFe_2As_2 under 12 T field with two orientation $H\parallel c$ and $H\parallel ab$. Inset: the Knight shift K_n of the sample with both fields.

timated to be $T_1^c/T_1^{ab} \approx 1.3$, holds for all temperatures above T_C . From 100 K and above, both the transport¹⁴ and our $1/^{75}\text{T}_1$ deviate from a simple Fermi-liquid behavior. This feature has also been observed in previous NMR measurements of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ with low different doping concentrations.¹⁶ The origin of such a deviation is not completely understood.

We took similar measurements on KFe_2As_2 . The superconducting transition temperature of our sample is about 3 K from resistivity, close to earlier reports.^{14,23,24} The ^{75}As spectrum is very narrow, with a full width at half maximum only 16 KHz under 12 T $\parallel c$ field at 200 K, which indicates the high quality of the sample. We studied the SLRR of ^{75}As by NMR under 12 T field with $H\parallel c$ and $H\parallel ab$, as shown in Fig. 3. As both fields are much higher than the H_{C2} ,²⁴ we were able to measure the normal-state SLRR down to 1.5 K. The comparison between two different field orientations gives an anisotropy factor of the SLRR $T_1^c/T_1^{ab} \approx 1.4$.

We first discuss the normal-state properties of both dopings. Our low-temperature resistivity is close to a T^2 dependence for both samples, which is consistent with other reports.¹⁴ However, our NMR data suggest the existence of strong spin fluctuations and indicates a deviation from a simple Fermi-liquid behavior in $x=1.0$ as we discussed below.

First, our NMR data show a prominent change in the spin dynamics with doping close to $x=1.0$. In Fig. 4, the normal-state SLRR at $T=30$ and 200 K is plotted for different dopings. Naively, a decrease in 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 surprising.

Second, 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 $1/^{75}\text{T}_1 \sim T^{\alpha_n}$ with the exponent $\alpha_n \approx 0.75$, as shown in Fig. 3, over two decades of temperature above 1.5 K for both field orientations. Similar power-law behavior and power-law exponent $\alpha_n \approx 0.8$ were reported by a NQR measurement on KFe_2As_2 powders.²⁶ The change in the Knight shift, as shown in Fig. 3 (inset), is negligibly small up to 200 K. Taking account the power-law

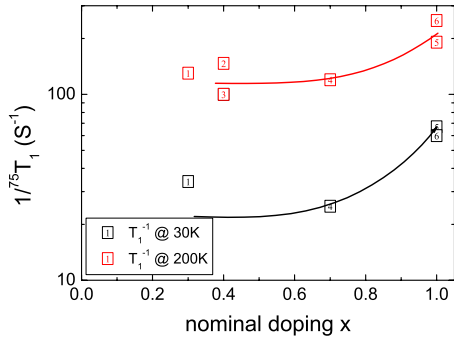


FIG. 4. (Color online) The normal-state spin-lattice relaxation rate $1/T_1$ at 30 and 200 K in 1: $x=0.3$ (Ref. 16), 2: $x=0.4$ (Ref. 18), 3: $x=0.4$ (Ref. 17), 4: $x=0.7$ (current work), 5: $x=1.0$ (current work), and 6: $x=1.0$ (NQR, Ref. 26) $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ samples.

behavior of the SLRR, the ratio $1/TT_1K_n^2(T)$ does not follow the modified Korringa relation [$1/TT_1K_n^2(T) \sim \text{const}$]. Instead, $1/T_1TK_n^2(T) \propto T^{-0.25}$ increases as temperature drops, which is a signature of spin fluctuations.

The strong fluctuations observed at $x=1.0$ is not consistent with the Fermi-liquid behavior as expected for a highly overdoped sample. In contrast, a Fermi-liquid behavior and a Korringa relation have been reported in overdoped electron-type compounds.^{28,29} From the doping dependence, we believe the spin fluctuations at $x=1.0$ is unrelated to the parent spin-density wave ordering. The spin fluctuations are probably driven by the intraband scattering rather than interband scattering since the electron pockets disappear at $x=1.0$.¹⁵ Given that superconductivity disappears close to $x=1.0$, the spin fluctuations at $x=1.0$ and/or the reduced interband scattering may be detrimental to the superconductivity.

The enhancement of the SLRR and the non-Korringa temperature dependence in KFe_2As_2 suggest that a new type of spin fluctuation develops at $x=1.0$. Since the KFe_2As_2 is a 50% hole-doped sample and no long-range order is observed, such high-temperature spin fluctuations suggest that the system is close to a quantum critical point of a new magnetic ordering. Introducing potassium vacancy to increase the doping level or applying high pressure may be possible to locate the quantum critical point. Theoretical, first-principles calculations proposed a new antiferromagnetic quantum-critical point but with a lower critical doping $x_c \approx 0.8$.³⁰ It is also worthwhile to mention that FeAs single crystals although with a different lattice structure, has a helimagnetic order.³¹

Next we discuss the superconducting properties of overdoped samples. We first analyze the SLRR of $x=0.7$ sample with $\mu_0H=12$ T $\parallel c$. Under this field, the T_c is suppressed to 16 K and a few features are seen in the SLRR. (i) The $1/T_1$ drops below T_c , and the Hebel-Slichter coherence peak is not seen in our crystal. Although $1/T_1$ is slightly enhanced at T_c , we have verified that the enhancement is due to a vortex dynamics effect because the enhancement strongly depends on the field strength and orientation. (ii) The $1/T_1$ data has a steplike feature at $T \approx T_c/2$ (8.5 K), which is consistent with a two-gap superconductivity.^{16,32}

Importantly, below $T_c/2$, the $1/T_1$ shows a power-law scaling with temperature, $1/T_1 \approx T^{\alpha_s}$. The scaling exponent

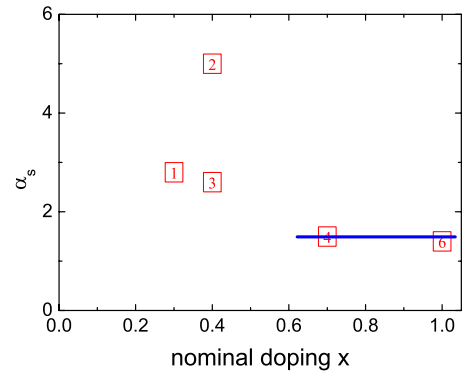


FIG. 5. (Color online) The power-law exponent α_s of $1/T_1 \sim T^{\alpha_s}$ of 1: $x=0.3$ (Ref. 16), 2: $x=0.4$ (Ref. 18), 3: $x=0.4$ (Ref. 17), 4: $x=0.7$ (current work), and 6: $x=1.0$ (NQR, Ref. 26) $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ samples.

$\alpha_s \approx 1.5$ holds down to our lowest temperature 1.5 K. The reported KFe_2As_2 samples²⁶ shows a similar power-law exponent $\alpha_s = 1.4-1.5$ below T_c . Therefore, the power-law exponent α_s is quite universal over 30% range of doping concentration. In contrast, the power-law exponent is much larger and nonuniversal in the underdoped samples. In Fig. 5, we plotted the power-law exponents in samples with different doping levels reported by different groups. Below the optimal doping ($x \leq 0.4$), the power-law exponent ranges from 5 down to 2.8.

The small power-law exponent in the overdoped samples indicates strong low-energy excitations in the superconducting state, relative to those at low dopings. All our spin recovery is fitted nicely by a single T_1 component across the whole spectrum, which indicates that our SLRR data are intrinsic properties of a high-quality sample. There are several possible origins of strong low-energy excitations. 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.^{8,9} Second, the effect of spin fluctuations on low-energy excitations can be quite different in the overdoped region. Our normal-state SLRR suggests a 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. For comparison, a strong low-energy excitations has been observed in a $\text{La}_{0.87}\text{Ca}_{0.13}\text{FePO}$ system,³³ which is proposed to be associated with ferromagnetic fluctuations. Finally, the nonmagnetic impurities could lead to a dirty s -wave or a d -wave superconductor^{34,35} behavior. 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.

In summary, our study of the doping and the temperature dependence of the spin-lattice relaxation rate in heavily overdoped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ suggest that another type of spin fluctuations develops as the doping close to $x=1.0$. These results rule out a simple Fermi-liquid description of the normal state and strongly suggest that system evolves toward a new magnetic quantum critical point. In the superconducting state, the

SLRR 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 underdoped or optimally doped samples. Such low-energy excitation may be correlated with the nonmagnetic impurities or the new type of spin fluctuations in the overdoped side.

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