\( T_c \) enhancement under pressure in the La1111 pnictide
LaFeAsO\(_{1-x}\)H\(_x\) (\( x=0.2 \)) studied by NMR

N. Fujiwara*, N. Kawaguchi, S. Iimura\(^1\), S. Matsuishi\(^1\), and H. Hosono\(^1\)

\(^1\)Graduate School of Human & Environmental Studies, Kyoto University, Kyoto, Kyoto 606-8501, Japan
\(^2\)Material and Structures Laboratory (MSL) & Frontier Research Center (FRC), Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama 226-8503, Japan

*naoki@fujiwara.h.kyoto-u.ac.jp

Abstract. Nuclear magnetic resonance (NMR) measurements under a pressure of 3.0 GPa were performed for a prototypical iron-based high-\( T_c \) superconductor LaFeAsO\(_{1-x}\)H\(_x\) (\( x=0.2 \)). At ambient pressure, this compound has superconducting (SC) double domes with the \( T_c \) minimum of 26 K at \( x=0.2 \) in the electronic phase diagram. Pressure application merges the double domes into a single dome, and the \( T_c \) minimum at \( x=0.2 \) goes up to 45 K, the \( T_c \) maximum, at 3.0 GPa. Despite that \( T_c \) enhancement under pressure was confirmed from the \(^{75}\)As relaxation rate divided by temperature (1/\( T_1T \)) around \( T_c \), 1/\( T_1T \) at high temperatures was almost the same with that at ambient pressure and hardly showed Curie-Weiss behaviour. These features are also seen for 14% F-doped LaFeAsO\(_{1-x}\)F\(_x\), suggesting that spin fluctuations are not essential to achieve high \( T_c \) over 45 K.

1. Introduction

The R1111 series such as RFeAsO\(_{1-x}\)F\(_x\) or RFeAsO\(_{1-x}\)H\(_x\) (R=La, Ce, Ne, Pr, Sm) is very unique among iron-based high-\( T_c \) superconductors in the points that high \( T_c \) over 50 K has been marked only in this series and only this series can accept high electron doping due to H substitution. Owing to the capability of electron doping, the H-doped La1111 series undergoes novel phenomena in the electronic phase diagram: (i) H doping leads to superconducting (SC) phase with double domes following a stripe-type antiferromagnetic (AF) phase [1], and (ii) further H doping leads to spatially inhomogeneous AF ordering following double SC domes [2-4]. Pressure application merges the SC double domes to a single dome: at 20% H-doping level, \( T_c \) marks the minimum of 26 K at ambient pressure, and intriguingly the minimum turns to the maximum of 45 K at 3.0 GPa [1, 5]. This specific situation allows one to investigate the high \( T_c \) mechanism in iron-based superconductors.

To investigate what causes the \( T_c \) maximum on a microscopic level, we performed \(^{75}\)As nuclear magnetic resonance (NMR) measurements on the 20% H-doped La1111 samples at 3.0GPa and compared the results with those obtained at ambient pressure.

2. Experimental conditions

2.1. Pressure cell

Figure 1 shows an illustration of a piston-cylinder type NiCrAl pressure cell [6]. The length of the NiCrAl cylinder is 30.0 mm, and it’s inner and outer diameters are 6.0-, and 16.0-mm, respectively. A
CuBe sleeve with an outer diameter of 40.0 mm covers the NiCrAl cylinder, as shown in Fig. 1. A Teflon capsule of 6.0 mm outer diameter and 15.0 mm length and a CuBe sealing ring were attached on a CuBe plug, forming a liquid container. Powder samples packed in a sample holder was inserted in the liquid container. Ruby powders were attached on the top of an optical fiber, and they were also inserted in the liquid container. Pressure inside the sample cell was monitored by Ruby fluorescence measurements. The initial volume of the sample space was 4.4 mm diameter × 11.0 mm length. A mixture of fluorinate liquids, Fluorinert FC-70 and FC-77, was used as a pressure-mediation liquid. The pressure cell potentially reaches 4.6 GPa by applying a load of 16 ton, despite that the length of the sample space becomes extremely small.

Figure 1. Illustration of a piston-cylinder-type NiCrAl pressure cell.  

Figure 2. Shift of the resonance frequency of the tank circuit, which corresponds to the AC susceptibility measurements.

2.2. AC susceptibility and NMR measurements
NMR measurements were performed using a conventional coherent-pulsed NMR spectrometer. A NMR probe equipped with two variable capacitors was used for AC susceptibility measurements as well as NMR measurements. For the measurements under pressure, a single coil wounded around the sample holder and capacitors outside the pressure cell form a tank circuit. The AC susceptibility was measured via the resonance frequency of the tank circuit. The resonance frequency was monitored by using a network analyzer.

The resonance frequency shifts to high frequency region when the samples undergo a superconducting state owing to the large demagnetization. On the other hand, $T_c$ can be also determined from the relaxation rate divided by temperature ($T$), $1/T_1T$: a superconducting gap opens below $T_c$ and thus $1/T_1T$ decreases more rapidly than that in the normal state. The measurements of $T_1$ were performed for the signals of the central transition ($J=-1/2 \leftrightarrow 1/2$) of $^{75}$As ($J=3/2$). The NMR spectra broaden owing to the electric quadrupole interaction, and $T_1$ was measured for the powder samples with FeAs planes parallel to the applied field, as described below.

Despite that one can estimate $T_c$ from both measurements, the $T_c$ values may be not always coincide with each other: all powder samples are involved in the resonance frequency measurements, whereas only powder samples with FeAs planes parallel to the applied field are involved in the $1/T_1T$ measurements.
3. Experimental results

3.1. Resonance frequency

Figure 2 shows the shift of the resonant frequency. We define $\text{Shift} = f / f_0 - 1$, where $f$ is the resonance frequency and $f_0$ is the estimation extrapolated from the normal state. At ambient pressure, $T_c$ determined from the onset is about 22 K, and that determined from the extrapolation is about 18 K, as shown by a dashed line in Fig. 2. At 3.0 GPa, $T_c$ determined from the onset is about 48 K, and that determined from the extrapolation is about 40 K. The discrepancy of $T_c$ at 3.0 GPa is about 8 K and is larger than that estimated at ambient pressure. In fact, the resonance frequency at 3.0 GPa changes gradually with decreasing temperature. This could be caused since applied pressure becomes less hydrostatic at low temperature than at room temperatures.

![Figure 3](image1.png)

**Figure 3.** NMR spectra of $^{75}$As ($I=1/2$) and $^{139}$La ($I=7/2$) measured at 3.0 GPa at 35.1MHz.

![Figure 4](image2.png)

**Figure 4.** Temperature dependence of $1/T_1 T$ for $^{75}$As. The inset shows the expansion around $T_c$.

3.2. NMR spectra

Figure 3 shows the NMR spectra of $^{75}$As ($I=1/2$) and $^{139}$La ($I=7/2$) measured at 3.0 GPa at 35.1MHz. The $^{75}$As signals of the central transition ($I=-1/2 \leftrightarrow 1/2$) appear at 47-50 KOe as a double peak pattern due to large electric field gradient (EFG). All $^{139}$La signals appear around 58 KOe due to small EFG. The central peak and six satellite edges of $^{139}$La should be observable in pure samples, however, broad signals were observed instead of six edges due to the distribution of EFG at La sites. The distribution mainly originates from H doping. The NMR spectra were almost unchanged as shown in Fig. 3, implying that the EFG in FeAs planes is almost $T$ independent. The relaxation rate was measured at the lower-field peak as shown by an arrow in Fig. 3. Only the powders with FeAs planes parallel to the applied field are involved in this peak.
3.3. Relaxation rate

Figure 4 shows the $T$ dependence of $1/T_1 T$, which gives a measure of spin fluctuations. At both ambient pressure and 3.0 GPa, $1/T_1 T$ exhibits a plateau just above $T_c$ and increases monotonously with increasing temperature. One can determine $T_c$ as deviation from the plateau. By applying pressure, $T_c$ goes from 15 K at ambient pressure up to 48-50 K. These values are consistent with $T_c$ determined from the resonance frequency. The increase in $1/T_1 T$ at high temperatures is not attributable to spin fluctuations but to the increase in the density of states $N(\epsilon_F)$ involved in Fermi surface at high temperatures. In conventional metals where strong spin fluctuations are absent, $1/T_1 T$ is described by Korringa relation,

$$\frac{1}{T_1 T} \propto A_{hf}^2 N(\epsilon_F)^2 K(\alpha)$$

(1)

where $A_{hf}$ is the hyperfine coupling, and $K(\alpha)$ gives a measure of electron interactions. At high temperatures, $1/T_1 T$ at 3.0 GPa is almost the same as that at ambient pressure, implying that $A_{hf}$ and $K(\alpha)$ are unchanged by pressure application up to 3.0 GPa. In the present case, the $T$ dependence of $1/T_1 T$ at 3.0 GPa is attributed to that of $N(\epsilon_F)$; $N(\epsilon_F)$ is a constant just above $T_c$ and increases monotonously with increasing temperature. The similar features have also been observed for 14% F-doped LaFeAsO$_{1-x}$F$_x$, the maximally F-doped samples [7, 8]. In this case, $T_c$ rises from 20 K to 40 K by applying a pressure of 3.0 GPa. These facts give advantage for the superconducting mechanism via orbital fluctuations rather than the mechanism via spin fluctuations.

4. Conclusion

We performed NMR measurements on LaFeAsO$_{1-x}$H$_x$ ($x$=0.2) at 3.0 GPa. Pressure application raises $T_c$ from 15 K at ambient pressure to 48 K without observable enhancement of AF fluctuations. The effect of high $T_c$ is observable in $1/T_1 T$ as enhancement of $N(\epsilon_F)$. These facts give advantage for the superconducting mechanism via orbital fluctuations rather than the mechanism via spin fluctuations.

References

[1] Iimura S, Matsuishi S, Sato H, Hanna T, Muraba Y, Kim SW, Kim JE, Takata M, and Hosono H, 2012 Nat. Commun. 3 943
[2] Fujiwara N, Tsutsumi S, Iimura S, Matsuishi S, Hosono H, Yamakawa Y, and Kontani H, 2013 Phys. Rev. Lett. 111 097002
[3] Sakurai R, Fujiwara N, Kawaguchi N, Y. Yamakawa, Kontani H, Iimura S, Matsuishi S, Hosono H, 2015 Phys. Rev. B 91 064509
[4] Yamakawa Y, Onari S, Kontani H, Fujiwara N, Iimura S, Hosono H, 2013 Phys. Rev. B 88 041106(R)
[5] Takahashi H, Soeda H, Nukii M, Kawashima C, Nakanishi T, Limura S, Muraba Y, Matsuishi S, and Hosono H, 2015 Sci. Rpt. 5 7829
[6] Fujiwara N, Matsumoto T, Koyama-Nakazawa K, Hisada A and Uwatoko Y, 2007 Rev. Sci. Instrum. 78 073905
[7] Nakano T, Fujiwara N, Tatsumi K, Okada H, Takahashi H, Kamihara Y, Hirano M, and Hosono H, 2010 Phys. Rev. B 81 100510(R)
[8] Tatsumi K, Fujiwara N, Okada H, Takahashi H, Kamihara Y, Hirano M, and Hosono H, 2009 J. Phys. Soc. Jpn. 78 023709