PHYSICAL REVIEW B **78**, 020512(R) (2008)

Ferromagnetic spin fluctuation in $LaFeAsO_{1-x}F_x$

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(Received 12 March 2008; revised manuscript received 19 June 2008; published 29 July 2008)

The F-doped LaFeAsO—a recently discovered superconductor with the high T_c of 26 K—has been studied using the resistivity (ρ), magnetic-susceptibility (χ), and heat-capacity (C_p) measurements in the F doping range $0 \leq x \leq 0.14$ ($LaFeAsO_{1-x}F_x$). In the low-temperature region, a $T^3 \ln T$ term in C_p and a T^2 term in χ—which are derived from the spin fluctuation—are observed. The nearly ferromagnetic nature evidenced by a large Wilson ratio (6.5 for $x=0$ and 11.2 for $x=0.025$) suggests that the superconductivity in the LaFeAsO system is mediated by ferromagnetic spin fluctuation.

DOI: 10.1103/PhysRevB.78.020512 PACS number(s): 74.70.Dd, 65.40.−b, 74.25.Bt, 74.25.Jb

Since the discovery of high-temperature superconductivity in cuprate oxide compounds,[1] a number of experimental and theoretical studies have been devoted to understanding the superconducting mechanism.[2–4] The most widely accepted physical picture for explaining such a high transition temperature (T_c) is that the antiferromagnetic (AF) spin fluctuation gives rise to the strong pair interaction of the Cooper pairs.[2,3] So far, it has been demonstrated that this mechanism is successfully realized in various superconductors such as the Pu-based compound $PuCoGa_5$ (T_c=18.5 K),[5] organic compounds k-$(BEDT\text{-}TTF)_2X$ ($T_c \sim 10$ K),[6] and so on. In contrast, there are only a few superconductors mediated by ferromagnetic (FM) spin fluctuation. These show significantly low T_c.[7,8] Therefore, a system having FM spin fluctuation was believed to be an unlikely candidate for producing high T_c.

Recently, we found that aliovalent ion doping of fluorine into a layered oxyarsenide LaFeAsO produces superconductivity with a high transition temperature of $T_c \sim 26$ K (Ref. 9) and a high upper critical field.[10] LaFeAsO has a layered structure belonging to the ZrCuSiAs structure with space group $P4/nmm$.[9] Co-based,[11] Fe-based,[9,12] and Ni-based[13] analog compounds show metallic conductivity without carrier doping. Fe-based and Ni-based compounds exhibit superconductivity, and Co-based compounds have FM metal properties [e.g., LaCoPO (Ref. 11) and LaCoAsO (Ref. 11) having Curie temperatures of 43 and 66 K, respectively]. The occurrence of itinerant ferromagnetism means that the interaction between quasiparticles can be considered to be FM and the presence of FM spin fluctuation may be expected in the LaFeAsO system.

If the presence of FM spin fluctuation in this system is demonstrated, it would be evidence that the high T_c in the system is mediated by FM spin fluctuation. In general, FM spin-fluctuation effects manifest themselves in a T^2 term in susceptibility[14] and $T^3 \ln(T/T_{SF})$ term in heat capacity,[15] well below the characteristic temperature of spin fluctuation (T_{SF}). In this Rapid Communication, we present the results of resistivity, magnetic-susceptibility, and heat-capacity measurements in $LaFeAsO_{1-x}F_x$ (x=0, 0.025, 0.05, 0.11, and 0.14) and show the characteristic properties of FM spin fluctuation.

Polycrystalline samples of $LaFeAsO_{1-x}F_x$ (x=0, 0.025, 0.05, 0.11, and 0.14) were prepared by solid-state reactions of LaAs, FeAs, Fe_2As, La, LaF_3, and La_2O_3 powders in an evacuated quartz tube, as reported previously.[9] The value of x was estimated from the Vegard law.[9] Powder x-ray diffraction showed that the samples with x=0.025, 0.11, and 0.14 contained impurities of FeAs (~3%) and LaOF (~3%). Samples with x=0 and 0.05 contained only a small amount of FeAs (~1%).

Resistivity, magnetic-susceptibility, and heat-capacity measurements were performed between 2 and 300 K using a physical property measurement system (PPMS) from Quantum Design Inc.

Figure 1 shows the heat capacity (C_p), magnetic susceptibility (χ), and resistivity (ρ) of $LaFeAsO_{1-x}F_x$ (x=0, 0.025, 0.05, 0.11, and 0.14). A sharp drop in χ and ρ, corresponding to superconducting transition, is observed for x=0.05, 0.11, and 0.14. For x=0 and 0.025, no such drop appears until 2 K. Another anomaly is observed at ~150 K, as also seen in C_p and ρ. The bulk nature of superconductivity for x=0.05 and 0.11 is now confirmed by the present C_p measurement. The inset in Fig. 1(a) shows the heat-capacity difference (C_p^*) between superconducting samples (x=0.05, 0.11, and 0.14) and nonsuperconducting LaFeAsO below 35 K, i.e., the difference in electronic contribution; $C_p^* = [C_{ele}(x) + C_{lat}(x)] - [C_{ele}(x=0) + C_{lat}(x=0)] \sim C_{ele}(x) - C_{ele}(x=0)$, where C_{ele} and C_{lat} are the electronic and the lattice contribution, respectively. Taking into account the entropy conservation between the superconducting and normal states, the heat-capacity jump at T_c (DC_p^*/T_c) is estimated to be 6.2 mJ mol^{-1} K^{-2} (T_c=20.5 K) and 6.4 mJ mol^{-1} K^{-2} (T_c=21.1 K) for x=0.05 and 0.11, respectively. For x=0.14, the heat-capacity jump is small and smears out, implying the small superconducting volume fraction. In fact, the diamagnetism signal of this sample is one-third to one-fifth of that of x=0.05 or 0.11, as shown in the inset of Fig. 1(b).

Figure 2(a) shows C_p values below 8 K in the plot of C_p/T versus T^2. For x=0.05, 0.11, and 0.14, the data points lie on straight lines with finite intercepts at T=0, indicating the following temperature dependence: $C_p = \gamma_{SC} T + \beta T^3$, where γ_{SC} is the electronic heat-capacity coefficient sup-

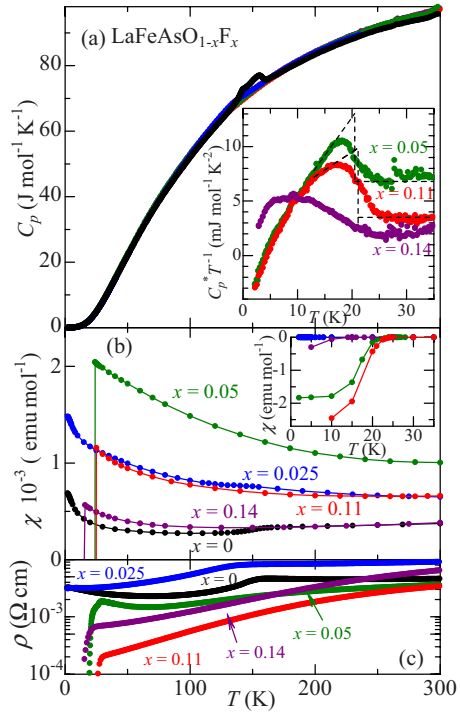

FIG. 1. (Color online) Thermal and magnetic properties for $LaFeAsO_{1-x}F_x$ (x=0, 0.025, 0.05, 0.11, and 0.14). (a) Temperature dependence of C_p. The inset shows the heat-capacity difference (C_p^*) between superconducting samples and the nonsuperconducting LaFeAsO divided by temperature ($C_p^*T^{-1}$). (b) Temperature dependence of χ. The data in the normal state are estimated from the slope of the magnetization curve between 1 and 2 T. The data in the superconducting state are estimated from the slope of the magnetization curve below 0.01 T. The inset of this figure shows the data below 35 K. (c) Temperature dependence of ρ.

pressed by the occurrence of a superconducting gap and β is the lattice heat-capacity coefficient. The finite values of γ_{SC} for the superconducting samples would be attributed to the presence of impurities, as observed in various systems.[16,17] The Debye temperature (Θ_D) estimated from β is 319 (x=0.05), 308 (x=0.11), and 332 K (x=0.14), which is lower than that of LaFePO (Θ_D=371 K),[16] probably because of the heavier mass of As compared to P.

For x=0 and 0.025, C_p/T distinctly departs from linear dependence below 6 K. This temperature dependence can be fitted with the characteristic $T^3 \ln(T/T_{SF})$ term of spin-fluctuation system. The total heat capacity can then be written as

$$C_p = \gamma_{SF}T + \beta T^3 + \delta T^3 \ln(T/T_{SF}), \quad (1)$$

where γ_{SF} represents the electronic heat-capacity coefficient enhanced by spin fluctuation and δ is the coefficient of the spin-fluctuation term.[15] Assuming that the average of β in these superconducting samples is equal to that in nonsuperconducting samples (x=0 and 0.025), Eq. (1) yields T_{SF} =12±1 and 13±1 K for x=0 and 0.025, respectively (where the error bars on T_{SF} are estimated from the standard deviation of β). Figure 2(b) displays the χ versus T^2 plots of

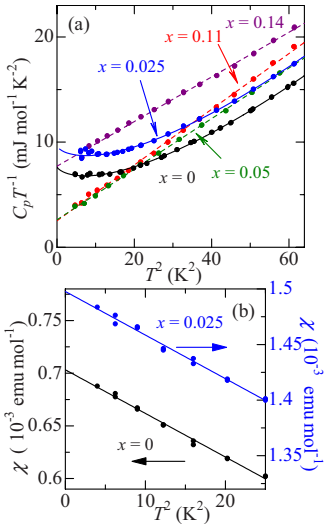

FIG. 2. (Color online) Detection of spin fluctuation in LaFeAsO system. (a) C_pT^{-1} versus T^2 plot. The broken lines indicate the best fits of $C_p=\gamma_{SC}T+\beta T^3$, in which γ_{SC}=2.6 mJ K^{-2} mol^{-1} and β=0.24 mJ K^{-4} mol^{-1} for x=0.05, γ_{SC}=2.5 mJ K^{-2} mol^{-1} and β=0.27 mJ K^{-4} mol^{-1} for x=0.11, and γ_{SC}=7.7 mJ K^{-2} mol^{-1} and β=0.21 mJ K^{-4} mol^{-1} for x=0.14. The solid curves indicate the fits of $C_p=\gamma_{SF}T+\beta T^3+(T/T_{SF})$, in which γ_{SF} =7.6 mJ K^{-2} mol^{-1} and δ=0.23 mJ K^{-4} mol^{-1} for x=0, and γ_{SF} =9.6 mJ K^{-2} mol^{-1} and δ=0.24 mJ K^{-4} mol^{-1} for x=0.025. The other parameters are denoted in the text. (b) χ versus T^2 plot for x=0 and 0.025.

x=0 and 0.025 samples in the low-temperature region. χ shows a linear dependence on T^2 rather than the Curie-Weiss law. Béal-Monod *et al.*[14] reported that the characteristic temperature dependence of χ in the FM spin-fluctuation system can be approximated as $\chi=\chi_0[1-(3.2\pi^2/24)(T/T_{SF})^2]$, where χ_0 is the magnetic susceptibility at 0 K. Following this expression, we obtain T_{SF} of 15±1 and 22±1 K for x=0 and 0.025, respectively. Considering the fact that the difference in T_{SF} between C_p and χ measurements has been reported in previous studies,[18,19] T_{SF} values derived from these two independent measurements appear to be consistent with each other. In any case, the two measurements clearly demonstrate the presence of FM spin fluctuation in x=0 and 0.025 samples.

Here, it is noted that the extrapolation of the high-temperature linear part in C_p/T gives an electronic heat-capacity coefficient without the spin-fluctuation effect (γ).[20] The values of γ obtained from this method are 1.6±1 and 3.2±1 mJ K^{-2} mol^{-1} for x=0 and 0.025, respectively. Assuming that the lattice contribution of LaFeAsO is the same as those of $LaFeAsO_{1-x}F_x$, the C_p^*/T above the T_c [see inset of Fig. 1(a)] corresponds to the difference in γ, $C_p^*/T=\gamma(x)-\gamma(x=0)$. This assumption allows us to estimate γ=8.4±2, 5.1±2, and 3.8±2 mJ K^{-2} mol^{-1} for x=0.05, 0.11, and 0.14, respectively, where the error bar takes into account the uncertainties in C_p^*/T above T_c and γ of the x=0 sample. Using these values, the normalized heat-capacity jump ($\Delta C_p^*/\gamma T_c$) is estimated to be 0.60–0.97 and 0.90–2.0 for x=0.05 and 0.11, respectively. Although the

large error bars in the data do not allow a conclusive interpretation of superconductivity, the value for $x=0.05$ is smaller than the weak-coupling BCS value of 1.43.

The electronic density of states (N_D) can be calculated from γ using the relation of $\gamma=(1/3)\pi^2 k_B^2 N_D$, where k_B is the Boltzmann constant. This equation gives $N_D=0.7$, 1.4, 3.6, 2.2, and 1.6 states/eV for $x=0$, 0.025, 0.05, 0.11, and 0.14, respectively, which are smaller than that of LaFePO (4.5 states/eV at $T_c=3.3$ K).[16] The smaller N_D and Θ_D values in LaFeAsO should lead to lower T_c within the framework of the phonon mediated BCS theory,[21] which is inconsistent with higher T_c. On the other hand, χ in a metal measures the density of states enhanced by the FM spin fluctuations via $\chi=\mu_B^2 N_D^*$, where μ_B is the Bohr magneton and N_D^* is the enhanced density of states. The N_D^* values calculated from the data at 300 K (12, 20, 31, 20, and 12 states/eV for $x=0$, 0.025, 0.5, 0.11, and 0.14, respectively) are one orders of magnitude larger than N_D obtained from C_p. This large enhancement can be understood in terms of the FM spin fluctuation.

The ratio of χ to γ at 0 K, which is known as the Wilson ratio (R_W), is commonly used as a measure to assess the electric and magnetic correlations between quasiparticles. In general, the ratio gives a dimensionless value of $R_W=1$ for free-electron systems and $R_W=2$ for strongly correlated systems. Nearly FM systems show very large values of R_W [e.g., Pd, $R_W=6-8$;[22] $TiBe_2$, $R_w=12$ (Ref. 22); and $Sr_3Ru_2O_7$, $R_W=10$ (Ref. 23)] because of the enhancement of χ. In the present compounds, we obtain significantly large R_W values of 6.5 and 11 for $x=0$ and 0.025, respectively,[18] indicating that LaFeAsO is considered to be a system containing FM spin fluctuation. These values are two to three times larger than that of the isostructural oxyphosphide LaFePO ($R_W=4.6$, $T_c=3.3$ K)[16] and implying that the stronger spin fluctuation induces a larger Wilson ratio and leads to enhancement of T_c. Such a relationship between T_c and R_W was found in the pressure dependence of superfluid transition in ^{3}He.[24]

For $x=0$ and 0.025, C_p, χ, and ρ show an anomaly at about 150 K, as shown in Fig. 1. To estimate the excess heat capacity (C_{ex}) associated with the anomaly, we assume a smoothly varying background [as shown in Fig. 3(a)] and subtract it from the total measured C_p. Figure 3(b) shows the C_{ex} value near the anomaly. Apparently, two peaks are present at 142 and 153 K for $x=0$—together with a small drop in χ [Fig. 3(c)]. In contrast, there is only one peak at 134 K for $x=0.025$. The entropy corresponding to the anomaly can be estimated to be $S=0.53$ ($0.09R$ ln 2) and 0.38 J mol^{-1} K^{-1} ($0.07R$ ln 2) for $x=0$ and 0.025, respectively, which are significantly smaller than the entropy associated with the antiferromagnetic spin ordering (R ln 2) usually seen in the Mott transition of cuprates.[25]

Figure 4 shows the phase diagram obtained by the data points of the present measurements and by that of Ref. 12, together with the variation of the overall thermodynamic quantities. With increasing x, the anomaly at ~150 K is driven down both in temperature and entropy, and the superconducting state emerges rapidly. The superconducting state appears for $x \geq 0.035$ with a maximum T_c of ~26 K at

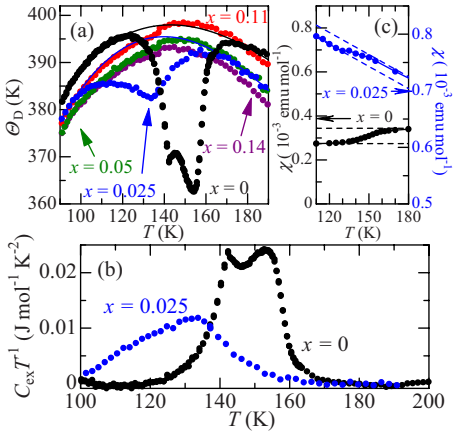

FIG. 3. (Color online) Thermal and magnetic property around 150 K. (a) Temperature dependence of Debye temperature (Θ_D) calculated form the heat capacity using the relation of $C=9rR(T/\Theta_D)^3\int_0^{\Theta_D/T} x^4 e^x/(e^x-1)^2 dx$, where r is the number of atoms in the chemical formula. The solid curves are the polynomial fit and correspond to the background. (b) Excess heat capacity (C_{ex}) divided by temperature ($C_{ex}T^{-1}$). C_{ex} is calculated by the subtracting the background in Fig. 3(a). (c) Temperature dependence of χ around 150 K.

$x=0.11$. For doping in the region of $x<0.035$, enhancements in T_{SF} and R_W are observed. Together with the enhancement in the density of states estimated from χ and C_p, this behavior indicates an increase in the FM fluctuation in this region.[26] In the whole region of x, both densities of states show similar x dependence; there is a cusplike maximum at $x=0.05$. The cusplike behavior and the larger value of N_D^* than N_D are similar to the critical behavior near the FM instability.[26] Therefore, the $x=0.05$ sample may be located closest to an FM instability. These results suggest that FM spin fluctuation can induce a high superconducting transition temperature in the LaFeAsO system, in sharp contrast to high-T_c cuprates driven by AF spin fluctuation.

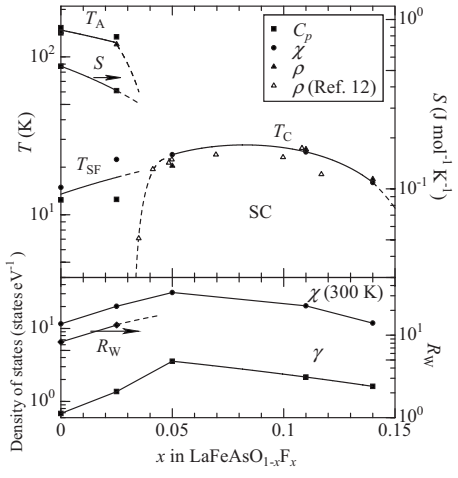

FIG. 4. Upper panel: Superconductivity phase diagrams of the $LaFeAsO_{1-x}F_x$ system. Lower panel: Density of states and Wilson ratio as a function of F content. Lines are visual guides.

χ and C_p of $LaFeAsO_{1-x}F_x$ ($x=0-0.025$) exhibit the characteristic temperature dependence expected for a FM spin-fluctuation system. Qualitative analysis of these data leads to an experimental definition of the characteristic temperature (T_{SF}), the Wilson ratio (R_W), and the densities of states (N_D and N_D^*). These values indicate that the LaFeAsO system can be considered as a nearly FM metal. Although the phase diagram obtained as a function of x is analogous to the antiferromagnetism-superconductivity phase diagram found in high-T_c cuprates, the observed entropy change and magnetic behavior associated with the anomaly at ~150 K are clearly different from an antiferromagnetic transition. Considering the significantly high-T_c value observed in the LaFeAsO system, further efforts are certainly warranted.

After this Rapid Communication was submitted, we learned that the heat capacity of isostructural oxyphosphide LaFePO also shows the $T^3 \ln(T/T_{SF})$ term (Ref. 27). This supports our conclusion that the FM spin fluctuation is an intrinsic property in LaFeAsO system.

We thank K. Ishida and M. Tachibana for the stimulating discussions. This work was supported by Grant-in-Aid JSPS (Grant No. 19.9728).

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B: Condens. Matter **64**, 189 (1986).
[2] T. Moriya, Y. Takahashi, and K. Ueda, J. Phys. Soc. Jpn. **59**, 2905 (1990).
[3] P. Monthoux, A. V. Balatsky, and D. Pines, Phys. Rev. Lett. **67**, 3448 (1991).
[4] J. Zaanen and O. Gunnarsson, Phys. Rev. B **40**, 7391 (1989).
[5] Y. Bang, A. V. Balatsky, F. Wastin, and J. D. Thompson, Phys. Rev. B **70**, 104512 (2004).
[6] J. Schmalian, Phys. Rev. Lett. **81**, 4232 (1998).
[7] S. S. Saxena, P. Agarwal, K. Ahilan, F. M. Grosche, R. K. W. Haselwimmer, M. J. Steiner, E. Pugh, I. R. Walker, S. R. Julian, P. Monthoux, G. G. Lonzarich, A. Huxley, I. Sheikin, D. Braithwaite, and J. Flouquet, Nature (London) **406**, 587 (2000).
[8] N. T. Huy, A. Gasparini, D. E. de Nijs, Y. Huang, J. C. P. Klaasse, T. Gortenmulder, A. de Visser, A. Hamann, T. Görlach, and H. v. Löhneysen, Phys. Rev. Lett. **99**, 067006 (2007).
[9] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
[10] F. Hunte, J. Jaroszynski, A. Gurevich, D. C. Larbalestier, R. Jin, A. S. Sefat, M. A. McGuire, B. C. Sales, D. K. Christen, and D. Mandrus, Nature (London) **453**, 903 (2008).
[11] H. Yanagi, R. Kawamura, T. Kamiya, Y. Kamihara, M. Hirano, T. Nakamura, H. Osawa, and H. Hosono, Phys. Rev. B **77**, 224431 (2008).
[12] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, J. Am. Chem. Soc. **128**, 10012 (2006).
[13] T. Watanabe, H. Yanagi, T. Kamiya, Y. Kamihara, H. Hiramatsu, M. Hirano, and H. Hosono, Inorg. Chem. **46**, 7719 (2007).
[14] M. T. Béal-Monod, S. K. Ma, and D. R. Fredkin, Phys. Rev. Lett. **20**, 929 (1968).
[15] S. Doniach and S. Engelsberg, Phys. Rev. Lett. **17**, 750 (1966).
[16] Y. Kohama, Y. Kamihara, H. Kawaji, T. Atake, and H. Hosono, arXiv:0806.3139, J. Phys. Soc. Jpn. (to be published).
[17] N. E. Phillips, R. A. Fisher, J. E. Gordon, S. Kim, A. M. Stacy, M. K. Crawford, and E. M. McCarron, III, Phys. Rev. Lett. **65**, 357 (1990).
[18] R. J. Trainor, M. B. Brodsky, and H. V. Culbert, Phys. Rev. Lett. **34**, 1019 (1975).
[19] P. H. Frings and J. J. M. Franse, Phys. Rev. B **31**, 4355 (1985).
[20] M. S. Wire, G. R. Stewart, W. R. Johanson, Z. Fisk, and J. L. Smith, Phys. Rev. B **27**, 6518 (1983).
[21] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[22] S. R. Julian, A. P. Mackenzie, G. G. Lonzarich, C. Bergemann, R. K. W. Haselwimmer, Y. Maeno, S. Nishizaki, A. W. Tyler, S. Ikeda, and T. Fujita, Physica B **259–261**, 928 (1999).
[23] S. Ikeda, Y. Maeno, S. Nakatsuji, M. Kosaka, and Y. Uwatoko, Phys. Rev. B **62**, R6089 (2000).
[24] C. Enss and S. Hunklinger, *Low-Temperature Physics* (Springer, Berlin, 2005).
[25] Y. Kimishima and H. Kittaka, Physica C **160**, 136 (1989).
[26] E. Bucher, W. F. Brinkman, J. P. Maita, and H. J. Williams, Phys. Rev. Lett. **18**, 1125 (1967).
[27] T. M. McQueen, M. Regulacio, A. J. Williams, Q. Huang, J. W. Lynn, Y. S. Hor, D. V. West, M. A. Green, and R. J. Cava, Phys. Rev. B **78**, 024521 (2008).