Breakdown of single spin-fluid model in heavily hole-doped superconductor CsFe$_2$As$_2$

D. Zhao,$^1$ S. J. Li,$^1$ N. Z. Wang,$^1$ J. Li,$^1$ D. W. Song,$^1$ L. X. Zheng,$^1$ L. P. Nie,$^1$ X. G. Luo,$^{1,2,3}$ T. Wu,$^{1,2,3}$, and X. H. Chen$^{1,2,3}$

$^1$Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China
$^2$Key Laboratory of Strongly-coupled Quantum Matter Physics, University of Science and Technology of China, Chinese Academy of Sciences, Hefei 230026, China
$^3$Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

Although Fe-based superconductors are multiorbital correlated electronic systems, previous nuclei magnetic resonance (NMR) measurement suggests that a single spin-fluid model is sufficient to describe its spin behavior. Here, we firstly observed the breakdown of single spin-fluid model in a heavily hole-doped Fe-based superconductor CsFe$_2$As$_2$ by site-selective NMR measurement. At high temperature regime, both of Knight shift and nuclei spin-lattice relaxation at $^{133}$Cs and $^{75}$As nuclei exhibit distinct temperature-dependent behavior, suggesting the breakdown of single spin-fluid model in CsFe$_2$As$_2$. This is ascribed to the coexistence of both localized and itinerant spin degree of freedom at 3$d$ orbits, which is consistent with orbital-selective Mott phase. However, single spin-fluid behavior is gradually recovered by developing a coherent state among 3$d$ orbits with decreasing temperature. A Kondo liquid scenario is proposed for the low-temperature coherent state. The present work sets strong constraint on the theoretical model for Fe-based superconductors.

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In high-$T_c$ cuprate superconductors, single spin-fluid model has been widely adopted as a theoretical starting point although at least one 3$d$ or two 2$p$ orbits from copper and oxygen sites should be considered together in theoretical model in principle[1]. The basis of such hypothesis is mostly based on the celebrated concept of Zhang-Rice singlet[2], which successfully converts the complex reality into single band t-J model. Such single spin-fluid model has been validated by early site-selective nuclei magnetic resonance (NMR) measurement on $^{89}$Y, $^{63}$Cu and $^{17}$O nuclei in YBa$_2$Cu$_3$O$_{6.9}$[3, 4].

In Fe-based superconductors, the multiorbital nature is a key factor to understand its basic properties[4]. Considering correlation effect due to Hund’s coupling, single spin-fluid model should be insufficient in this case. However, previous site-selective NMR measurement on F-doped LaOFeAs found that Knight shift and nuclei spin-lattice relaxation on different nuclei are nearly identical[5], including $^{75}$As, $^{57}$Fe, $^{19}$F and $^{139}$La nuclei. This result suggests a single spin-fluid model, which is consistent with weak coupling theory based on itinerant nature of Fe 3$d$ electrons[5, 6]. Similar behavior was also observed in many other Fe-based superconductors[10–12]. On the other hand, strong coupling theory based on local nature of Fe 3$d$ electrons has also been proposed for Fe-based superconductors[13], in which the coexistence of itinerant and localized electrons at different 3$d$ orbits would appear in a so-called orbital-selective Mott phase[14–16]. Recently, orbital-selective Mott phase has been widely observed in FeSe-derived superconductors by angle-resolved photoemission spectroscopy (ARPES)[17, 18]. However, site-selective NMR experiment has not yet observed any breakdown of single spin-fluid model in FeSe-derived superconductors[10].

Very recently, a similar orbital-selective Mott phase has also been proposed in heavily hole-doped Fe-based superconductors AFe$_2$As$_2$ (A = K, Rb, Cs)[19–20]. Furthermore, a so-called “Knight shift anomaly” phenomenon has been observed by $^{75}$As NMR in AFe$_2$As$_2$ (A = K, Rb, Cs)[21], which hints a possible deviation from single spin-fluid model. In order to further examine the single spin-fluid model in heavily hole-doped Fe-based superconductors AFe$_2$As$_2$ (A = K, Rb, Cs), we conducted a site-selective NMR experiment on CsFe$_2$As$_2$ single crystal by measuring $^{133}$Cs and $^{75}$As nuclei.

As shown in Fig.1a, considering the spatial distribution of 3$d$ orbits, the 3$d$ orbits at Fe sites could be divided into two categories. The first category includes 3$d_{xy}$ and 3$d_{xz, yz}$ and the second one includes 3$d_{z^2}$, 3$d_{yz}$ and 3$d_{zx}$. It’s very obvious that the orbits in second category have much larger spatial distribution along c-axis than that in the first one. In Fe-based superconductors, the dominated hyperfine interaction between 3$d$ electrons at Fe site and $^{75}$As nuclei is verified to be transferred hyperfine interaction mediated by 4$s$ orbit of $^{75}$As[22]. In this case, the overlap between 3$d$ and 4$s$ orbits would largely determine the strength of the transferred hyperfine interaction. Therefore, in principle, the electrons on different 3$d$ orbits have different transferred hyperfine interaction with $^{75}$As nuclei as shown in Fig.1a. We could express the spin part of Knight shift from different 3$d$ orbits as the following equation:

$$K_s(T) = \sum_{\sigma} A_{\sigma} \chi_{\sigma}(T), (\sigma = xz, yz, xy, z^2, x^2 + y^2)$$ (1)

$A_{\sigma}$ is the hyperfine coupling tensor from different 3$d$ orbits. $\chi_{\sigma}(T)$ is the orbital-dependent local spin suscepti-
FIG. 1: (color online). (a) Illustration of the microscopic process of the transferred hyperfine interaction on $^{75}$As and $^{133}$Cs nuclei. The crystalline structure of CsFe$_2$As$_2$ is shown in the side view along Fe-Fe direction. The hyperfine interaction of $^{75}$As and $^{133}$Cs are dominated by the transferred hyperfine interaction through the hybridization of onsite 4s or 6s orbit with 3d orbits at the nearest-neighbour Fe atoms. We performed NMR measurements on both $^{75}$As and $^{133}$Cs nuclei. The full spectrum at 2 K are shown in (b) for $^{133}$Cs nuclei and (c) for $^{75}$As nuclei.

...ability. Considering similar transferred hyperfine interaction, the $^{133}$Cs nuclei in spacer layer with distinct out-of-plane distance to Fe site would only have significant overlap with the 3d orbits in above second category, suggesting an orbital-selective NMR probe. Based on this fact, the site-selective NMR by measuring both $^{75}$As and $^{133}$Cs nuclei would have the ability to examine single spin-fluid model in our case. Our following results unambiguously confirm the breakdown of single spin-fluid model in CsFe$_2$As$_2$.

High-quality CsFe$_2$As$_2$ single crystals are grown by the self-flux technique. All NMR measurement on $^{75}$As and $^{133}$Cs nuclei are conducted from 2 K to 300 K under an external magnetic field of 14 Tesla parallel to c axis. The nuclei spin number $I_{nuclei}$ for $^{75}$As and $^{133}$Cs nuclei are 3/2 and 7/2 respectively. The standard full spectrum of $^{75}$As and $^{133}$Cs nuclei are shown in Fig.1b. There are three transition lines for $^{75}$As nuclei and seven transition lines for $^{133}$Cs nuclei. For $^{133}$Cs nuclei, all NMR peaks have a similar linewidth of ~20 kHz at 2 K, suggesting a magnetic broadening origin. This is also consistent with small quadrupole frequency below. For $^{75}$As nuclei, the linewidth for satellite peaks and central peak are ~300 KHz and ~30 KHz at 2 K, indicating that the linewidth of satellite peaks is dominated by quadrupole broadening. Similar behavior has already been seen in previous study. By measuring the separation between each transition lines, the quadrupole frequency $v_Q$ for $^{75}$As and $^{133}$Cs nuclei are determined to be ~13.6 MHz and ~0.658 MHz respectively. Both of Knight shifts for $^{75}$As and $^{133}$Cs nuclei are determined by measuring the frequency position of the central transition line. Nuclei spin-lattice relaxations rate $1/T_1$ are also measured on the central transition line for both $^{75}$As and $^{133}$Cs nuclei.

The main results in this letter are shown in Fig.2. As shown in Fig.2a, the temperature-dependent Knight shift of $^{75}$As ($^{75}$K) nuclei exhibits a characteristic crossover behavior. At high temperature regime, $^{75}$K is gradually increasing as temperature decreasing. This is also consistent with high-temperature bulk magnetic susceptibility, which suggests a localized spin behavior. As temperature further decreasing, $^{75}$K shows a maximum and then starts to decrease with lowering temperature. Below 20 K, $^{75}$K becomes saturated and shows a temperature-independent behavior. Above temperature-dependent behavior has been ascribed to an incoherent-to-coherent electronic crossover, which is also observed in KFe$_2$As$_2$ and RbFe$_2$As$_2$ with different crossover temperature.

In sharp contrast, the remarkable crossover behavior in temperature-dependent Knight shift of $^{75}$As nuclei is completely absent in that of $^{133}$Cs nuclei. As shown in Fig.2a, the temperature dependent Knight shift of $^{133}$Cs ($^{133}$K) nuclei shows a monotonous decreasing in the whole temperature range. The localized spin behavior as shown in high-temperature bulk susceptibility and $^{75}$K does not show up in $^{133}$K. This result indicates that the localized spin behavior probably comes from 3d$_{xy}$ or 3d$_{x^2+y^2}$ orbits. As we mentioned before, the hyperfine interaction between 3d electrons and $^{133}$Cs nuclei is dominated by the transferred hyperfine interaction which is dependent on the overlap between 3d orbits at Fe site and 6s orbits at Cs site. Since both of 3d$_{xy}$ or 3d$_{x^2+y^2}$ orbits at Fe site has less overlap with 6s orbits at Cs site due to limited spatial distribution along c axis, the transferred hyperfine interaction would be not sensitive to 3d$_{xy}$ or 3d$_{x^2+y^2}$ orbits. In this case, we could ascribe the origin of electronic crossover behavior observed by $^{75}$As nuclei to the 3d$_{xy}$ or 3d$_{x^2+y^2}$ orbits. Based on previous theoretical calculation, the 3d$_{x^2+y^2}$ orbit has much less mass renormalization effect than other 3d orbits. Considering this point, the high-temperature localized spin behavior could only be ascribed to 3d$_{xy}$ orbit, which is also consistent with that the 3d$_{xy}$ orbit has the maximum mass renormalization effect among all 3d orbits. Therefore, we believe that the temperature dependence of $^{133}$K is dominated by itinerant 3d orbits but the temperature dependence of $^{75}$K, especially for the incoherent-to-coherent crossover, is mainly dominated by localized 3d$_{xy}$ orbit. This result strongly proves the breakdown of single spin-fluid model in CsFe$_2$As$_2$. By scaling both temperature-dependent $^{75}$K and $^{133}$K, we found an identical temperature dependent behavior below T$^\ast$ ~ 75 K. As shown in the inset of Fig.2a, single spin-fluid behavior is recovered below T$^\ast$. This result indicates that, although single spin-fluid model is broken above T$^\ast$ due to coexistence of localized and itinerant...
3$d$ electrons, a coherent state involving both localized and itinerant 3$d$ electrons appears below $T^*$ which still follows single spin-fluid model. Similar crossover behavior was also observed in FeSe-derived superconductors by ARPES, in which the high-temperature incoherent state is ascribed to orbital-selective Mott phase\textsuperscript{[14-18]}. Here, we also believe that a similar orbital-selective Mott phase might appear above $T^*$ in CsFe$_2$As$_2$. Low-temperature ARPES and STM experiments have already observed a coherent peak from 3$d_{xy}$ orbit close to Fermi level below 20 K in KFe$_2$As$_2$\textsuperscript{[26]}. Further ARPES experiment with whole temperature range is needed to verify the exact nature of the high-temperature incoherent state in CsFe$_2$As$_2$.

In Fig.2b, we also measured the temperature dependent $1/T_1$ for both $^{75}$As and $^{133}$Cs nuclei. Similar to Knight shift result, the temperature-dependent $1/T_1$ also shows a distinct temperature-dependent behavior for both $^{75}$As and $^{133}$Cs nuclei above $T^*$. For $^{133}$Cs nuclei, the temperature-dependent $1/T_1$ follows an approximate power-law behavior with $1/T_1 \sim T^{1.36}$, which looks like a strange metallic behavior. For $^{75}$As nuclei, the temperature-dependent $1/T_1$ is almost temperature independent, which is consistent with a localized moment behavior\textsuperscript{[21]}. This result further confirms the above conclusion on the breakdown of single spin-fluid model above $T^*$. Below $T^*$, an identical temperature dependent behavior for both $^{75}$As and $^{133}$Cs nuclei with $1/T_1 \sim T^{0.75}$ appears as shown in the inset of Fig 2b. This result is consistent with the formation of a coherent state below $T^*$. A deviation from $T^{0.75}$ power-law behavior is also observed at very low temperature. This is due to the appearance of two-component behavior in spin-lattice relaxation decay. The details has been discussed in our previous work and we found that such two-component behavior is dependent on external magnetic field\textsuperscript{[21-24]}. When we measure nuclei spin-lattice relaxation under zero field, a perfect spin-lattice relaxation decay with single component is observed and the $T^{0.75}$ power-law behavior is extended to the lowest temperature\textsuperscript{[21]}. Based on this observation, we ascribe the low-temperature $T^{0.75}$ power-law behavior to the characteristic property of the low-temperature coherent state. The field-induced deviation from $T^{0.75}$ power-law behavior due to two-component behavior in spin-lattice relaxation decay might be other novel effect but this is not the focus in this letter.

Based on above results on Knight shift and nuclei spin-lattice relaxation, we found that the high-temperature incoherent state above $T^*$ looks like a so-called orbital-selective Mott phase\textsuperscript{[14-16]}, in which $3d_{xy}$ orbit is probably localized and other 3$d$ orbits remain itinerant. As shown in Fig.3a, orbital-selective Mott phase has already been proposed in phase diagram based on strong coupling theory\textsuperscript{[13-12]}. Previous theoretical study suggests that the $3d_{xy}$ orbit would firstly occurs orbital-selective Mott localization among all 3$d$ orbits in AFe$_2$As$_2$ ($\mathbf{A} = K, \text{Rb}, \text{Cs}$)\textsuperscript{[19-23]}. This is consistent with our present site-selective NMR results. In detail, the contrasting temperature dependence of $^{133}K$ and $^{75}K$ suggests that the orbital-selective Mott localization or at least the strongest correlation effect happens on $3d_{xy}$ orbit, which leads to a localized spin behavior above $T^*$. Further ARPES experiment would be expected to verify the exact nature of $3d_{xy}$ orbit above $T^*$.

Below $T^*$, a coherent state between localized and itinerant 3$d$ orbits is developed, which is also verified by low-temperature ARPES and STM results on KFe$_2$As$_2$\textsuperscript{[26]}. How to understand the underlying mechanism of such incoherent-to-coherent crossover? In fact, incoherent-to-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{(color online). (a) Temperature dependent Knight shift for both $^{75}$As and $^{133}$Cs nuclei. The red squares represent the Knight shift of $^{133}$Cs nuclei. The blue triangles represent the Knight shift of $^{75}$As nuclei. The red dash line is a guiding line for temperature dependent $^{75}K$ at high temperature. Both Knight shifts below $T^*$ follow a same temperature dependent behavior, which is also confirmed by the $^{133}K - ^{75}K$ plot in the inset. (b)Temperature dependent nuclei spin-lattice relaxation for both $^{75}$As and $^{133}$Cs nuclei. The blue triangles represent the nuclei spin-lattice relaxation of $^{133}$Cs nuclei. The red squares represents the nuclei spin-lattice relaxation of $^{75}$As. Both nuclei spin-lattice relaxation below $T^*$ follow a same power-law behavior, which is also confirmed by the $^{133}T_1 - ^{75}T_1$ plot in the inset. The fitting formula of spin-lattice relaxation decay is $I(t) = I_0 + I_1(0.1e^{-\frac{t}{1/T_1}} + 0.9e^{-\frac{t}{1/T_2}})$ for $^{75}$As nuclei and $I(t) = I_0 + I_1e^{-\frac{t}{1/T_1}}$ for $^{133}$Cs nuclei.}
\end{figure}
coherent crossover has already been proposed in early dynamical mean field theory (DMFT) by K. Haule and G. Kotliar, in which each 3d electron be- comes coherent through Kondo-type coupling. In Kondo liquid state, the localized spin degree of freedom would be screened out by itinerant electrons, which leads to the deconfinement of localized moments. In our case, we also believe that a similar deconfinement of localized 3d electrons happens due to certain Kondo-type coupling between localized and itinerant 3d electrons, such as off-site Kondo coupling. If this scenario is finally validated, the Kondo-type coupling between localized and itinerant spin degree of freedom for 3d electrons should be an important ingredient in effective theoretical model for Fe-based superconductors. This would stimulate further theoretical investigation in AFe$_2$As$_2$ (A = K, Rb, Cs) system and bring new understanding on the mecha-nism of superconducting pairing in Fe-based supercon-ductors.

Finally, we would like to address that the strong coupling feature observed in AFe$_2$As$_2$ (A = K, Rb, Cs) is probably due to the Mott insulating phase at 3d$^5$ configuration. Based on DMFT calculation, the realization of Mott insulating phase would be much easier at half filling than other integer fillings. For example, the critical mutual Coulomb repulsion ($U_c$) for Mott transition has a minimum at half filling. For 3d electron system, the half filling is 3d$^5$ configuration. In Fe-based superconductors, the parent compound with 3d$^6$ configuration is indeed a bad metal but not Mott insulator. However, we could expect a real Mott insulating phase appears at 3d$^5$ configuration and this has already been proposed in previous theory. In this case, when we doped considerable holes from parent compound with 3d$^6$ configuration, the system is actually approaching to Mott insulating phase at 3d$^5$ configuration. Therefore, the emergence of orbital-selective Mott phase between 3d$^5$ configuration and 3d$^6$ configuration is not a surprising in strong coupling scenario. In sharp contrast, when we doped electrons from parent compound with 3d$^6$ configuration, the correlation effect would become weaker during the evolution from 3d$^6$ configuration towards 3d$^7$ configuration. This is consistent with experimental results on Co-doped BaFe$_2$As$_2$. In cuprate superconductors, the most novel strongly correlated physics (such as pseudogap, stripe, nematicity, charge order, etc.) always emerges in the underdoped regime with hole doping. Here, in Fe-based superconductors, considering above Mott physics at 3d$^5$, the most novel strongly correlated physics would happen in the overdoped regime with hole doping from parent compound at 3d$^6$. It needs further experimental and theoretical survey to figure out the exact nature of strongly correlated physics in this regime.

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* Electronic address: wutao@ustc.edu.cn

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