75 As NMR study of the growth of paramagnetic-metal domains due to electron doping near the superconducting phase in LaFeAsO$_{1-x}$Fx


Fujiwara, N. ...[et al]. 75 As NMR study of the growth of paramagnetic-metal domains due to electron doping near the superconducting phase in LaFeAsO$_{1-x}$Fx. Physical Review B 2012, 85(9): 094501.

ISSUE DATE:
2012-03-02

URL:
http://hdl.handle.net/2433/241756

RIGHT:
© 2012 American Physical Society
In strongly correlated electron systems, including high-transition temperature (high-$T_c$) superconductors, the electric and magnetic behavior at the phase boundary between antiferromagnetic (AF) and superconducting (SC) phases has attracted significant research interest. In iron-based high-$T_c$ pnictides, the AF state is a stripe-type spin-density-wave (SDW) state arising from interband nesting between hole and electron pockets, and the relationship between AF and SC states is deeply connected with the pairing symmetry. Some theoretical investigations predict that SDW and SC order parameters are compatible near the phase boundary, and the homogeneous coexistence of SDW and SC states is possible for superconductors with $S_{\pm}$ symmetry. In fact, this coexistence is experimentally suggested for compounds that exhibit the crossover regime such as Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ (Ba122 series), which is a representative high-$T_c$ superconductor along the horizontal axis, implying the possibility of $S_{\pm}$ symmetry.

The vertical axis in Fig. 1 corresponds to the saturation-recovery method after a single pulse. A pressure cell, which was applied by using a conventional clump-type cell, was used to measure the $T_c$ values at high pressures. The $T_c$ values were determined from the Neel temperature, which is defined as the temperature at which the magnetization changes sign. The $T_c$ values were measured by using nuclear magnetic resonance (NMR) spectra for the undoped samples measured at 3.5 T. The $T_c$ values were found to be nearly the same for all compounds, with the exception of the La1111 series, which exhibited a smaller $T_c$ value.

The conditions in which phase segregation or homogeneous coexistence appear to be elucidated for a variety of pnictides. Starting from the La1111 series, an empirical and systematic understanding of the crossover regime appears to be possible. In the pulsed-NMR measurements, field-swept-NMR spectra were obtained from the spin-echo intensity after two coherents. The relaxation rates $(1/T_1)$ were measured by using the saturation-recovery method after a single pulse. A pressure cell, which was applied by using a conventional clump-type cell, was used to measure the $T_c$ values at high pressures. The $T_c$ values were determined from the Neel temperature, which is defined as the temperature at which the magnetization changes sign. The $T_c$ values were measured by using nuclear magnetic resonance (NMR) spectra for the undoped samples measured at 3.5 T. The $T_c$ values were found to be nearly the same for all compounds, with the exception of the La1111 series, which exhibited a smaller $T_c$ value.

II. EXPERIMENTAL RESULTS

In the pulsed-NMR measurements, field-swept-NMR spectra were obtained from the spin-echo intensity after two coherent pulses. The relaxation rates $(1/T_1)$ were measured by using the saturation-recovery method after a single pulse. A pressure cell, which was applied by using a conventional clump-type cell, was used to measure the $T_c$ values at high pressures. The $T_c$ values were determined from the Neel temperature, which is defined as the temperature at which the magnetization changes sign. The $T_c$ values were measured by using nuclear magnetic resonance (NMR) spectra for the undoped samples measured at 3.5 T. The $T_c$ values were found to be nearly the same for all compounds, with the exception of the La1111 series, which exhibited a smaller $T_c$ value.
measurements, respectively. Some data were cited from Refs. 20
and 22. (b) $^{75}$As NMR spectra at 3.0 GPa measured at 45.1 MHz. Two peaks correspond to the transition $T_N$ at 3.0 GPa expanded around the phase boundary. Solid circles and open squares represent superconducting ($T_c$) transition temperatures determined from the resistivity and NMR measurements, respectively.

**FIG. 2.** (Color online) $^{75}$As $(I = \frac{3}{2})$ NMR spectra measured at 35.1 MHz for undoped LaFeAsO. (a) NMR spectra at ambient pressure. Two sharp peaks correspond to the transition $I = -\frac{1}{2} \Leftrightarrow \frac{1}{2}$, and the broad low-field signal corresponds to the transition $I = -\frac{3}{2} \Leftrightarrow -\frac{1}{2}$. A double-peak structure appears due to the quadrupole interaction. At low temperatures, the signal corresponding to $I = -\frac{1}{2} \Leftrightarrow \frac{1}{2}$ is distributed to a wide field region because of the internal field arising from the ordered moments. (b) NMR spectra at 3.0 GPa.

**FIG. 3.** (Color online) (a) Phase diagram of LaFeAsO$_{1-x}$F$_x$ at 3.0 GPa expanded around the phase boundary. Solid circles and open squares represent $T_N$ determined from resistivity and NMR measurements, respectively. Some data were cited from Refs. 20 and 22. (b) $^{75}$As NMR spectra at 3.0 GPa measured at 45.1 MHz. Two peaks correspond to the transition $I = -\frac{1}{2} \Leftrightarrow \frac{1}{2}$, and the broad signal corresponds to the transition $I = -\frac{3}{2} \Leftrightarrow -\frac{1}{2}$. The signals which originate from the paramagnetic-metal phase below $T_N$ are highlighted in the spectra. (c) Detuning of the NMR tank circuit measured at a doping level of 2.6% shown by an arrow in (a) under a pressure of 3.0 GPa. The bend indicates the onset of superconductivity. (d) Phase diagram of LaFeAsO$_{1-x}$F$_x$ at ambient pressure. (e) $^{75}$As NMR spectra at ambient pressure measured at 45.1 MHz. (e) Detuning of the NMR tank circuit measured at a doping level of 2.6% shown by an arrow in (d) at ambient pressure.

The AF phase at low temperatures, the double-peak structure disappears and the signal corresponding to $I = -\frac{1}{2} \Leftrightarrow \frac{1}{2}$ is distributed to a wide field region because the internal fields arising from the AF ordering affect the resonance position. Intriguingly, the paramagnetic-metal (PM) state survives even for the 2.6% F-doped La1111 series located near the phase boundary [see Figs. 3(a) and 3(d)]. Figures 3(b) and 3(e) show $^{75}$As NMR spectra at 3.0 GPa and at ambient pressure, respectively.
As NMR study of the growth of...

**FIG. 4.** (Color online) (a) $^{75}$As NMR spectra at 10 K measured at 35.1 MHz. Broad bumps at 3.0 GPa and at ambient pressure originate from superconducting and paramagnetic-metal phases, respectively. (b) Relaxation rates ($1/T_1$) measured at the lower-field peaks within the double-structure peaks corresponding to $I = -\frac{1}{2} \leftrightarrow \frac{1}{2}$. $1/T_1$ has a maximum at $T_N$, reflecting antiferromagnetic fluctuations from neighboring AF domains. $1/T_1 T$ for the undoped samples at ambient pressure were reported in Refs. 20, 24, and 25.

measured at 45.1 MHz. At high temperatures, the NMR spectra are qualitatively the same as the undoped spectra. At low temperatures below $T_N$ (~100 and 80 K at ambient pressure and 3.0 GPa, respectively), the NMR spectra consist of two components: the broad signal originating from the AF state, and central bumps originating from the PM state as highlighted in Figs. 3(b) and 3(e). The central bumps are robust because they survive even at 10 K [see Fig. 4(a)], implying the occurrence of phase segregation or domain formation. At 3.0 GPa, PM domains become superconducting at low temperatures, as seen from the detuning of the NMR tank circuit [see Fig. 3(c)]. The detuning measured at 45.1 MHz indicates a $T_c$ value of 18 K. Therefore, at 3.0 GPa, SC and AF phases become segregated on a microscopic level, although AF and SC phases apparently overlap in the phase diagram [see Fig. 3(a)]. The phase segregation between the AF and SC phases has been observed even for a doping level of 5.5% by means of muon-spin rotation ($\mu$SR), and pressure application causes an increase in the SC volume fraction against the AF volume fraction.23 Interestingly, at ambient pressure the absence of the detuning as shown in Fig. 3(f) indicates that phase segregation between the AF and PM phases occurs, which is not expected from the existing phase diagram that indicates the AF phase at the 2.6% doping level. The existence of the PM phase is the most important result from the present experiments and raises fundamental doubts about the existing paradigm that focuses only on the relationship between SC and AF states. Why does the PM phase occur at the doping level where the AF phase is expected in the existing diagram? The answer is deeply connected with the size of PM domains, which are not macroscopic but on the scale of several lattice units. At a doping level of 2.6%, the PM domains are so small that some experimental techniques may not detect them. This assertion is supported by the fact that the relaxation rates...
(1/\(T_\text{c}\)) have a maximum at \(T_N\), reflecting AF fluctuations from neighboring AF domains [see Fig. 4(b)]. Note that PM domains are due to neither a nonuniform charge distribution nor some second phase. The former possibility is ruled out because domains with excess charge carriers would be not in a PM state but in a SC state. The latter possibility is also ruled out because \(1/\(T_\text{c}\) would be free from AF fluctuations of neighboring domains.

### III. Discussion

The phase segregation between PM and AF phases cannot be explained by the existing paradigm: To understand the phenomenon together with the phase segregation between SC and AF phases at high pressure, two factors should be considered: (i) the growth of PM domains due to increasing electron doping level as illustrated in Fig. 5(a), and (ii) the location of the onset of superconductivity. PM domains undergo a superconducting transition depending on \(P\) and \(x\) as shown in Fig. 5(b). In the underdoped regime [regime A in Fig. 5(b)], PM domains are maintained, even below \(T_N\), as isolated seeds because of supercooling; however, they finally disappear at low temperatures. Therefore, the ground state is the SC state, which is consistent with existing observations. In the intermediate-doping regime [regime B in Fig. 5(b)], PM domains grow with increasing doping level and become robust even at low temperatures, causing phase segregation with AF domains. Whether the ground state is a SC or PM state depends on the location of the onset of superconductivity. The onset, which is at \(\sim 3.5\%\) doping level at ambient pressure [see Fig. 5(b)], shifts to the underdoped regime upon applying pressure and crosses the \(2.6\%\) doping level at 3.0 GPa. Therefore, two kinds of segregation are possible depending on pressure. In the intermediate-doping regime, applying pressure would not change the size of PM domains if one considers the NMR spectral intensity shown in Fig. 4(a). Taking account of a bulk volume fraction, PM domains would somehow link with neighboring PM domains, unlike in the underdoped regime. In the overdoped regime [region C in Fig. 5(b)], PM domains cover the entire system and exhibit superconducting properties at low temperatures, independent of pressure application. The PM state is free from AF (i.e., SDW) ordering, implying that a factor other than interband nesting is crucial. Recently, a ferroquadrupole (FQ) ordering state between SDW and SC states has been suggested based on orbital fluctuation theory. A phase diagram based on the theory is shown in Fig. 5(c). AF and PM domains in the central panel of Fig. 5(a) correspond to different doping levels, indicated by the arrows in Fig. 5(c). PM domains at ambient pressure would be in the FQ ordering phase, while they become superconducting at 3.0 GPa because the SC phase boundary shifts to the underdoped regime by applying pressure. The electronic phase diagram shown in Fig. 5(c) allows us to reproduce the phase diagram in Fig. 1 because the volume fraction of AF domains is predominant around the phase boundary, and therefore the contribution from AF domains is apparently emphasized for some experimental techniques.

### IV. Conclusion

In conclusion, we have observed phase segregation between AF and PM domains at ambient pressure in the La1111 series by using \(^{75}\text{As}\) NMR. By increasing the electron doping level, we observed growth of PM domains accompanied by the onset of superconductivity. The PM state is independent of the AF ordering that arises from interband nesting, suggesting that the existing paradigm that focuses only on the relationship between superconductivity and antiferromagnetism is not valid. The FQ state predicted by orbital fluctuation theory is a leading candidate to explain the anomalous PM domains.

### Acknowledgments

The NMR work is supported by a Grant-in-Aid (Grant No. KAKENHI 23340101) from the Ministry of Education, Science, and Culture, Japan. This work was supported in part by the JPSJ First Program. The authors would like to thank H. Kontani for discussion.
As NMR STUDY OF THE GROWTH OF... 


