As-NMR Study of the Iron Pnictide $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ under High Pressure

T. Yamazaki$^{a}$, N. Takeshita$^{b,c}$, K. Kondo$^{a}$, R. Kobayashi$^{a}$, Y. Yamada$^{a}$, H. Fukazawa$^{a,c,*}$, Y. Kohori$^{a,c}$, P. M. Shirage$^{b}$, K. Kihou$^{b}$, H. Kito$^{b,c}$, H. Eisaki$^{b,c}$, A. Iyo$^{b,c}$

$^a$Department of Physics, Chiba University, Chiba 263-8522, Japan
$^b$National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8562, Japan
$^c$JST, TRIP, Chiyoda-ku, Tokyo 102-0075, Japan

E-mail: hideto@nmr.s.chiba-u.ac.jp

Abstract. We performed resistivity and zero-external-field (ZF) $^{75}\text{As}$ nuclear magnetic resonance (NMR) measurements of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x = 0$ and 0.4) under high pressure. ZF $^{75}\text{As}$ NMR measurements revealed that the magnetic ordered state is robust against pressure. On the other hand, superconducting transition temperature $T_c$ has a tendency to decrease monotonically under pressure. The spin-lattice relaxation rate $1/T_1$ in antiferromagnetic and superconducting states suggests that the coexistence of the both states is not microscopic but is phase separated.

1. Introduction
The discovery of superconductivity in F-doped LaFeAsO with a superconducting transition temperature $T_c = 26$ K [1] has accelerated worldwide investigations of related superconductors [2, 3, 4, 5, 6, 7, 8, 9]. The 3d electrons originating from an FeAs layer form multiple bands at the Fermi level and play an important role in superconductivity in these materials [10, 11]. The common feature of these compounds is the possession of a FeAs layer which is analogous to the CuO$_2$ plane in high-superconducting-transition-temperature (high-$T_c$) cuprates. In addition, nondoped materials commonly exhibit an antiferromagnetic (AF) order with adjacent structural phase transition, which also resembles the parent materials of high-$T_c$ cuprates. Hence, the relation between magnetic order and superconductivity is one of the vital issues in the investigations of such compounds.

K-doped BaFe$_2$As$_2$ is the firstly reported oxygen-free iron-pnictide superconductor with $T_c = 38$ K [6]. The crystal structure of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ is of the ThCr$_2$Si$_2$-type. This structure possesses an FeAs layer similar to that realized in LaFeAsO. The parent material BaFe$_2$As$_2$ exhibits AF anomaly at $T_N = 140$ K [12]. Neutron diffraction measurements revealed an ordered moment of 0.87 $\mu_B$ (Bohr magneton) at the Fe site with a $q$ vector of $(1, 0, 1)$ for the orthorhombic structure [13]. It is important to note that this compound exhibits structural phase transition as well as AF anomaly [12, 13]. The zero-field $^{75}\text{As}$-NMR spectrum also revealed that the magnetically ordered state of this compound is commensurate [14, 15].

Several groups reported the phase diagram of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [16, 17]. The most striking feature of the phase diagram is that the SC region widely spreads for $0.2 \leq x \leq 1$ and...
thus the possibility of the coexistence of the AF and SC states exists for $0.2 \leq x \leq 0.4$. Moreover, it is demonstrated that the pressure effect is quite important in the iron-pnictide superconductors [18, 19, 20]. To understand the relationship between the AF instability and superconductivity in Ba$_{1-x}$K$_x$Fe$_2$As$_2$, we performed resistivity and ZF-NMR measurements under high pressure.

2. Experiment
Polycrystalline Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($x = 0$ and 0.4) samples were synthesized by a high-temperature and high-pressure method. The NMR experiment on the $^{75}$As nucleus ($I = 3/2$, $\gamma = 7.292$ MHz/T) was carried out using phase-coherent pulsed NMR spectrometers. The samples were crushed into powder for use in the experiments. A CuBe-NiCrAl hybrid piston cylinder cell was used for the NMR measurements under pressure $P$ up to about 2.5 GPa. We used Daphne 7373 for the pressure transmitting medium. Electrical resistivity was measured by a conventional dc four-probe method with cubic anvil apparatus in which Fluorinerts was used for transmitting medium. The values of $P$ and its homogeneity were determined from the nuclear quadrupole resonance frequency and full width at half maximum of $^{63}$Cu of Cu$_2$O at 4.2 K, respectively [21, 22].

3. Results and Discussion
In Fig. 1(a), we show ZF $^{75}$As-NMR spectra of BaFe$_2$As$_2$ at pressures of 0-2.49 GPa. We show only center lines for the pressures of 1.22 and 1.93 GPa. The $P$ dependence of the $^{75}$As-NMR spectra is small up to 2.5 GPa. Satellite lines at around 7 and 11 MHz for the pressure of 2.49 GPa are broader than those for the ambient pressure since pressure inhomogeneity yields distribution of electric field gradient at the As site. As described in refs. xiv and xv, we can evaluate the internal magnetic field $H_{\text{int}}$ at the As site from the frequency of the center line of the ZF $^{75}$As-NMR spectra. The $H_{\text{int}}$ gradually decreases with increasing $P$. Although the spectrum becomes broader, the existence of the ZF $^{75}$As-NMR spectrum indicates the static antiferromagnetic ordered state at 2.49 GPa. Moreover, the satellite lines at 2.49 GPa evidences that the Zeeman energy ($\sim 8.7$ MHz) is sufficiently larger than the electric quadrupole interaction ($\sim 2$ MHz).

As already reported in ref. xix, we also performed resistivity $\rho$ measurement up to 13 GPa, which exhibits metallic behavior. At ambient pressure, $\rho$ rapidly decreases below approximately 131 K ($= T_N$) [23]. This is due to AF anomaly associated with structural phase transition. The AF anomaly becomes broader above 1 GPa. In order to determine the AF transition temperature, we took derivative $d\rho/dT$ of BaFe$_2$As$_2$, and determined the AF transition temperature from the peak in $d\rho/dT$. Because the steep decrease of $\rho$ below the anomaly temperature can be interpreted as the suppression of magnetic scattering, this anomaly is attributable to AF transition.

In addition to AF anomaly at higher temperature, there is another anomaly in $\rho$ below approximately 20-30 K at $P$ values above 3.0 GPa. This anomaly can be interpreted as the onset of superconductivity. However, we should note that we obtained no zero resistivity at every pressure. We confirmed its reproducibility with different batches of samples. Simultaneously, we obtained the current dependence of $\rho$ below these temperatures. Therefore, this anomaly is related to superconductivity. Indeed, recent pressure studies on the isomorph compound SrFe$_2$As$_2$ ($T_N = 200$ K) have revealed that the SrFe$_2$As$_2$ is quite sensitive to the uniaxial stress [24, 25]. This suggests that the anomaly related with superconductivity in polycrystalline BaFe$_2$As$_2$ is due to the local inhomogeneous stress at grain boundary.

Contrast to $\rho$ of BaFe$_2$As$_2$, $\rho$ of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ shows no anomalies associated with magnetic ordering, while anomalies associated with SC transition becomes clear, and exhibits zero resistivity below approximately 38 K (Fig. 2). $T_c$ gradually decreases with decreasing $P$, and
reaches approximately 19 K at 17 GPa. This tendency itself is quite similar to that of the anomalies associated with superconductivity for \( x = 0 \), and the suppression of \( T_c \) is more gradual than that of higher-\( T_c \) superconductor NdFeAsO\(_{0.7}\) [18].

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** (a) ZF \(^{75}\)As-NMR spectra of BaFe\(_2\)As\(_2\) at pressures of 0-2.49 GPa. (b) ZF \(^{75}\)As-NMR spectra of Ba\(_{0.6}\)K\(_{0.4}\)Fe\(_2\)As\(_2\) at 0 and 1.02 GPa.

**Figure 2.** (Color online) Electrical resistivity of Ba\(_{0.6}\)K\(_{0.4}\)Fe\(_2\)As\(_2\) at pressures of 1.0-17.0 GPa. The inset shows the resistivity up to about 250 K.

In Fig. 1(b), we show ZF \(^{75}\)As-NMR spectra of Ba\(_{0.6}\)K\(_{0.4}\)Fe\(_2\)As\(_2\) at 0 and 1.02 GPa. This is consistent with the broadening of the field-sweep NMR spectra of Ba\(_{0.6}\)K\(_{0.4}\)Fe\(_2\)As\(_2\) below about 90 K in the previous study [26]. Though no anomalies associated with magnetic ordering were found in \( \rho \) measurement, this NMR result is a strong evidence for the existence of the static magnetic ordering domain in Ba\(_{0.6}\)K\(_{0.4}\)Fe\(_2\)As\(_2\). The spectra become much broader than those of the parent compound BaFe\(_2\)As\(_2\). Furthermore, it is difficult to distinguish satellite lines in spectra, which is due to the distribution of internal magnetic field and/or nuclear quadrupole frequency arising from the large distribution of K in the material. Rough estimation of \( H_{int} \) is approximately 1.2(1) T at ambient \( P \), and has little \( P \) dependence. Note that the observed spectra is induced mainly by the internal magnetic field is the AF state, and is not induced by the electric field gradient, which should exist at around 5 MHz [26].

We evaluated the spin-lattice relaxation rate \( 1/T_1 \) at ambient pressure in the AF state of Ba\(_{0.6}\)K\(_{0.4}\)Fe\(_2\)As\(_2\) according to the procedure described in ref. xxvi. The \( 1/T_1 \) at 1.5 K in the AF state is an order of magnitude larger than that in the SC state [26]. Therefore, we may conclude that the coexistence of the both states is not a microscopic coexistence but a phase separation. Further study using single crystals is required to discuss the nature between AF and SC states more accurately.

### 4. Summary

We performed resistivity and ZF \(^{75}\)As NMR measurements of Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) (\( x = 0 \) and 0.4) under high pressure. ZF \(^{75}\)As NMR measurements revealed that the internal magnetic field is
robust against $P$. On the other hand, $T_c$ has a tendency to decrease monotonically under $P$. The $1/T_c$ in AF and SC states suggests that the coexistence of the AF and SC states is not microscopic but phase separated.

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References
[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono: J. Am. Chem. Soc. 130 (2008) 3296.
[2] H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. 77 (2008) 063707.
[3] Z. A. Ren, J. Yang, W. Lu, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao: Euro. Phys. Lett. 82 (2008) 57002.
[4] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang: Phys. Rev. Lett. 100 (2008) 247002.
[5] X. H. Chen, T. Wu, G. Wang, R. H. Liu, H. Chen, and D. F. Fang: Nature 453 (2008) 761.
[6] M. Rotter, M. Tegel, and D. Johrendt: Phys. Rev. Lett. 101 (2008) 107006.
[7] F. C. Hsu, J. Y. Luo, K. W. Yeh, T. K. Chen, T. W. Huang, P. M. Wu, Y. C. Lee, Y. L. Huang, Y. Y. Chu, D. C. Yan, and M. K. Wu: Proc. Natl. Acad. Sci. U.S.A 105 (2008) 14262.
[8] X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin: arXiv:0806.4688.
[9] S. Matsuishi, Y. Inoue, T. Nomura, H. Yanagi, M. Hirano, and H. Hosono: J. Am. Chem. Soc. 130 (2008) 14428.
[10] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du: Phys. Rev. Lett. 101 (2008) 057003.
[11] K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki: Phys. Rev. Lett. 101 (2008) 087004.
[12] M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes, and R. Pöttgen: Phys. Rev. B 78 (2008) 020503(R).
[13] Q. Huang, Y. Qiu, W. Bao, J. W. Lynn, M. A. Green, Y. C. Gasparovic, T. Wu, G. Wang, and X. H. Chen: Phys. Rev. Lett. 101 (2008) 257003.
[14] H. Fukazawa, K. Hirayama, K. Kondo, T. Yamazaki, Y. Kohori, N. Takeshita, K. Miyazawa, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. 77 (2008) 093706.
[15] H. Fukazawa, T. Yamazaki, K. Kondo, K. Hirayama, Y. Kohori, N. Takeshita, K. Miyazawa, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. 77 (2008) Suppl. C 138.
[16] M. Rotter, M. Pangerl, M. Tegel, and D. Johrendt: Angew. Chem. Int. Ed. 47 (2008) 7949.
[17] H. Chen, Y. Ren, Y. Qiu, W. Bao, R. H. Liu, G. Wu, T. Wu, Y. L. Xie, X. F. Wang, Q. Huang, and X. H. Chen: Euro. Phys. Lett. 85 (2009) 17006.
[18] N. Takeshita, A. Iyo, H. Eisaki, H. Kito, and T. Ito: J. Phys. Soc. Jpn. 77 (2008) 075003.
[19] H. Fukazawa, N. Takeshita, T. Yamazaki, K. Kondo, H. Hirayama, Y. Kohori, K. Miyazawa, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. 77 (2008) Suppl. C 138.
[20] H. Fukazawa, K. Hirayama, T. Yamazaki, Y. Kohori, and H. Hosono: Nature 453 (2008) 376.
[21] H. Fukazawa, K. Hirayama, T. Yamazaki, Y. Kohori, and T. Matsumoto: J. Phys. Soc. Jpn. 76 (2007) 125001.
[22] A. P. Reyes, E. T. Ahrens, R. H. Heffner, P. C. Hammel, and J. D. Thompson: Rev. Sci. Instrum. 63 (1992) 3120.
[23] Y. Tomioka: private communications.
[24] K. Matsubayashi, N. Katayama, K. Ohgushi, A. Yamada, K. Munakata, T. Matsumoto, and Y. Uwatoko: J. Phys. Soc. Jpn. 78 (2009) 037003.
[25] H. Kotegawa, T. Kawazoe, H. Sugawara, K. Murata, and H. Tou: arXiv:0904.4631; to appear in J. Phys. Soc. Jpn.
[26] H. Fukazawa, T. Yamazaki, K. Kondo, Y. Kohori, N. Takeshita, P. M. Shirage, K. Kihou, K. Miyazawa, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. 78 (2009) 033704.