

Multiple Phase Transitions in Single-Crystalline $\text{Na}_{1-\delta}\text{FeAs}$

G. F. Chen, W. Z. Hu, J. L. Luo, and N. L. Wang

*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences,
Beijing 100190, People's Republic of China*

(Received 21 February 2009; published 4 June 2009)

Specific heat, resistivity, susceptibility, and Hall coefficient measurements were performed on high-quality single-crystalline $\text{Na}_{1-\delta}\text{FeAs}$. This compound is found to undergo three successive phase transitions at around 52, 41, and 23 K, which correspond to structural, magnetic, and superconducting transitions, respectively. The Hall effect result indicates the development of energy gap at low temperature due to the occurrence of spin-density-wave instability. Our results provide direct experimental evidence of the magnetic ordering in the nearly stoichiometric NaFeAs .

DOI: 10.1103/PhysRevLett.102.227004

PACS numbers: 74.70.-b, 74.25.Fy, 74.25.Gz

The recent discovery of superconductivity with transition temperature $T_c \sim 26$ K in $\text{LaFeAsO}_{1-x}\text{F}_x$ (abbreviated as 1111) has attracted a great deal of research interest [1]. Substituting La with other rare earth elements dramatically enhances the T_c up to 41–55 K [2–5]. At room temperature, all these parent compounds crystallize in a tetragonal ZrCuSiAs -type structure, which consists of alternate stacking of edge-sharing Fe_2As_2 tetrahedral layers and La_2O_2 tetrahedral layers along the c axis. Soon after this discovery, another group of compounds $A\text{Fe}_2\text{As}_2$ ($A = \text{Ba, Sr, Ca}$)(122), which crystallize in a tetragonal ThCr_2Si_2 -type structure with identical Fe_2As_2 tetrahedral layers as in LaFeAsO , were also found to be superconducting with T_c up to 38 K upon hole doping [6–8].

In these so called “1111” and “122” compounds, it is well known that the Fe ions tend to form magnetically ordered states and participate in building up a high density of states at the Fermi level, which is responsible for the superconductivity [9]. However, very recently, LiFeAs and NaFeAs (111), with the PbFCl structure type and containing Fe_2As_2 tetrahedral layers, were reported to be superconducting ($T_c \sim 18$ K and 9–25 K, respectively) at ambient pressure without purposely doping carriers, and no signature of magnetic order was detected at temperature up to 300 K [10–13]. If the absence of magnetic order is an intrinsic property for the “111” compounds, it would strongly challenge the generally accepted picture that magnetic fluctuations play a crucial role in the superconducting pairing. While band structure calculation [14–16] on stoichiometric $\text{LiFeAs}/\text{NaFeAs}$ suggests that they should be similar to the parent compounds of 1111 and 122, and they should display magnetic orders rather than superconductivity in the ground state.

Experimentally, it is difficult to synthesize the stoichiometric LiFeAs and NaFeAs , because of the evaporation loss of Li/Na during the high-temperature reaction. It is reasonably convinced that carriers are introduced in $\text{LiFeAs}/\text{NaFeAs}$ by self-doping due to Li/Na deficiencies. It has been confirmed in the Li deficient sample $\text{Li}_{1-\delta}\text{FeAs}$

[10,11]. The absence of superconductivity was indeed found in the nearly stoichiometric LiFeAs synthesized by high pressure method. However, there is little experimental evidence for structural or magnetic transition. It may be due to Li deficiency, which introduces the level of carrier density close to a “critical value” just suppressing the spin-density-wave (SDW) order.

It is of great interest to investigate the electronic properties of the high-quality single crystal of these materials (111) and compare them with 1111 and 122 systems. Here we report on a comprehensive study of the transport, specific heat, and magnetic susceptibility on nearly stoichiometric single crystals of $\text{Na}_{1-\delta}\text{FeAs}$. We find that $\text{Na}_{1-\delta}\text{FeAs}$ single crystal undergoes three successive phase transitions at 52, 41, and 23 K, which might correspond to structural, magnetic and superconducting transitions, respectively. Hall coefficient measurement indicates the development of energy gap at low temperature in $\text{Na}_{1-\delta}\text{FeAs}$, which is similar to LaFeAsO and SrFe_2As_2 . This is consistent with the expectation of recent density functional calculation which shows the SDW instability for stoichiometric NaFeAs [14]. The present work provides a strong evidence that a stoichiometric NaFeAs has a magnetic ground state, similar to the parent compounds of 1111 and 122.

High-quality single crystals of $\text{Na}_{1-\delta}\text{FeAs}$ have been grown by the self-flux technique. The starting compositions were selected as $\text{Na}_{1.5}\text{FeAs}$. The mixtures of Na, and FeAs were put into an alumina crucible and sealed in Ta crucible under 2 atm of argon gas. The Ta crucible was then sealed in an evacuated quartz ampoule and heated to 1100 °C and cooled slowly (at 5 °C/h) to grow single crystals. The obtained crystals with sizes up to 8 mm × 5 mm × 0.5 mm have the form of platelets with shiny surfaces. These crystals were characterized by x-ray diffraction (XRD). Figure 1 shows the x-ray diffraction pattern of $\text{Na}_{1-\delta}\text{FeAs}$ with the 00ℓ reflections. The lattice constant $c = 7.028$ Å was calculated from the higher order peaks, comparable to that of polycrystalline sample [13].

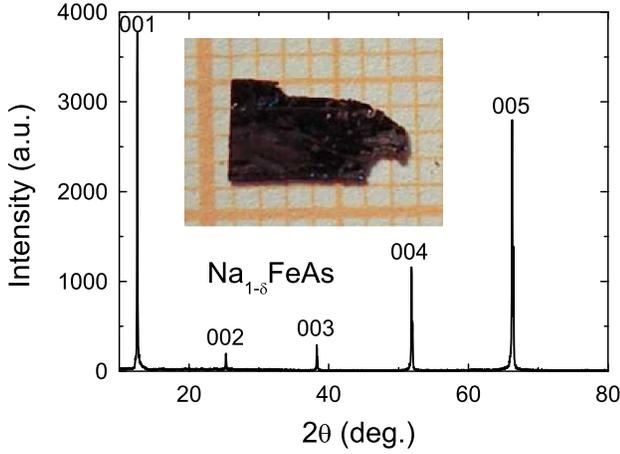


FIG. 1 (color online). Single crystal x-ray diffraction pattern for $\text{Na}_{1-\delta}\text{FeAs}$. The inset shows the photograph of a $\text{Na}_{1-\delta}\text{FeAs}$ single crystal (length scale 1 mm).

The elemental composition of the single crystal was checked by Inductively Coupled Plasma (ICP) analysis. Several crystals from the same batch were analyzed and the deficiency of sodium was found to be less than 1%; that is, the elemental composition of the single crystal is very close to a stoichiometric 1:1:1. The resistivity was measured by a standard 4-probe method. The dc magnetic susceptibility was measured with a magnetic field of 0.1 T. The Hall coefficient measurement was done using a five-probe technique. The specific heat measurement was carried out using a thermal relaxation calorimeter. These measurements were performed down to 2 K in a physical property measurement system (PPMS) of Quantum Design.

Figure 2(a) shows the temperature dependence of in-plane resistivity ρ_{ab} of $\text{Na}_{1-\delta}\text{FeAs}$ at zero field. At high temperature, ρ_{ab} shows a metallic behavior, whereas ρ_{ab} increases steeply below 52 K with a shoulder around 41 K, and then shows a superconducting transition near 23 K (drops to zero resistivity at 8 K). The superconducting transition seems to be broad, similar to that of polycrystal (not shown here). Here the former two anomalies may correspond to the structural and magnetic phase transitions. The increase of the electrical resistivity at the phase boundary might be attributed to the opening of a gap on part of the Fermi surfaces. This gap formation is very likely to be induced by the occurrence of an antiferromagnetic (AF) SDW, similar to the 1111 compounds. One consequence of this gap is to reduce the effective number of conduction electrons. We have also attempted to probe the influence of magnetic fields H on $\rho(T)$ with H up to 14 T, as shown in Figs. 2(b) and 2(c). We find that the magnetic phase transition temperature is insensitive to the applied field H and ρ is field-independent in the AF state for $H \parallel ab$ plane ($I \parallel ab$). However, when H is applied along the c axis, $[\rho_{ab}(14 \text{ T}) - \rho_{ab}(0 \text{ T})]/\rho_{ab}(0 \text{ T})$ reaches as high as 18% at 25 K. The large positive magnetoresistance was also observed in 1111 and 122 compounds [9,17].

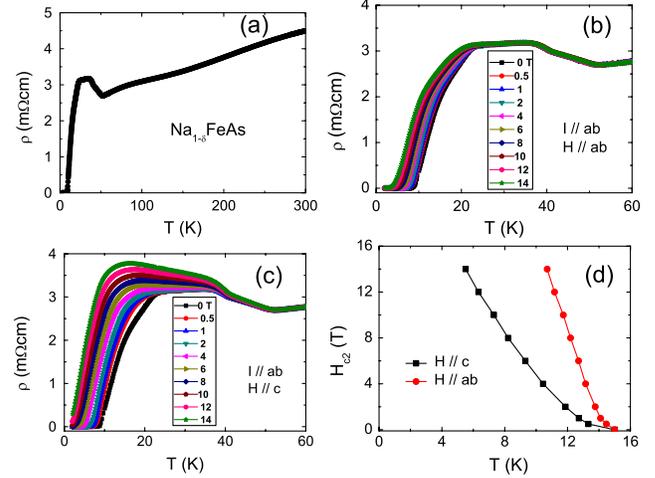


FIG. 2 (color online). (a) The in-plane resistivity ρ_{ab} for $\text{Na}_{1-\delta}\text{FeAs}$ at zero field. (b)–(c) Temperature dependence of the in-plane electrical resistivity for $\text{Na}_{1-\delta}\text{FeAs}$ in low temperature region at fixed fields up to 14 T for the $H \parallel ab$ plane and $H \parallel c$ axis. (d) $H_{c2}(T)$ plots for the $H \parallel ab$ plane (closed circle) and $H \parallel c$ axis (closed square), respectively.

Note that ρ increases more rapidly below 40 K at high magnetic fields, one might speculate that the magnetic order is formed at this temperature, and the structural phase transition occurs at higher temperature of 50 K in $\text{Na}_{1-\delta}\text{FeAs}$, in analogy to 1111 compounds, where the neutron experiment has revealed that the structural phase transition occurs prior to magnetic ordering.

Now let us see the magnetic field effect on superconductivity as shown in Figs. 2(b)–2(d). We can find the superconducting transition is broadened slightly in magnetic fields up to 14 T, although it has a broad transition at zero field. This behavior is rather different from polycrystalline LaFeAsO where the superconducting transition is broadened strongly in magnetic fields due to the weak link between superconducting grains [18]. Figure 2(d) shows $H_{c2} - T_c$ curves for both $H \parallel ab$ and $H \parallel c$, respectively, where T_c is defined by a criterion of 50% of normal state resistivity. The curves $H_{c2}(T)$ are very steep with slopes $-dH_{c2}^{ab}/dT|_{T_c} = 3.98 \text{ T/K}$ for $H \parallel ab$ and $-dH_{c2}^c/dT|_{T_c} = 2.19 \text{ T/K}$ for $H \parallel c$. Using the Werthamer-Helfand-Hohenberg formula [19] $H_{c2}(0) = -0.69(dH_{c2}/dT)T_c$ and taking $T_c = 15 \text{ K}$, the upper critical fields are estimated as $H_{c2}^{ab} = 41.2 \text{ T}$ and $H_{c2}^c = 22.7 \text{ T}$, respectively. Regarding the relatively low value of T_c , the upper critical fields $H_{c2}(0)$ seem to be very high. The anisotropy ratio $\gamma = H_{c2}^{ab}/H_{c2}^c \approx 1.8$ is rather small, which is close to that of $\text{Sr}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ with $\gamma \approx 2.0$ [17]. It is much lower than high T_c cuprates, for example $\gamma \approx 7\text{--}10$ for YBCO [20]. The lower value of γ indicates that the interplane coupling in $\text{Na}_{1-\delta}\text{FeAs}$ is relative strong and the energy band with strong dispersion along the z direction may play an important role in understanding the superconductivity of Fe-based superconductors.

In Fig. 3(a), we present the temperature dependence of magnetic susceptibility χ for $\text{Na}_{1-\delta}\text{FeAs}$ in a field of 0.1 T with the $H \parallel ab$ plane and $H \parallel c$ axis, respectively. At high-temperature, χ decreases monotonically with decreasing temperature. This non-Pauli and non-Curie-Weiss-like paramagnetic behavior, is consistent with those observed in 1111 and 122 parent compounds above T_{SDW} [1,17,21]. At low temperature, χ tends to show a small upturn, and followed by a clear diamagnetic drop corresponding to superconductivity at around 10 K, which corresponds to the zero resistivity temperature. To show the low temperature part clearly, we have plotted in the inset of Fig. 3(a) the susceptibility in the temperature interval from 30 to 60 K. Two humps found in χ with magnetic field H parallel to the ab plane at 40 and 50 K give that the magnetic easy axis of this compound is along the ab plane (There is no detectable anomaly observed in χ with $H \parallel c$). That is to say, the Fe spins in NaFeAs order antiferromagnetically with spin direction parallel to the ab plane, similar to that of SrFe_2As_2 which has been confirmed by neutron scattering experiment [22].

To get more information about the structural or magnetic phase transition, we performed specific heat measurements for $\text{Na}_{1-\delta}\text{FeAs}$. Figure 3(b) shows the temperature dependence of C/T from 2 to 60 K. Two successive jumps in C/T at $T_1 \sim 41$ K and $T_2 \sim 52$ K show the bulk nature of phase transitions which have been observed in susceptibility and resistivity data as well. However, the anomalies around T_1 and T_2 are very broad and small, which would be characteristic of a second-order transition. Very similar properties have been reported on 1111 compounds, such as LaFeAsO , where two subsequent jumps at 155 and 143 K were observed in specific heat data corresponding to the structural and SDW transitions, respectively [23]. While the structural transition and SDW transition occur at same temperature in SrFe_2As_2 . The specific heat shows a very sharp peak which is the characteristic feature of first-order phase transitions [17]. The conversion of first-order

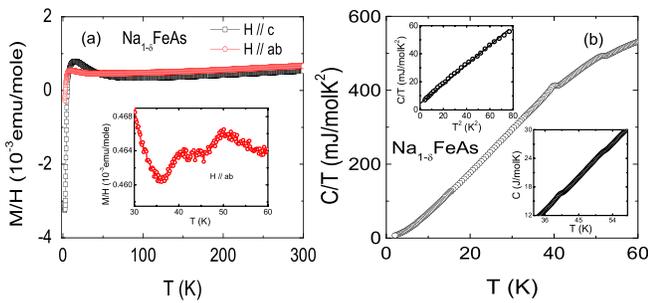


FIG. 3 (color online). (a) Magnetic susceptibility of $\text{Na}_{1-\delta}\text{FeAs}$ as a function of temperature with the $H \parallel ab$ plane and $H \parallel c$ axis, respectively. The inset shows the expanded view of χ between 30 and 60 K. (b) Temperature dependence of specific heat divided by temperature C/T for $\text{Na}_{1-\delta}\text{FeAs}$. The upper inset shows the fit of C/T vs T^2 in the low temperature region. The lower inset shows the plot of C vs T around the structural and magnetic phase transitions.

transition to second-order transition has also been observed in those of slightly underdoped samples of $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ ($x < 0.2$), in which the single structural or magnetic phase transition splits into two distinct phase transitions (The first-order phase transition starts rounding off and becomes smaller as more Co ions are added in the pure system) [24]. The onset of a second-order phase transition is probably related to a change of symmetry in the ground state [25,26]. Theoretical studies also suggest that whether the structural and magnetic transitions occur simultaneously or separately depends on the interlayer coupling [25,26]. The separation of structural distortion and the magnetic transition in the present compound indicates that the interlayer coupling is closer to that of 1111 compounds, but much weaker than 122 compounds.

At low temperature, there is no detectable anomaly observed around T_c , indicating a small superconducting volume fraction; the fit of C/T vs T^2 yields the electronic coefficient $\gamma \approx 5$ mJ/mol \cdot K², as shown in the upper inset of Fig. 3(b). Here the electronic coefficient for $\text{Na}_{1-\delta}\text{FeAs}$ is close to the values for LaFeAsO and SrFe_2As_2 (which are significantly smaller than the theoretical calculations due to the SDW partial gap) [9,17].

The Hall coefficient R_H as a function of temperature between 20 and 200 K for $\text{Na}_{1-\delta}\text{FeAs}$ is shown in Fig. 4. The Hall coefficient is negative at all temperatures, indicating conduction carriers are dominated by electrons. Above 50 K, the Hall coefficient is nearly temperature independent; the carrier density is estimated being $n \approx 9 \times 10^{21}$ cm⁻³ at 200 K if the one-band model is simply adopted. It is comparable to that of SrFe_2As_2 with $n \approx 1.5 \times 10^{22}$ cm⁻³ at 300 K obtained by the same method. The large carrier number for $\text{Na}_{1-\delta}\text{FeAs}$ indicates that it is a good metal. Noted that the band calculation on its sister compound of LiFeAs revealed its semimetallic behavior. As mentioned above, there is a possibility that Na defi-

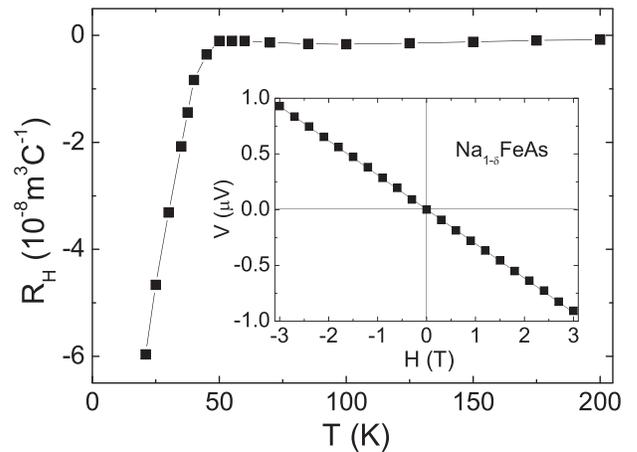


FIG. 4. Temperature dependence of Hall coefficient for $\text{Na}_{1-\delta}\text{FeAs}$. The inset shows the verification of the Hall voltage driven by magnetic field where a linear dependence of the transverse voltage on the applied magnetic field is observed up to 3 T at 40 K.

ciencies serve as a source of effective hole carriers. So it is an extremely rare case the measurement of a negative Hall coefficient in nominally hole-doped Fe-based superconductors. However, this behavior could be qualitatively understood by a simple two-band approximation. In a scenario where the Fermi surface contains both electron and hole pockets, the sign of R_H depends on the relative magnitude of the respective densities, n_e and n_h , and mobilities, μ_e and μ_h ($\mu = e\tau/m^*$, where e is the electron charge, $1/\tau$ is the scattering rate and m^* is the effective mass). And therefore, in the “hole”-doped sample, the negative R_H implies that μ_e is much larger than μ_h . Below 50 K, R_H drops dramatically to a very large negative value. The absolute value of R_H at 23 K is about 60 times larger than that at 60 K. The huge increase of the R_H value is seen in the undoped compounds of 1111 and 122, which is naturally explained by the gapping of the Fermi surface which removes a large part of free carriers. Evidence for the gap is also observed by optical spectroscopy measurement [27]. The band calculation shows that a hole pocket is lying around the center of Brillouin zone (BZ) and the electron pockets are lying at the BZ corners. Therefore, the low temperature behavior of the Hall effect for $\text{Na}_{1-\delta}\text{FeAs}$ may be understood with the following scenario: with temperature down to below T_{SDW} , the hole pocket is almost fully gapped while the electron pockets are partially gapped. The negative Hall coefficient R_H reflects mainly the ungapped electron density at the BZ corner.

In summary, we have succeeded in growing the high-quality single crystal of nearly stoichiometric $\text{Na}_{1-\delta}\text{FeAs}$ and studied the electronic properties by measurements of electrical resistivity, heat capacity, and Hall effect. This compound is found to undergo the structural, magnetic and superconducting transitions at low temperatures. The negative Hall coefficient R_H suggests that the electron type charge carriers dominate the conduction in this material. Although the present experiments cannot completely rule out a tiny amount of Na deficiencies, our present data provide the first direct experimental evidence confirming the existence of SDW instability in NaFeAs , which are consistent with the theoretical predication. We believe that our results are important to understand the mechanism of superconductivity and underline further the importance of magnetic fluctuations for the superconductivity pairing observed in Fe-based superconductors.

This work is supported by the NSFC, CAS, and the 973 project of the MOST of China.

Note added.—In the published version of [13], new μSR data were added to the original preprint indicating the presence of magnetic order near 40 K, which thus supports the conclusion of present work about magnetic ordering.

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).

- [2] 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**, 247002 (2008).
- [3] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, *Nature (London)* **453**, 761 (2008).
- [4] 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, *Europhys. Lett.* **82**, 57002 (2008).
- [5] C. Wang, L. J. Li, S. Chi, Z. W. Zhu, Z. Ren, Y. K. Li, Y. T. Wang, X. Lin, Y. K. Luo, S. Jiang, X. F. Xu, G. H. Cao, and Z. A. Xu, *Europhys. Lett.* **83**, 67006 (2008).
- [6] M. Rotter, M. Tegel, and D. Johrendt, *Phys. Rev. Lett.* **101**, 107006 (2008).
- [7] G. F. Chen, Z. Li, G. Li, W. Z. Hu, J. Dong, X. D. Zhang, P. Zheng, N. L. Wang, and J. L. Luo, *Chin. Phys. Lett.* **25**, 3403 (2008).
- [8] M. S. Torikachvili, S. L. Bud'ko, N. Ni, and P. C. Canfield, *Phys. Rev. Lett.* **101**, 057006 (2008).
- [9] J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Z. Hu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, Z. Fang, and N. L. Wang, *Europhys. Lett.* **83**, 27006 (2008).
- [10] 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, *Solid State Commun.* **148**, 538 (2008).
- [11] J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, Paul C. W. Chu, and A. M. Guloy, *Phys. Rev. B* **78**, 060505(R) (2008).
- [12] C. W. Chu, F. Chen, M. Gooch, A. M. Guloy, B. Lorenz, B. Lv, K. Sasmal, Z. J. Tang, J. H. Tapp, and Y. Y. Xue, arXiv:0902.0806.
- [13] D. R. Parker, M. J. Pitcher, P. J. Baker, I. Franke, T. Lancaster, S. J. Blundell, and S. J. Clarke, *Chem. Commun. (Cambridge)*, **2009**, 2189.
- [14] R. A. Jishi and H. M. Alyahyaei, arXiv:0812.1215.
- [15] D. J. Singh, *Phys. Rev. B* **78**, 094511 (2008).
- [16] I. A. Nekrasov, Z. V. Pchelkina, and M. V. Sadovskii, *JETP Lett.* **88**, 543 (2008).
- [17] G. F. Chen, Z. Li, J. Dong, G. Li, W. Z. Hu, X. D. Zhang, X. H. Song, P. Zheng, N. L. Wang, and J. L. Luo, *Phys. Rev. B* **78**, 224512 (2008).
- [18] G. F. Chen, Z. Li, G. Li, J. Zhou, D. Wu, J. Dong, W. Z. Hu, P. Zheng, Z. J. Chen, H. Q. Yuan, J. Singleton, J. L. Luo, and N. L. Wang, *Phys. Rev. Lett.* **101**, 057007 (2008).
- [19] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, *Phys. Rev.* **147**, 295 (1966).
- [20] K. K. Nanda, *Physica (Amsterdam)* **265C**, 26 (1996).
- [21] G. M. Zhang, Y. H. Su, Z. Y. Lu, Z. Y. Weng, D. H. Lee, and T. Xiang, arXiv:0809.3874 and references therein.
- [22] J. Zhao, D. X. Yao, S. Li, T. Hong, Y. Chen, S. Chang, W. Ratcliff, J. W. Lynn, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, E. W. Carlson, J. P. Hu, and P. C. Dai, *Phys. Rev. Lett.* **101**, 167203 (2008).
- [23] M. A. McGuire *et al.*, *Phys. Rev. B* **78**, 094517 (2008).
- [24] J. H. Chu, J. G. Analytis, C. Kucharczyk, and I. R. Fisher, *Phys. Rev. B* **79**, 014506 (2009).
- [25] C. Fang, H. Yao, W. F. Tsai, J. P. Hu, and S. A. Kivelson, *Phys. Rev. B* **77**, 224509 (2008).
- [26] Y. Qi and C. K. Xu, arXiv:0812.0016.
- [27] W. Z. Hu *et al.* (unpublished).