31P NMR investigation of the superconductor LiFeP ($T_c = 5K$)

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Abstract – We investigate the static and dynamic spin susceptibility of the “111”-type Fe-based superconductor LiFeP with $T_c \sim 5K$ through the measurement of the Knight shift. 31P and the spin-lattice relaxation rate $\frac{1}{T_1}$ at the 31P site by nuclear magnetic resonance. The constant $31K$, small magnitudes of $\frac{1}{T_1}$, along with the resistivity $\rho \sim T^2$ all point to the weak spin correlations in LiFeP. 31P $\frac{1}{T_1}$ display small enhancement toward $T_c$, indicating that the superconductivity is intimately correlated with the antiferromagnetic spin fluctuations.

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Introduction. – The discovery of superconductivity with $T_c = 26K$ in the layered structure La(O$_{1-x}$F$_x$)FeAs ($x = 0.05 \sim 0.12$) [1] has generated great interest in the research of Fe-based high-temperature superconductors. Over the past six years, hundreds of Fe-based superconductors have been reported and the list has expanded rapidly from the original LaFeAsO “1111” structure [1,2] to the MFe$_2$As$_2$ (M stands for alkali earth metal) “122” family [3], the MFeAs (M stands for alkali metal) “111” family [4], the iron chalcogenide FeSe “11” family [5], the “42622” family [6] and the “32522” family [7] etc. Despite the different crystalline structures, accumulating experimental and theoretical results have pointed to the unconventional superconducting pair symmetry of these Fe-based superconductors, and the common physical properties they share [8,9].

LiFeP is one of the prototypical superconductor in the “111” family, which was found to become superconducting below $T_c \sim 6K$ [10]. In addition to the much lower $T_c$, LiFeP has some properties different from other “111”-type superconductors LiFeAs [11] and NaFeAs [12]. For example, the measurements of the magnetic penetration depth $\lambda$ have indicated a nodal superconducting order parameter for LiFeP [13], different from the fully gapped state observed for LiFeAs [13]. Furthermore, no magnetic or structural transition has been observed in LiFeP and LiFeAs, but a structural transition at $T_s = 57K$ [14] and a SDW magnetic transition at $T_{SDW} = 45K$ [15] have been observed in NaFeAs. On the other hand, it has been shown in LiFeAs by NMR (nuclear magnetic resonance) that the antiferromagnetic spin fluctuations are strongly enhanced toward $T_c$ [16]. The feature of antiferromagnetic spin fluctuations enhancement toward $T_c$ has been observed in other Fe-based families [17–21], which provides convincing experimental evidences that the superconductivity is intimately correlated to the antiferromagnetic spin fluctuations. To the best of our knowledge, no NMR investigations of LiFeP have been reported. It will be interesting to investigate the spin dynamics and examine if such feature exists in the superconducting LiFeP.

In this paper, we conduct a NMR measurement on a polycrystalline sample in the paramagnetic state. We measure the static susceptibility and the spin dynamics through the Knight shift and $\frac{1}{T_1}$ measurements at the $31P$ site, respectively. We find that the static susceptibility is temperature independent throughout the measured temperature range of 4.2K and 280K. While the magnitude of antiferromagnetic fluctuations is almost an order of magnitude smaller than those of LiFeAs [16], a weak enhancement toward $T_c$ is observed. This indicates that the superconductivity is intimately correlated with the antiferromagnetic spin fluctuations despite the lower $T_c$ of LiFeP.

Experiments. – The LiFeP polycrystalline specimens were synthesized by the solid-state reaction method. The pallets of mixed high-purity Fe (99.9%) and P (99%) powders (Alfa Aesar) were sealed in an evacuated quartz tube and heated to 800°C for 10 hours to prepare the intermediate product FeP. FeP were then mixed with Li ingots (Alfa Aesar, 99.9%) with nominal concentration and heated to 800°C for 30 h. The specimens were then cooled down to...
room temperature with the furnace shutting off. The handling of materials were performed in a high-purity argon-filled glove box (the percentage of O2 and H2O \( \leq 0.1 \) ppm), to protect it from exposing to air. The color of the sample was shiny black, indicating the good crystallization.

The polycrystals were characterized by the X-ray powder diffraction and the dc magnetization with a Quantum Design superconducting quantum interference device (SQUID). The temperature dependence of electrical resistivity was measured on a thin bar-shaped sample (3.78 mm \( \times \) 1.02 mm \( \times \) 1.08 mm) in a Cryogenic Mini-CFM system by a standard four-probe method. We conducted the \( ^{31} \)P NMR measurements by using the standard pulsed NMR techniques. We obtained the NMR spin echo signal by applying 90°-180° pulses in a fixed external field of \( B_{\text{ext}} \) \( = 4.65 \) tesla.

**Results and discussion.** In fig. 1, we show the powder X-ray diffraction pattern of LiFeP polycrystal. The diffraction peaks can be well indexed into a \( Cu_2Sb \)-type tetragonal structure with \( P4/nmm \) symmetry [10], which is the same as the other two “111”-type iron-based superconductor LiFeAs [11] and NaFeAs [12]. A careful inspection indicates that a small amount of Fe2P exists at \( 2\theta = 40.28^\circ \). Fe2P is a ferromagnetic material with Curie temperature higher than 200 K [22]. This small amount of impurity will not affect our NMR measurements of the intrinsic properties of LiFeP since NMR is a local and site-selective microscopic probe and we conducted NMR measurements at the \( ^{31} \)P site of LiFeP. The lattice constants are \( a = 3.6938 \) Å and \( c = 6.0446 \) Å, which are consistent with the previous reported values [10]. Compared to the values of \( a = 3.9494 \) Å and \( c = 7.0396 \) Å for NaFeAs [12], and \( a = 3.77 \) Å and \( c = 6.36 \) Å for LiFeAs [11], both the \( ab \)-plane and the \( c \)-axis of LiFeP shrink to some extent. The smaller lattice constants of LiFeP have been attributed to the much smaller atomic size of Li and P atoms than that of Na and As. In the inset of fig. 1, we show the dc magnetic susceptibility of the LiFeP sample measured in both the ZFC and the FC condition with an applied field of 20 Oe. The diamagnetic signals confirm that the superconductivity takes place at \( \sim 5 \) K. The superconducting volume fraction reaches 100% for the ZFC mode at 2 K after the correction of the demagnetizing factors. The bulk superconductivity has also been confirmed through the observation of an abrupt change of the conduction frequency in a NMR coil.

In fig. 2, we show the temperature dependence of the electrical resistivity of LiFeP. The resistivity data indicates a sharp superconducting transition temperature at \( \sim 5 \) K. The residual resistivity in our specimen is 5.7 \( \mu \Omega \cdot \) cm, which is smaller than the value of previous reports [10,23], indicating the good quality of our polycrystalline specimen. We plot the resistivity vs. \( T^2 \) in the temperature range between 5 K and 40 K, and a linear dependence has been observed. We do not observe anomalies corresponding to the SDW transition or the structural transition that have been observed in the NaFeAs superconductor [12,14,15]. This situation is similar to the case of LiFeAs [11] where no anomalies have been observed in the curves of both electrical resistivity and magnetic susceptibility.

We carried out the \( ^{31} \)P NMR lineshapes measurements under the field \( B_{\text{ext}} \) \( = 4.65 \) tesla. This field is much higher than the second critical field \( \sim 2 \) tesla of LiFeP [24,25], and therefore it is in the paramagnetic state. \( ^{31} \)P has a nuclear spin \( I = \frac{1}{2} \) with a gyromagnetic ratio of \( ^{31} \gamma_n/2\pi = 17.235 \) MHz/tesla. We will observe a single resonance frequency for each individual \( ^{31} \)P site since there is no nuclear quadrupole interaction. In fig. 3, we display the

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Fig. 1: (Color online) Powder X-ray diffraction pattern of LiFeP. The star marks the small amount of Fe2P impurity. The inset displays the dc susceptibility of the LiFeP sample in both the ZFC and the FC mode, and the diamagnetic signals indicate that \( T_c \sim 5 \) K.

Fig. 2: (Color online) Temperature-dependent electrical resistivity for the LiFeP polycrystalline sample, showing the superconducting transition at \( \sim 5 \) K. The inset shows the expanded \( \rho(T^2) \) data, suggesting a linear behavior at low temperature. The black solid line is a fitting line with the function \( \rho = \rho_0 + A T^2 \) with \( \rho_0 = 0.0057 \) mΩ · cm and \( A = 4.5 \times 10^{-6} \) mΩ · cm/K².
temperature dependence of $^{31}\text{P}$ lineshapes for LiFeP from 280 K to the base temperature of 4.2 K. Only one resonance frequency is observed at $f \sim 80.143$ MHz. The Knight shift $K$ for each temperature by using the formula $^{31}\text{K} = (f - f_0)/f_0 \times 100\%$, where $f$ is the peak frequency of the lineshape. The temperature dependence of $^{31}\text{K}$ is plotted in fig. 5(a). $^{31}\text{K}$ of LiFeP is only $\sim 0.03\%$, which is much smaller than $^{75}\text{K} \sim 0.18\%$ at $^{75}\text{As}$ of LiFeAs [26,27] and NaFeAs [28]. More interestingly, $^{31}\text{K}$ hardly changes in the measured temperature range. This situation is different from the case of $^{75}\text{K}$ of LiFeAs, where $^{75}\text{K}$ smoothly decreases with the decreasing temperature [26,27].

To obtain the insight of the spin dynamics, we measure the spin-lattice relaxation rate $1/T_1$ at the peak frequency of $^{31}\text{P}$ NMR lines. $T_1$ represents the time scale during which the nuclear spins return to its thermal equilibrium after the absorption of the inverted radio-frequency pulse. The recovery of the nuclear magnetization after the inversion pulse, $M(t)$, was fitted to a stretched exponential equation, $M(t) = M_0[1 - A \exp[-(t/T_1)^\alpha]]$, where $M_0, A, T_1$ and $\alpha$ are the free parameters. We show typical nuclear spin recovery curves of the LiFeP sample for the $^{31}\text{P}$ site in fig. 4. The exponent $\alpha$ varies smoothly from $\sim 1.0$ at 280 K to $\sim 0.9$ at 4.2 K. Theoretically, the spin contribution to $1/T_1$ may be written using the imaginary part of the dynamical electron spin susceptibility $\chi''(q, f)$ as [29]

$$\frac{1}{T_1} = \frac{2\gamma_n^2 k_B T}{g^2 \mu_B^2} \sum_q |A(q)|^2 \chi''(q, f),$$

(1)

where $A(q)$ is the hyperfine form factor [29] and $f$ the measured frequency. $T_1$ can be as long as $\sim 250$ seconds for nonmagnetic insulators such as the direct gap semiconductor LiZnP, and become five orders shorter to $\sim 2.5$ milliseconds when strong magnetic fluctuations exist [30].

We show the T-dependence of the spin-lattice relaxation rate $1/T_1$ divided by $T$, $1/T_1/T$ in fig. 5(b). We note that the results of $1/T_1/T$ hardly change even if we fix the exponent $\alpha$ equal to 1.0 throughout the entire temperature range. The value of $1/T_1$ at the $^{31}\text{P}$ site of LiFeP is $\sim 0.065 \pm 1\%$, which is almost an order smaller than $\sim 0.45 \pm 1\%$ at $^{75}\text{As}$ sites of LiFeAs [16,26,27,31], implying much weaker spin fluctuations in the LiFeP system. This result also indicates that the electron correlation is much weaker in LiFeP than in LiFeAs, and is consistent with a more significant mass enhancement in LiFeP than in LiFeAs observed in high-field quantum oscillations [32]. In addition, we find that $1/T_1/T$ display a slight enhancement toward low temperature. This feature is qualitatively similar to the case of

Fig. 3: $^{31}\text{P}$ lineshapes of LiFeP measured over a wide temperature range from 4.2 K to 280 K under a field of 4.65 Tesla. The dashed line marks the position of $^{31}\text{K} = 0$. 

Fig. 4: (Color online) Typical nuclear spin recovery curves $M(t)$ after an inversion pulse for $^{31}\text{P}$. The solid curves represent appropriate fits to determine $T_1$ with the stretched exponential time dependence.
LiFeAs [16], indicating that antiferromagnetic spin fluctuations do exist in LiFeP although they are weaker.

We can also use the Korringa relation, $T_1TK^2 = \frac{h}{4\pi k_B} \frac{\gamma_e^2}{\gamma_n} \beta$, to evaluate quantitatively the strength of the electron correlations. Here, $\gamma_e$ and $\gamma_n$ are the electron and nuclear gyromagnetic ratios, respectively. $K_s$ is the spin susceptibility extracted from the Knight shift data in fig. 5(a). The Korringa factor $\beta$ reflects the magnitude of spin correlations [33]. Usually $\beta$ is equal to 1 for a noninteracting system, and strong ferromagnetic correlations give $\beta \gg 1$, while strong antiferromagnetic correlations give $\beta \ll 1$. We show the calculated $\beta$ in fig. 5(c). The values of $\beta$ in the whole measured temperature range are smaller than 1, indicating the existence of the antiferromagnetic fluctuations in LiFeP. $\beta$ is close to 1, which is much larger than $\beta \sim 0.2-0.5$ in LiFeAs [27,31], again indicating the weaker spin correlations in LiFeP.

A close inspection of the $\frac{1}{T_1TK}$ curve indicates that a small hump appears at $T \sim 20$ K, suggesting that some magnetic instabilities exist around this temperature. Currently we do not know the origin of this magnetic instability since no anomalies have been detected around this temperature in both dc magnetic susceptibilities and the electrical resistivity. A brave assumption is that this hump is related to the SDW magnetic transition which has not been observed in LiFeP and LiFeAs. A possible scenario is that Li concentrations affects the ground state of Li$_{1-\delta}$FeP, and a precise control of Li concentration may unveil this mystery.

**Summary and conclusion.** – In summary, we investigated the static and dynamic spin susceptibility of the superconducting LiFeP in the paramagnetic state by a NMR measurement at the $^{31}$P site. Through the measurement of electrical resistivity, Knight shift and $\frac{1}{T_1TK}$, we found that $\rho \sim T^2$, $^{31}$K $\sim$ constant and the Korringa ratio $\beta \sim 0.8$, which all point to the weak spin correlations in LiFeP. Our results indicate that the antiferromagnetic spin fluctuations are slightly enhanced toward $T_c$, although their magnitudes are much weaker than those of LiFeAs. This, on the one hand, indicates that antiferromagnetic fluctuations are important for the superconductivity in LiFeP, and on the other hand, may explain the much lower $T_c$ of LiFeP than that of LiFeAs. We also detected a magnetic instability around $\sim 20$ K, which may be related to the different ground states arising from Li off-stoichiometry. We are applying an electrochemical method to precisely control the amount of Li concentration in LiFeP and LiFeAs to elucidate their mysterious ground states.

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