As and $^{139}$La NMR/NQR investigations of iron-based superconductor LaFeAs(O$_{0.89}$F$_{0.11}$)

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Abstract. We report $^{75}$As and $^{139}$La NMR/NQR results in LaFeAs(O$_{0.89}$F$_{0.11}$). In the normal state, $1/T_1$ decreases with lowered temperature, which is reminiscent of the pseudogap behavior in the high-$T_c$ cuprates. In the superconducting (SC) state, $1/T_1$ decreases suddenly below $T_c$ without a Hebel-Slichter coherence peak, followed by a $T^3$ dependence, which is characteristics of unconventional superconductors with lines of nodes. However, the residual density of states in the low temperatures, which is usually observed in unconventional superconductors with crystal imperfections and/or impurity phases, was not observed. Knight shift measurements show that spin susceptibility decreases in the SC state.

1. Introduction
The recent discovery of iron-based superconductor LaFeAs(O$_{1-x}$F$_x$) with $T_c$ up to 43 K under pressure has renewed the record of $T_c$ among non-cuprate superconductors [1, 2]. One of the notable features is the highly two-dimensional (2D) crystal structure. Fe atoms form a 2D square lattice, and the cylindrical Fermi surfaces deriving from Fe-3$d$ orbitals are reported [3]. Besides, superconductivity occurs when carriers are doped into the parent compound LaFeAsO that undergoes a SDW transition at $T_N \sim 140$ K accompanied with a structural phase transition at $\sim 160$ K [4, 5, 6, 7]. These results imply interplay between magnetism and superconductivity in LaFeAs(O$_{1-x}$F$_x$). In order to reveal magnetic fluctuations in the normal state and the SC properties in LaFeAs(O$_{0.89}$F$_{0.11}$), we performed $^{75}$As and $^{139}$La NMR/NQR experiments.

2. Experimental
Polycrystalline samples of LaFeAs(O$_{0.89}$F$_{0.11}$) synthesized by solid-state reactions [1] are ground into powder for NMR/NQR measurements. The crystal structure, phase purity, and lattice constants of the sample were examined by powder X-ray diffraction [1]. Electrical resistivity measurements via a conventional four-probe method show that resistivity $\rho$ follows $\rho_0 + AT^2$ below 200 K down to $T_c$, which yields a large residual resistivity ratio $RRR=\rho(300 \text{ K})/\rho_0 \simeq 22.5$ with $\rho_0 \equiv \rho(T \rightarrow 0) = 0.153 \text{ m}\Omega\text{cm}$ (Fig. 1). $T_c$ determined from the zero-resistivity temperature is 22.5 K in zero magnetic field. This value of $T_c$ is in good agreement with
AC susceptibility measurements using an in situ NMR coil at \( \sim 12 \) MHz. A standard spin-echo technique was used for NMR/NQR measurements. The nuclear spin-lattice relaxation rate \( 1/T_1 \) was measured using a saturation recovery method. The recoveries of the nuclear magnetization \( M(t) \) of \( ^{75}\text{As} \) (\( I = 3/2 \)) and \( ^{139}\text{La} \) (\( I = 7/2 \)) after a saturation pulse were fitted with \( m(t) = (M(\infty) - M(t))/M(\infty) = 0.1e^{-t/(T_1)} + 0.9e^{-6t/(T_1)} \) and \( m(t) = 0.0119e^{-t/(T_1)} + 0.0682e^{-6t/(T_1)} + 0.2061e^{-15t/(T_1)} + 0.7137e^{-28t/(T_1)} \) respectively, which were measured at the intense peak of the central transition. For Knight shift measurements, the powder sample was mixed with epoxy (Stycast 1266), and then was aligned in a magnetic field of 5.5 T to obtain a narrow NMR linewidth as described in Ref. 8 [8].

3. Results and Discussions
Figure 2 shows \(^{75}\text{As}\) and \(^{139}\text{La}\) NMR spectra of the powder sample at 30 K obtained by sweeping magnetic field at 72.1 MHz. Note that this powder sample mostly aligned along the \( ab \)-plane, which was inferred from the NMR line shape of the aligned sample. From a splitting between the 1st satellites of the \(^{75}\text{As}\) NMR spectrum, we deduced the NQR frequency to be about 11 MHz, which is in good agreement with the previous report [8]. The \(^{75}\text{As}\) NQR signal arising from the \( \pm 1/2 \leftrightarrow \pm 3/2 \) transitions was observed at 11.2 MHz in zero magnetic field.

![Figure 1](image1.png)

**Figure 1.** Resistivity in zero magnetic field. Inset: \( T_c \) (22.5 K) was determined at the zero-resistivity temperature.

![Figure 2](image2.png)

**Figure 2.** Field-sweep \(^{75}\text{As}\) and \(^{139}\text{La}\) NMR spectra at 30 K at 72.1 MHz.

Figure 3 shows \( T \)-dependence of \( 1/T_1T \) of \(^{75}\text{As}\) in 9.82 T and \(^{139}\text{La}\) in 2.55 T. \( 1/T_1T \) of both of \(^{75}\text{As}\) and \(^{139}\text{La}\) decreases with lowered temperature, which is reminiscent of the pseudogap behavior in the underdoped regime of high-\( T_c \) cuprates [9, 10], and approaches a nearly constant value in a narrow \( T \)-region just above \( T_c \). The dashed line in Fig. 3 is a fit to \( \frac{1}{T_1T} = A + B \exp(-\Delta_{PG}/T) \) where \( A = 0.04 \) (sK)\(^{-1} \), \( B = 0.17 \pm 0.01 \) (sK)\(^{-1} \), and \( \Delta_{PG} = 172 \pm 17 \) K for \( 1/T_1T \) of \(^{75}\text{As}\). We point out a difference between the pseudogap behavior of LaFeAs(\( O_{0.89}F_{0.11} \)) and the underdoped cuprate. In the cuprate, \( 1/T_1T \) decreases from temperatures far above \( T_c \) and no clear anomaly is observed at \( T_c \). In contrast, in LaFeAs(\( O_{0.89}F_{0.11} \)), the Korringa behavior \((T_1T = \text{const.})\) is observed in the narrow \( T \)-region from 30 K to \( T_c \), which is related to the \( T^2 \) behavior of the resistivity, and a clear anomaly of \( 1/T_1T \) is observed at \( T_c \).

We now turn to \( 1/T_1 \) in the SC state. Fig. 4 shows \( T \)-dependence of \( 1/T_1 \) of \(^{75}\text{As}\) in 9.82 T. \( 1/T_1 \) decreases suddenly below \( T_c(H)(\sim 20 \) K) and exhibits a \( T^3 \) dependence down to the
The spin symmetry of the Cooper pair is inferred from Knight shift measurements in the SC state. The observed $T^3$ dependence of $1/T_1$ can be accounted for using a 2-D line-node ($\Delta(\phi) = \Delta_0 \sin(2\phi)$) model with $2\Delta/k_BT_c = 4$. The absence of a Hebel-Slichter coherence peak just below $T_c$ and the $T^3$ dependence of $1/T_1$ are similar with high-$T_c$ cuprates and heavy fermion superconductors, suggesting unconventional superconductivity in LaFeAs(O$_{0.89}$F$_{0.11}$). However, we point out that a residual density of states (DOS), which is usually inferred from the $1/T_1 \propto T$ behavior at the lowest temperatures, is not observed in LaFeAs(O$_{0.89}$F$_{0.11}$). In unconventional superconductors with line-node SC gap, $1/T_1$ follows a $T^3$ dependence below $T_c$, then turns into linear $T$ behavior at the lowest temperatures due to the residual DOS originating from lattice imperfections and/or impurities. The absence of the residual DOS appears to be contrary to the existence of line-nodes, but be favor for the extended $s$-wave scenario in which the SC gap vanishes along lines without sign change of the SC gap function. Further NMR measurements using high quality samples and impurity-doped samples are important in order to fully determine the SC gap function.

The spin symmetry of the Cooper pair is inferred from Knight shift measurements in the SC state. Fig. 5 shows the $^{75}$As NMR spectra of the aligned sample obtained by sweeping external field at a fixed frequency of 40.5 MHz. The spectral peak (corresponding to the magnetic field along the $ab$-plane direction) shifts toward higher fields with lowered temperature, indicating a decrease of the Knight shift in the SC state (see the inset). By measuring a splitting between the 1st satellites of $^{75}$As NMR spectrum at a series of different temperatures, we found that electric quadrupole interaction is $T$-independent in this temperature range. We also found that the entire shift cannot be ascribed to a SC diamagnetic effect, which was investigated from measuring $^{139}$La NMR spectrum. Therefore, the shift originates from the decrease of the spin susceptibility in the SC state, which is consistent with previous reports [8, 11, 12]. Detailed analysis of the Knight shift will be published elsewhere.

4. Conclusion
From $^{75}$As and $^{139}$La NMR/NQR measurements in LaFeAs(O$_{0.89}$F$_{0.11}$), we observed pseudogap behavior in $1/T_1T$ both at the $^{75}$As and $^{139}$La sites, , which is reminiscent of the high-$T_c$ cuprates. In the SC state, $1/T_1$ decreases suddenly below $T_c$ without a Hebel-Slichter coherence.
As NMR spectra of the central line of the aligned powder corresponding to the magnetic field along the $ab$-plane obtained by sweeping external field at 40.5 MHz.

peak followed by a $T^3$ dependence, suggesting that LaFeAs(O$_{0.89}$F$_{0.11}$) is an unconventional superconductor in which the SC gap vanishes along lines or possesses line-nodes in the SC gap. Knight shift measurements show that spin susceptibility decreases in the SC state. However, the absence of residual DOS at low $T$ is different from other unconventional superconductors with lines of nodes, further NMR studies using high-quality sample and impurity-doped sample are needed to identify the SC gap function.

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