Effect of Li-deficiency impurities on the electron-overdoped LiFeAs superconductor

Meng Wang,1 Miaoyin Wang,2 Hu Miao,1 S. V. Carr,2 D. L. Abernathy,3 M. B. Stone,3 X. C. Wang,1 Lingyi Xing,1 C. Q. Jin,1 Xiaotian Zhang,1 Jiangping Hu,1,4 Tao Xiang,1 Hong Ding,1 and Pengcheng Dai2,1

1Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
2Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200, USA
3Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6393, USA
4Department of Physics, Purdue University, West Lafayette, Indiana 47907, USA

We use transport, inelastic neutron scattering, and angle resolved photoemission experiments to demonstrate that the stoichiometric LiFeAs is an intrinsically electron-overdoped superconductor similar to those of the electron-overdoped NaFe1−xTnxAs and BaFe2−xTnxAs2 (T = Co, Ni). Furthermore, we show that transport properties of the stoichiometric superconducting LiFeAs and Li-deficient nonsuperconducting Li1−xFeAs are different, their electronic and magnetic properties are rather similar. Therefore, the nonsuperconducting Li1−xFeAs is also in the electron overdoped regime, where small Li deficiencies near the FeAs octahedra can dramatically suppress superconductivity through the impurity scattering effect.

PACS numbers: 74.25.Ha, 74.70.-b, 78.70.Nx

Superconductivity in iron pnictides occurs near an antiferromagnetic (AF) instability [1][2]. When the AF order in a nonsuperconducting (NSC) parent compound is suppressed by electron or hole doping, superconductivity emerges with the persistent short-range spin excitations directly coupled to the superconducting (SC) transition temperature $T_c$. While this general behavior is obeyed in most iron pnictide superconductors and suggests the importance of magnetism to the superconductivity of these materials [3][4], the only exception is the stoichiometric LiFeAs (Fig. 1a), which does not have a static AF ordered parent compound and superconductors with a relatively high $T_c$ of ~17 K without any doping [5][6]. Furthermore, a few percent of Li deficiencies in Li1−xFeAs can increase the resistivity and destroy superconductivity (Figs. 1b and 1c) [7]. Indeed, the absence of the AF order in LiFeAs is caused by the poor nesting condition between the shallow hole-like Fermi pocket near the $\Gamma(0,0)$ point and the large electron Fermi surface at the $M(1,0)/(0,1)$ points in the Brillouin zone (Fig. 1d) [8]. These observations have fueled the suggestion that the mechanism of superconductivity in LiFeAs is due to fermionic instability and p-wave triplet pairing [9][10]. This is fundamentally different from all other iron pnictides, where the singlet electron pairing superconductivity and AF order are both believed to be associated with the sign reversed quasiparticle excitations between the hole and electron Fermi surfaces near the $\Gamma(0,0)$ and $M(1,0)/(0,1)$ points [11][12].

Here we describe transport, inelastic neutron scattering, and angle resolved photoemission (ARPES) experiments on the stoichiometric SC LiFeAs and Li-deficient NSC Li1−xFeAs. We find that a few percent Li-deficiencies in Li1−xFeAs can completely suppress superconductivity and change transport properties but without much affecting the sizes of the Fermi surfaces [13] and incommensurate spin excitations in the SC LiFeAs [14]. By comparing our results with previous work on the SC LiFeAs [15,16], NaFe1−xCo$_x$As [17,18], BaFe$_{2−x}$T$_x$As$_2$ (T = Co, Ni) [19,20], and LaFe$_{1−y}$Zn$_y$AsO$_{1−x}$F$_x$ [21], we conclude that the stoichiometric LiFeAs is an intrinsically electron-overdoped superconductor, and that Li deficiencies affect its SC properties similar to the Zn impurity effects in the electron-overdoped iron pnictide superconductors [22]. Therefore, the mechanism of superconductivity in LiFeAs is associated with AF spin excitations and not fundamentally different from all other iron-based superconductors [13][16].

Our transport measurements on the SC and NSC Li1−xFeAs were carried out on a commercial physical properties measurement system using the four probe method. The inelastic neutron scattering experiments were performed on the ARCS time-of-flight chopper spectrometer at the spallation neutron source, Oak Ridge National Laboratory [23]. The ARPES experiments were performed at the PGM beaceline of the Synchrotron Radiation Center, Stoughton, Wisconsin. The energy and angular resolutions of the ARPES measurements were set at ±20 meV and 0.2°, respectively. The samples were cleaved in situ and measured at 20 K in a vacuum better than 4 × 10$^{-11}$ Torr. The incident photon energy was chosen to be $h\nu = 35$ eV. Our single crystals of the SC LiFeAs were grown using the self flux method with the $^7$Li isotope to minimize the neutron absorption effect. The method for growing the NSC Li1−xFeAs with natural Li were described previously [24]. The inductively coupled plasma analysis on the samples showed that the compositions of the NSC crystals are Li$_{0.94±0.01}$Fe$_{0.06}$As [25]. To within the errors of our measurements, the SC LiFeAs was found to be stoichiometric. Figure 1b shows temperature dependence of the resistivity for the SC and NSC Li1−xFeAs. Figure 1c plots the expanded view of the

Superconductivity through the impurity scattering effect.
FIG. 1: (color online). (a) Phase diagram of the electron doped NaFe$_{1-x}$Co$_x$As from Ref. [21]. The inset shows the structure of Na(Li)FeAs and the differences in the angles of the two alkali arsenic planes based on the structural parameters from Ref. [7] for LiFeAs and Ref. [20] for NaFeAs. (b) The temperature dependence of resistivity for the SC LiFeAs (solid line) and NSC Li$_{0.94}$FeAs (dashed line) up to room temperature. The data are normalized by the size and mass of the single crystals. (c) Expanded view of the temperature dependence of the resistivity for the SC and NSC Li$_{1-x}$FeAs. The SC LiFeAs has a clear transition to superconductivity at 16 K. (d) Schematic Fermi surfaces of LiFeAs from Ref. [17]. The red shadow indicates a flat band in the center of the Γ(0, 0) point. The incommensurability from the ARPES measurements is defined as $\delta K$, the mismatch of the inner hole Fermi surface and electron Fermi surfaces. (e) The energy dependence of the incommensurability for the incommensurate spin excitations from the SC LiFeAs (the red squared symbols), NSC Li$_{0.94}$FeAs (the olive diamond symbols), and the APRES measurements (the grey dash line). The violet solid line is the incommensurability value from Ref. [18]. The inset shows the locations of the incommensurate peaks near the in-plane AF wave vector $Q = (1, 0)$ in LiFeAs.

low-temperature resistivity for both samples, which reveals a $T_c = 16$ K for the SC LiFeAs and larger resistivity for the NSC Li$_{0.94}$FeAs. For inelastic neutron scattering measurements on ARCS, we co-aligned approximately 3.95 grams of the SC single crystals of LiFeAs with a mosaic of 2°. The NSC Li$_{0.94}$FeAs was the same sample used in our previous measurements [27]. They are mounted inside a He exchange gas filled thin aluminum can which was mounted directly to the cold-finger of a closed cycle He refrigerator for ARCS measurements, where the wave vector $Q$ at $(q_x, q_y, q_z)$ in Å$^{-1}$ is defined as $(H, K, L) = (q_x a/2\pi, q_y b/2\pi, q_z c/2\pi)$ reciprocal lattice units (rlu) with $a = b = 5.316$ Å, and $c = 6.306$ Å.

In our previous inelastic neutron scattering work on the NSC Li$_{0.94}$FeAs with natural Li [27], we have reported the presence of a large spin gap of $\Delta = 13$ meV at the AF ordering wave vector $Q = (1, 0, 3)$ using triple-axis spectroscopy. The gap was found to be temperature independent between 2 and 190 K [27]. More recently, inelastic neutron scattering experiments on the SC LiFeAs with the $^7$Li isotope found low-energy ($1.5 \leq E \leq 13$ meV) transverse incommensurate spin excitations that appear to couple to $T_c$ [18]. In the light of this development, we have carried out new measurements on ARCS with the incident neutron beam direction parallel to the $c$-axis and $E_i = 35$ meV for both the SC LiFeAs and NSC Li$_{0.94}$FeAs at 5 K. For the NSC Li$_{0.94}$FeAs with highly neutron absorbing $^6$Li, the scattering geometry at ARCS is much better than the earlier triple-axis measurements [27] because neutrons only have to pass the thinnest part of the platelet samples. Figure 2 summarizes the outcome of these measurements. For the SC LiFeAs, Figures 2a-2d show the two-dimensional constant-energy $(E)$ images of the scattering in the $(H, K)$ plane for $E = 7 \pm 1$, 9 \pm 1, 11 \pm 1, and 15 \pm 1$ meV, respectively. Consistent
FIG. 3: (color online). Constant-energy cuts of spin excitations along the [1, K] direction for the SC LiFeAs and NSC Li$_{0.94}$FeAs at energy transfers of (a) $E = 5 \pm 1$ meV; (b) $7 \pm 1$ meV; (c) $11 \pm 1$ meV; (d) $13 \pm 1$ meV; (e) $17 \pm 1$ meV; (f) $19 \pm 1$ meV; all with $E_i = 35$ meV. The solid lines are fits to two Gaussian peaks. The dashed vertical lines in (c), marked the center of peaks, indicate the definition of incommensurability of spin excitations as in previous work [18]. The cuts for the SC and NSC spin excitations spectra were subtracted by the same fitted NSC background at the identical energy. The intensity is in absolute units, and error bars indicate one standard deviation. For presentation, the SC data are offset vertically by 2 units for all panels.

with previous work [18], we can see clear transverse incommensurate peaks centered near the in-plane AF wave vector $Q = (1, 0)$ at all the probed energies. Figures 2e-2h plot two-dimensional scattering images for the NSC Li$_{0.94}$FeAs at $E = 7 \pm 1, 9 \pm 1, 11 \pm 1$, and $15 \pm 1$ meV, respectively. These results reveal the presence of low-energy spin excitations in the NSC Li$_{0.94}$FeAs, different from the earlier triple-axis measurement [27]. While spin excitations are clearly incommensurate at the probed energies for the SC LiFeAs (Figs. 2a-2d), the incommensurability is less well-defined for the NSC Li$_{0.94}$FeAs (Figs. 2e-2h).

To quantitatively determine the differences in spin excitations of the SC and NSC Li$_{1-x}$FeAs, we cut through the transverse direction of the two-dimensional scattering images in Fig. 2 for both samples. Figures 3a-3f show constant-energy cuts along the [1, K] direction for energies of $E = 5 \pm 1, 7 \pm 1, 11 \pm 1, 13 \pm 1, 17 \pm 1$, and $19 \pm 1$ meV, respectively. Inspection of the Figure reveals that the incommensurabilities of spin excitations for both the SC and NSC Li$_{1-x}$FeAs are very similar and nearly energy independent within the probed excitation energy range of $5 \leq E \leq 19$ meV. However, the incommensurate spin excitations in the SC LiFeAs have better defined peaks with longer spin-spin correlation lengths compared with that of the NSC Li$_{0.94}$FeAs (Fig. 3). Simple Gaussian fits to the data in Fig. 3 are able to extract the incommensurate peak position, $\delta_K$, as a function of energy transfer. This is shown in Fig. 1e, again illustrating the similar amount of and the lack of change of incommensurability with energy transfer in both compounds. Based on these data, we see that the low-energy spin excitations in the superconductivity-suppressed Li$_{0.94}$FeAs are remarkable similar to those of the SC LiFeAs. Therefore, Li-deficiency induced suppression of superconductivity does not fundamentally alter the magnetic properties of the SC LiFeAs.

If we assume that the Li-deficiencies in Li$_{1-x}$FeAs remove electrons from the FeAs octahedra, the SC LiFeAs should have a larger electron-doping level than that of the NSC Li$_{0.94}$FeAs and therefore should have a larger electron Fermi surface size. Figures 4a and 4b show the ARPES intensity mappings of the SC LiFeAs and NSC Li$_{0.94}$FeAs, respectively. Figure 4c plots the corresponding hole and electron Fermi pockets near the $\Gamma(0,0)$ and $M(1,0)/(0,1)$ points, respectively, for the SC and NSC samples. To within the errors of our measurements, we find that the SC LiFeAs and NSC Li$_{0.94}$FeAs have the same Fermi surface topology (Fig. 4c). Therefore, a few percent Li-deficiencies in Li$_{1-x}$FeAs do not dramatically change the hole and electron Fermi pocket sizes and alter the Fermi surface nesting conditions. This is consistent with the similar incommensurate spin excitations in the SC and NSC Li$_{1-x}$FeAs (Figs. 2 and 3), but con-
tary to the naive expectation that the Li-deficiencies in Li_{1-x}FeAs should reduce the sizes of the electron Fermi surface and enlarge the hole Fermi surface.

In previous work, nonmagnetic Zn impurities were found to severely suppress superconductivity for LaFeAsO_{1-x}F_x in the electron-overdoped regime but were much less effective in reducing T_c for the under and optimally electron doped samples [26]. Similarly, Zn impurities were found to be effective in suppressing superconductivity in BaFe_{2-x}Co_xAs_2 [23]. This behavior is consistent with the s±-wave SC state, where the nonmagnetic impurity scattering should rapidly decrease T_c [27]. If we assume that the Li-vacancies in Li_{1-x}FeAs indeed have a limited impact on the size of the electron and hole Fermi surfaces, the rapid suppression of superconductivity by small amount of Li-deficiencies may indicate that superconductivity in the stoichiometric LiFeAs is in the electron-overdoped regime [29]. To see why this may be the case, we consider the lattice structure near the FeAs octahedra can act as impurity centers which scatter off conduction band electrons. The LiFeAs near the FeAs octahedra can act as impurity centers which scatter off conduction band electrons. The LiFeAs near the FeAs octahedra can act as impurity centers which scatter off conduction band electrons. The stoichiometric LiFeAs is an intrinsically electron-overdoped superconductor.

Moreover, recent systematic scanning tunneling microscopy (STM) measurements on NaFe_{1-x}Co_xAs reveal that the tunneling spectra dI/dV change from the symmetric lineshape of the electron- [20] to a strong asymmetric lineshape in the electron overdoped regime (x = 0.061) [22]. Since STM measurements on the SC LiFeAs (see Fig. 1b in Ref. [12]) show strong asymmetric tunneling spectra consistent with that of the electron overdoped NaFe_{1-x}Co_xAs with x = 0.061 [22], it is inevitable that the SC and NSC Li_{1-x}FeAs are in the electron overdoped regime similar to the electron overdoped NaFe_{1-x}Co_xAs (Fig. 1a).

We thank P. Richard, T. Qian, Zhuan Xu, Shiliang Li, and Yayu Wang for helpful discussions. The work in IOP is supported by the MOST of China through 973 projects: 2012CB821400, 2010CB833102, and 12J2010CB923001. The work at UTK is supported by the U.S. DOE BES No. DE-FG02-05ER46202. The research at ORNL’s SNS was sponsored by the Scientific User Facilities Division, BES, U.S. DOE. The ARPES work at SRC is primarily funded by the University of Wisconsin-Madison with supplemental support from facility Users and the University of Wisconsin-Milwaukee.
Electronic address: pdai@utk.edu

[1] Y. Kamihara et al., J. Am. Chem. Soc. 130, 3296 (2008).
[2] C. de la Cruz et al., Nature (London) 453, 899 (2008).
[3] M. D. Lumsden and A. D. Christianson, J. Phys.: Condens. Matter 22, 203203 (2010).
[4] J. W. Lynn and P. C. Dai, Physica C 469, 469 (2009).
[5] X. C. Wang et al., Solid State Commun. 148, 538 (2008).
[6] J. H. Tapp et al., Phys. Rev. B 78, 060505(R) (2008).
[7] M. J. Pitcher et al., Chem. Commun., 5918 (2008).
[8] F. L. Pratt et al., Phys. Rev. B 79, 052508 (2009).
[9] C. W. Chu et al., Physica C 469, 326 (2009).
[10] S. V. Borisenko et al., Phy. Rev. Lett. 105, 067002 (2010).
[11] P. M. R. Brydon et al., Phys. Rev. B 83, 060501(R) (2011).
[12] T. Hänke et al., Phys. Rev. Lett. 108, 127001 (2012).
[13] P. J. Hirschfeld, M. M. Korshunov, I. I. Mazin, Rep. Prog. Phys. 74, 124508 (2011).
[14] K. Kuroki et al., Phys. Rev. Lett. 101, 087004 (2008).
[15] A. V. Chubukov, Annu. Rev. Condens. Matter Phys. 3, 13 (2012).
[16] F. Wang et al., Phys. Rev. Lett. 102, 047005 (2009).
[17] K. Umezawa et al., Phys. Rev. Lett. 108, 037002 (2012).
[18] N. Qureshi et al., Phys. Rev. Lett. 108, 117001 (2012).
[19] A. E. Taylor et al., Phys. Rev. B 83, 220514 (R) (2011).
[20] S. L. Li et al., Phys. Rev. B 80, 020504(R) (2009).
[21] D. R. Parker et al., Phys. Rev. Lett. 104, 057007 (2010).
[22] X. D. Zhou et al., [arXiv:1204.4237].
[23] C. Lester, J.-H. Chu, J. G. Analytis, T. G. Perring, I. R. Fisher, and S. M. Hayden, Phys. Rev. B 81, 064505 (2010).
[24] J. T. Park et al., Phys. Rev. B 82, 134503 (2010).
[25] H. Q. Luo et al., [arXiv:1206.0653].
[26] Y. K. Li et al., New J. Phys. 12, 083008 (2010).
[27] M. Wang et al., Phys. Rev. B 83, 220515 (R) (2011).
[28] J. Li et al., Solid State Communications 152, 671 (2012).
[29] R. M. Fernandes, M. G. Vavilov, and A. V. Chubukov, Phys. Rev. B 85, 140512 (R) (2012).
[30] M. A. Tanatar et al., Phys. Rev. B 85, 014510 (2012).
[31] Y. Bang, H.Y. Choi, H. Won, Phys. Rev. B 79, 054529 (2009).
[32] C. Putzke et al., Phys. Rev. Lett. 108, 047002 (2012).
[33] S. Graser, A. F. Kemper, T. A. Maier, H.-P. Cheng, P. J. Hirschfeld, and D. J. Scalapino, Phys. Rev. B 81, 214503 (2010).
[34] C. L. Zhang et al., Scientific Reports 1, 115 (2011).
[35] J.-P. Castellan et al., Phys. Rev. Lett. 107, 177003 (2011).