NMR evidence of strong-correlated superconductivity in LiFeAs: tuning toward an SDW ordering

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In this letter, we reported the results of NMR study on LiFeAs single crystals. We find a strong evidence of the low temperature spin fluctuations; by changing sample preparation conditions, the system can be tuned toward an spin-density-wave (SDW) quantum-critical point. The detection of an interstitial Li(2) ion, possibly located in the tetrahedral hole, suggests that the off-stoichiometry and/or lattice defect can probably account for the absence of the SDW ordering in LiFeAs. These facts show that LiFeAs is a strongly correlated system and the superconductivity is likely originated from the SDW fluctuations.

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The interplay of magnetism and superconductivity is one of the dominant themes in the study of unconventional superconductors, such as high-T_c cuprates, organic superconductors and heavy fermions, where the magnetic fluctuations are crucial to the superconductivity in general [1,8]. This subject has also been extensively studied both experimentally and theoretically in the recent discovered iron pnictides [4], where high-temperature superconductivity is achieved by suppressing a competing spin-density-wave (SDW) state upon chemical doping or pressure [5,6]. Here the superconductivity emerging in proximity to a spin-density-wave (SDW) quantum critical point (QCP), as well as the persisting spin fluctuations shown above T_C [8], support strongly that superconducting pairing is mediated by spin fluctuations.

However, in an iron pnictide LiFeAs, bulk superconductivity up to 18 K, instead of long-range antiferromagnetism (AFM), is found in the ground state without nominal doping [9,11]. Angle-resolved photoemission spectroscopy (ARPES) studies [12,14] do not see evidence of spin fluctuations. In particular, the superconducting gap seems to be a single isotropic gap with a moderate amplitude [12,14], in contrast to the multiple gaps in other iron pnictides which is likely originated from Fermi surface nesting and spin fluctuations [13,20]. The μSR studies show that LiFeAs has a different Uemura relation with other pnictide superconductors [21]. These facts lead to an ever-lasting proposal that LiFeAs is a conventional superconductor, rather than a strongly correlated superconductor.

Theoretically, the local density approximation (LDA) calculations indicate that LiFeAs has a similar band structure with LaFeAsO, BaFe2As2 and NaFeAs, and therefore a similar magnetic ordering in the undoped and a universal origin of superconductivity in the doped materials are expected among all compounds [22,23]. Indeed, particularly for the sister compound NaFeAs with the same 111 structure, the magnetism [26,27] and superconducting properties [28,29] (upon doping) are very similar to the 1111 (such as RFeAsO1−xFx [30,31]) and the 122 (such as Ba1−xKxFe2As2 and Ba(Fe1−xCo)x2As2 [32,33]) families. It is conjectured that the absence of AFM in LiFeAs is probably caused by lithium deficiency [10]. However, the lack of evidences for chemical non-stoichiometry, and the absence of Curie-Weiss-like low-temperature SDW spin fluctuations from NMR [32,34], different from the results in Ba(Fe1−xCo)x2As2 [38], do not seem to support this scenario.

Therefore the study of whether LiFeAs is a strongly correlated superconductor is certainly important for understanding the correlation among the band structure, the magnetism and the mechanism of superconductivity of the high T_c pnictides. In order to resolve this problem, we performed NMR studies on LiFeAs single crystals. We first searched for possible SDW order and SDW fluctuations in our high-quality single crystals. For the first time, we found evidences of anisotropic spin fluctuations, which can be tuned toward an SDW quantum critical point. We further show spectral evidence that the absence of antiferromagnetism in LiFeAs is likely caused by the doping and/or the scattering effect from an additional Li(2) site.

The single crystals of LiFeAs were grown by self-flux method with two different growth conditions. LiAs was firstly synthesized as precursor by reacting Li (3N) and As (5N) in Ta tube sealed in evacuated quartz ample and heated at 600 °C for 10 hours. Mixtures of LiAs and Fe (4N) powder with the composition of Li5FeAs5 were sealed into Ta tubes under 1.5 atmosphere of argon gas, then the Ta tubes were vacuum sealed into quartz tubes. For the sample 1 (S1), the ample was heated to 1050 °C, held for 24 hours and cooled slowly to 650 °C over 200 hours, then the furnace is shut down and naturally cooled down to room temperature. The sample 2 (S2) was obtained by heating the ample to 1170 °C, held...
The relaxation rate is deduced from an inversion-recovery NMR studies were performed with the magnetic field along the NMR crystals were chosen with typical dimension of 3×2×0.1 mm³. Both ⁷Li (S = 3/2) and ⁷⁵As (S = 3/2) NMR studies were performed with the magnetic field along the ab-plane and the c-axis. All spectral measurements use the spin-echo technique. The spin-lattice relaxation rate is deduced from an inversion-recovery method, and the spin magnetization is fit with the S = 3/2 nuclear recovery $m(t)/m(0) = 1 - 0.1e^{-t/T_1} - 0.9e^{-6t/T_1}$ for both ⁷Li and ⁷⁵As.

We first study the spin fluctuations through the spin-lattice relaxation rate $1/T_1$ of ⁷⁵As in LiFeAs. In Fig. 2 (a), the $1/^{75}T_1^{T_1}T$ of the superconducting crystal S1 ($T_c ≈ 17$ K) is shown with an 8 T magnetic field along the ab-plane. The Superconducting onset is shown by a sharp drop of the $1/^{75}T_1T$ below $T_c$. There is a small upturn while temperature decrease from 50 K down to $T_c$, which indicate spin fluctuations. Following Moriya’s 2D spin fluctuation theory in a paramagnet, we fit the data with a Curie-Weiss behavior $1/T_1T = A/(T + Θ) + b$ at low temperatures (see Fig. 2 (a)). Here A is proportional to the electron density of state (DOS) on the Fermi surface, and the value of Θ is correlated with band mass $m^*$, whose sign usually switches from negative to positive if the system is tuned from an antiferromagnetic ground state to a quantum disordered paramagnet. The b term is obtained phenomenologically, assuming a Korringa (Fermi liquid) contribution from the multiple band system. Our fitting parameter Θ = 30 ± 5 K is comparable with the optimal-doped Ba(Fe₁₋ₓCoₓ)₂As₂, indicating a similar strength of spin fluctuations with other iron pnictide superconductors.

To check the sample dependence of spin fluctuations, we investigated the spin-lattice relaxation of sample S2 with a less superconducting volume and a lower $T_c$. The spin-lattice relaxation rate (SLRR) of the crystal S2 is measured with field applied both along the ab-plane ($1/^{75}T_1^{ab}T$) and along the c-axis ($1/^{75}T_1^{c}T$) (see Fig. 2 (b)). Comparing with S1, the low-temperature $1/^{75}T_1^{ab}T$ of S2 are very different. The $1/^{75}T_1^{ab}T$ increase dramatically as temperature drops under a 12 T magnetic field with Θ ≈ 10 ± 5 K, which is close to a diverging behavior (i.e., Θ ≤ 0 K) at finite temperatures. Such behavior is a clear indication that the system is close to a magnetic ordering.

Next we discuss the nature of the low-temperature spin fluctuations. As shown in Fig. 2 the Curie-Weiss behavior is also seen in $1/^{75}T_1^{c}T$ (Θ ≈ 20 ± 5 K), but much weaker than that of the $1/^{75}T_1^{ab}T$. The anisotropy of the spin-lattice relaxation rate, defined as $T_1^{c}/T_1^{ab}$, increases as temperature drops, which is well described as signatures of the stripe AFM (or the SDW) correlations.
The Knight shift of Li(2) with field along the ab-plane is estimated with a concentration of $\pm 0.1\%$, much larger than that of Li(1). Li(2) is also found with field along the c-plane, and Knight shift is estimated as $7K_n^{ab} \sim -0.05\%$. Early x-ray studies on LiFeAs suggest an interstitial Li site located above the Fe site and enclosed in an As$_4$ tetrahedron. Since Li has a small quadrupole moment, the quadrupole correction to the center frequency of Li(2) is probably negligible.

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The Li(2) spectra shift to higher frequency and broaden right below $T_c$, which indicates that Li(2) is intrinsic in a superconducting state. We are not able to find the satellite of Li(2) and assign the lattice position of Li(2) directly, possibly because the satellite intensity of Li(2) is too low. According to the spectrum and the spin-lattice relaxation measurements, it is natural to conclude that the Li(2) comes from an interstitial site in the lattice (see Fig. 1 (a)), which is located just above the Fe site and enclosed in an As$_4$ tetrahedron. Since Li has a very small quadrupole moment, the quadrupole correction to the center frequency of Li(2) is probably negligible. The Knight shift of Li(2) with field along the ab-plane is estimated with $7K_n^{ab} \sim -0.1\%$, much larger than that of Li(1). Li(2) is also found with field along the c-plane, and Knight shift is estimated as $7K_n^{ab} \sim -0.05\%$. Early x-ray studies on LiFeAs suggest an interstitial Li site located above the Fe site and enclosed in an As$_4$ tetrahedron.

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sibilities. If the actual concentration of Li(2) is higher in S1, a larger electron-doping effect is expected to suppress the SDW and induces the superconductivity, which is seen in S1. On the other hand, if the actual concentration of Li(2) is higher in S2, additional doping effect such as Li(1) deficiency, may exist to cancel the Li(2) effect. Then a higher concentration of Li(2) in S2 result in the low \(T_c\) and bring the system back toward the SDW ordering \(^{12}\). In fact, lithium-deficiency on Li(1) has been speculated to coexist with Li(2) doping \(^{10, 22, 41}\). Besides, disorder could also play an essential role here. Since S2 is made with a fast growth condition, disorder scattering may suppress the superconductivity and favor the competing SDW ordering. Finally, we should also point out that although Li(2) is coupled to superconductivity, we cannot completely rule out the possibility that the Li(2) is from a minor superconducting phase. More work is needed to verify the position and the role of Li(2) proposed in LiFeAs.

To summarize, we found two independent evidences for strong-correlated superconductivity in LiFeAs. First, evidence of strong spin fluctuations is found in the normal state right above \(T_c\), which increase as temperature drops. Such effect supports that superconductivity is probably mediated by spin fluctuations. In particular, a suppression of \(T_c\) with different growth conditions leads to a significant enhancement of anisotropic spin fluctuations toward an SDW quantum critical point. Second, our data shows a Li(2) signal with a concentration of (6 ± 2)/% in superconducting LiFeAs, and the absence of the long range AFM in LiFeAs could be caused by a doping effect. Combining both evidences, our data unifies LiFeAs with the 1111 and the 122 iron pnictides with the same magnetic origin and the same mechanism of superconductivity. We believe that our results are important to understand the mechanism of superconductivity and underline further the importance of magnetic fluctuations for the superconductivity pairing observed in iron-based superconductors.

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