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

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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−xTixAs and BaFe2−xTixAs2 (T = Co, Ni). Furthermore, we show that although 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.

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I. INTRODUCTION

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 Tc.3,4 While this general behavior is obeyed in most iron pnictide superconductors and suggests the importance of magnetism to the superconductivity of these materials,3–5 the only exception is the stoichiometric LiFeAs [Fig. 1(a)], which does not have a static AF ordered parent compound and superconducts with a relatively high Tc of ~17 K without any doping.6–10 Furthermore, a few percent of Li deficiencies in Li1−xFeAs can increase the resistivity and destroy superconductivity [Figs. 1(b) and 1(c)].6,11 If antiferromagnetism is a common thread for the electron pairing and superconducting in iron-based superconductors,12 one would expect that spin excitations in the SC and NSC Li1−xFeAs have some common features with other iron-based superconductors.3–5 On the other hand, if antiferromagnetism is not important in iron-based superconductors, the mechanism of superconductivity in LiFeAs could be principle be different from other iron-based materials. Indeed, based on early angle-resolved photoemission spectroscopy (ARPES) experiments, the absence of the static AF order in LiFeAs is believed to be caused by the poor nesting condition between the shallow hole-like Fermi pocket near the Γ(0,0) point and the large electron Fermi surface at the M(1,0)/(0,1) points in the Brillouin zone [Fig. 1(d)].13 These observations have fueled the suggestion that the mechanism of superconductivity in LiFeAs is due to the ferromagnetic instability and p-wave triplet pairing.13–15 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 Γ(0,0) and M(1,0)/(0,1) points.16–19

More recently, high-resolution ARPES experiments revealed the presence of nodeless SC gaps in the hole and electron Fermi pockets near the Γ(0,0) and M(1,0)/(0,1), respectively, in the SC LiFeAs, consistent with AF instead of ferromagnetic interactions.20,21 Based on inelastic neutron scattering experiments on the SC single crystal LiFeAs, the low-energy spin excitations (1.5 ≤ E ≤ 13 meV) were found to respond to superconductivity and occur at the incommensurate wave vectors transverse to the in-plane AF electron-hole pocket nesting wave vector QAF = (1,0).21 By noting that the electron-underdoped iron pnictide BaFe2−xTixAs2 (T = Co, Ni)22,23 have transverse incommensurate static AF (spin-density-wave) order, the authors conclude that the SC LiFeAs should be compared with the electron-doped materials although its electron doping status is still unknown.21 These results are different from the earlier neutron scattering experiments on powder SC LiFeAs24 and single crystal NSC LiFeAs,25 where a large normal-state spin gap (~10 meV) has been reported. Given the rather confusing experimental situation, it is important to carry out new transport, neutron scattering, and ARPES experiments to sort out the differences in the electronic structures and spin excitations between the SC and NSC Li1−xFeAs, and determine why Li1−xFeAs has no static AF order and why its superconductivity is so sensitive to a small amount of Li deficiency.11

Here we describe transport, inelastic neutron scattering, and ARPES experiments on the stoichiometric SC LiFeAs and Li-deficient NSC Li1−xFeAs. We find that a few percent Li deficiency can completely suppress superconductivity and change transport properties but without significant effect on the sizes of the Fermi surfaces,20 and incommensurate spin excitations.21 By comparing our results with previous work on the SC LiFeAs,20,21 NaFe1−xCo1−xAs,26–28 BaFe2−xTixAs2,29,31 and LaFe1−xZnxAsO1−xFy,32 we conclude that the stoichiometric LiFeAs is an intrinsically electron-overdoped superconductor similar to NaFe1−xCo1−xAs with x ~ 0.065, and that Li deficiencies affect its SC properties similar to the Zn-impurity effects in the electron-overdoped iron pnictide superconductors.33 These results naturally explain the absence of the static AF order in Li1−xFeAs, and why superconductivity in LiFeAs is so sensitive to the Li deficiency. Therefore, the
ARPES measurements is defined as near the in-plane AF wave vector \( Q \) in the center of the planes based on the structural parameters from Ref. 8 for LiFeAs and Na(Li)FeAs and the differences in the angles of the two alkali arsenic. The violet solid line is the incommensurability value from olive diamond symbols, and the APRES measurements (the gray dash line). 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 neutron absorption. The method for growing the NSC Li\(_{1-x}\)FeAs with natural Li was described previously. The inductively coupled plasma analysis on the samples showed that the compositions of the NSC crystals are Li\(_{0.94}\)Fe\(_{0.01}\)FeAs. Previous Rietveld analysis of the powder neutron diffraction data suggests that NSC Li\(_{1-x}\)FeAs also has a small amount of As deficiency that we cannot determine from the inductively coupled plasma analysis. To within the errors of our measurements, the SC LiFeAs was found to be stoichiometric. Figure 1(b) shows temperature dependence of the resistivity for the SC and NSC Li\(_{1-x}\)FeAs. Figure 1(c) plots the expanded view of the low-temperature resistivity for both samples, which reveals a \( T_c = 16 \) K for the SC LiFeAs and larger resistivity for the NSC Li\(_{0.93}\)FeAs. For inelastic neutron scattering measurements, we co-aligned approximately 3.95 grams of 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. These samples were mounted inside a He-exchange-gas-filled thin aluminum can which was mounted directly to the cold finger of a closed-cycle He refrigerator, where the wave vector \( Q \) at \((q_x, q_y, q_z)\) in \( \text{Å}^{-1} \) is defined as \( Q = (H, K, L) = (q_x/a, 2\pi, q_y/b, 2\pi, q_z/c, 2\pi) \) 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, we 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. 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 \( T_c \). 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\(_{0.93}\)FeAs at 5 K. Figure 2 summarizes the outcome of these measurements. For the SC LiFeAs, Figures 2(a)–2(d) show 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 with previous work, we can see clear transverse incommensurate peaks centered near the in-plane AF wave vector \( Q = (1, 0) \) at all the probed energies. Figures 2(e)–2(h) 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. While spin excitations are clearly incommensurate at the probed energies for the SC...
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FIG. 2. (Color online) Two-dimensional constant-energy plots of the spin excitations in the \( \{H, K\} \) plane at the spin excitation energies indicated (a)–(d) for the SC LiFeAs and (e)–(h) for the NSC \( \text{Li}_{0.94}\text{FeAs} \) at 5 K. The incident neutron energy was \( E_i = 35 \text{ meV} \) oriented along the \( c \) axis. The intensity has been normalized to be in absolute units using a vanadium standard as discussed in Ref. 25.

LiFeAs [Figs. 2(a)–2(d)], the incommensurability is less well defined for the NSC \( \text{Li}_{0.94}\text{FeAs} \) [Figs. 2(e)–2(h)].

To quantitatively determine the differences in spin excitations of the SC and NSC \( \text{Li}_{1-x}\text{FeAs} \), we cut through the transverse direction of the two-dimensional scattering images in Fig. 2. Figures 3(a)–3(f) show constant-energy cuts along the \( \{1, K\} \) direction for energies of \( E = 5 \pm 1 \text{ meV} \), \( 7 \pm 1 \text{ meV} \), \( 11 \pm 1 \text{ meV} \), \( 13 \pm 1 \text{ meV} \), \( 17 \pm 1 \text{ meV} \), \( 19 \pm 1 \text{ meV} \); all with \( E_i = 35 \text{ meV} \). The solid lines are fits to two Gaussian peaks. The dashed vertical lines in (c) marking peak centers indicate the definition of incommensurability of spin excitations as in previous work. 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.

FIG. 3. (Color online) Constant-energy cuts of spin excitations along the \( \{1, K\} \) direction for the SC LiFeAs and NSC \( \text{Li}_{0.94}\text{FeAs} \) at energy transfers of (a) \( E = 5 \pm 1 \text{ meV} \), (b) \( 7 \pm 1 \text{ meV} \), (c) \( 11 \pm 1 \text{ meV} \), (d) \( 13 \pm 1 \text{ meV} \), (e) \( 17 \pm 1 \text{ meV} \), (f) \( 19 \pm 1 \text{ meV} \); all with \( E_i = 35 \text{ meV} \).

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 \( \text{Li}_{0.94}\text{FeAs} \) are remarkably similar to those of the SC LiFeAs. This implies that the 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 \( \text{Li}_{1-x}\text{FeAs} \) remove electrons from the FeAs octahedra, the SC LiFeAs should have a larger electron-doping level than that of the NSC \( \text{Li}_{0.94}\text{FeAs} \) and therefore should have a larger electron Fermi surface size. Figures 4(a) and 4(b) show the ARPES intensity mappings of the SC LiFeAs and NSC \( \text{Li}_{0.94}\text{FeAs} \), respectively. Figure 4(c) 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 \( \text{Li}_{0.94}\text{FeAs} \) have the same Fermi surface topology [Fig. 4(c)]. Therefore, a few percent of Li deficiencies in \( \text{Li}_{1-x}\text{FeAs} \) does 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 \( \text{Li}_{1-x}\text{FeAs} \) [Figs. 2 and 3] but is contrary to the naive expectation that the Li-deficiencies in \( \text{Li}_{1-x}\text{FeAs} \) should reduce the sizes of the electron Fermi surface and enlarge the hole Fermi surface (hole doping).
Assuming that the electric conductivity in LiFeAs arises from the hopping of itinerant electrons between the Fe atoms through the As bridge, the Li-vacancies in LiFeAs near the FeAs octahedra can act as impurity centers which scatter off conduction-band electrons. If there are also As deficiencies in the NSC Li$_{1-x}$Fe$_{x}$, they may also act as impurity scattering to suppress superconductivity, whereas Na deficiencies are far removed from the FeAs octahedra and play a role of hole doping. The correction to $T_c$ by the impurity scattering is a universal function of the impurity scattering rate $\Gamma$. For the $s^\pm$-wave superconductor, it was shown that the SC transition temperature is completely suppressed if the ratio between $\Gamma$ and the $T_c$ value without impurities is approximately larger than 1.\cite{417}

The value of $\Gamma$ can be estimated from the resistivity difference $\Delta\rho$ between the Li-deficient and stoichiometric Li$_{1-x}$Fe$_{x}$ via $\Delta\rho_l = m^*\Gamma/(e^2n)$, where $m^*$ is the effective mass of quasiparticle and $n$ is the electron density per unit cell. From Figure 1(c), we see that $\Delta\rho_l$ is about 0.03 m$\Omega$ cm. For LiFeAs, the effective mass is $\sim 5$ times the bare electron mass.\cite{34} If there are two itinerant electrons per Fe, we find that $\Gamma \approx 2.27\tau$, which is larger than the critical value of $\Gamma$ that is needed for completely suppressing $T_c$. This is consistent with the picture that the out-of-plane Li vacancies in LiFeAs play the same role as the nonmagnetic Zn impurities in the electron-overdoped LaFe$_{1-x}$Zn$_x$As$_{1-x}$F$_x$.\cite{32}

If the stoichiometric LiFeAs is indeed an electron-overdoped superconductor, it should be located away from the AF instability as NaFe$_{1-x}$Co$_x$As near $x \approx 0.065$ [Fig. 1(a)] without static AF order.\cite{26} The electron doping of $x \approx 0.065$ is roughly estimated from a comparison of incommensurate spin excitations in BaFe$_{2-x}$Ni$_x$As$_2$\cite{31} with the expected location of incommensurate spin excitations in NaFe$_{1-x}$Co$_x$As.\cite{27} The quasiparticle excitations between the mismatched hole and electron Fermi surfaces due to the self-electron-doping should produce incommensurate spin fluctuations along the direction transverse to the AF ordering wave vector $Q = (1,0)$ [Figs. 1(d) and 1(e)] consistent with the calculated spin susceptibility $\chi''(Q,\omega)$ based on a random phase approximation of a three-dimensional 5-orbital tight-binding model for BaFe$_2$As$_2$.\cite{30,31,38} Experimentally, the transverse incommensurate spin fluctuations with $\delta K \approx 0.1$ were found at $E = 7$ meV for the electron-overdoped BaFe$_{2-x}$Ni$_x$As$_2$ at $x = 0.15$.\cite{31} Using the ARPES measurements (Fig. 4), we plot in Fig. 1(d) the hole and electron Fermi surfaces of the SC and NSC Li$_{1-x}$Fe$_x$. Assuming that the large hole pocket near $\Gamma(0,0)$ is unfavorable for the Fermi surface nesting, we see that the nesting of the small hole pocket near $\Gamma(0,0)$ and the electron pockets near $M(1,0)/(1,0)$ should yield incommensurate spin excitations at $\delta K$ as shown in Fig. 1(e). This nesting condition is consistent with previous work on LiFeAs\cite{21} and our own measurements. These results are also in agreement with the Fermi surface nesting interpretation of the low-energy spin excitations in the electron-\cite{31,30} and hole-doped\cite{39,40} BaFe$_2$As$_2$ and thus suggest that the stoichiometric LiFeAs is an intrinsically electron-overdoped superconductor. This is also consistent with the fact that further electron-doping in the SC LiFeAs via Ni and Co substitution can systematically reduce $T_c$.\cite{11,41}

We note that, for the electron-underdoped BaFe$_{2-x}$As$_2$ with static transverse incommensurate spin-density-wave order,\cite{22,23} low-energy ($<10$ meV) spin excitations are commensurate.\cite{31}

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.\cite{32} Similarly, Zn impurities were found to be effective in suppressing superconductivity in BaFe$_{2-x}$Co$_x$As$_2$.\cite{23} This behavior is consistent with the $s^\pm$-wave SC state, where the nonmagnetic impurity scattering should rapidly decrease $T_c$.\cite{34} If we assume that the Li vacancies in Li$_{1-x}$Fe$_x$As indeed have a limited impact on the size of the electron and hole Fermi surfaces, the rapid suppression of superconductivity by a small amount of Li deficiency may indicate that superconductivity in the stoichiometric LiFeAs is in the electron-overdoped regime.\cite{34} To see why this may be the case, we consider the lattice structure of LiFeAs shown in the inset of Fig. 1(a). Compared with the AF ordered Na$_{1-x}$Fe$_x$, the FeAs octahedron in LiFeAs is much more compressed with an Fe-As distance of $\sim 2.417$ Å\cite{8} similar to the Fe-As distance of $\sim 2.42$ Å in the electron-overdoped NaFe$_{1-x}$Co$_x$As with $x = 0.2$.\cite{27} Although we cannot make a direct extrapolation to the LiFeAs electron doping level from this comparison, we note that lattice structure of LiFeAs is close to that of the electron-overdoped NaFe$_{1-x}$Co$_x$As. To understand why small Li deficiencies can dramatically suppress superconductivity of the stoichiometric LiFeAs while the Na deficiencies in Na$_{1-x}$Fe$_x$As actually promotes superconductivity,\cite{35} we note that the Na ions in Na$_{1-x}$Fe$_x$As form a buffer layer rather far removed from the FeAs octahedra whereas the Li ions in LiFeAs are almost in the As-layer of the FeAs octahedra.\cite{8,27}

FIG. 4. (Color online) (a) and (b) ARPES intensity mappings of the SC and NSC Li$_{1-x}$Fe$_x$ samples recorded with $h\nu = 35$ eV photons (corresponding to the $c$ axis momentum transfer $k_z = \pi$) and integrated within $\pm 20$ meV with respect to the Fermi energy $E_F$. The extracted Fermi surface contours from (a) and (b) are plotted together in (c).
and different from the low-energy incommensurate spin excitations in the SC and NSC Li$_{1-x}$FeAs (Fig. 2). Therefore, the SC LiFeAs cannot be in the electron-underdoped regime, where Li deficiencies should have weak effect on superconductivity and further electron doping should increase $T_c$.

Moreover, recent systematic scanning tunneling microscopy (STM) measurements on NaFe$_{1-x}$Co$_x$As reveal that the tunneling spectra $dI/dV$ change from the symmetric line shape near Fermi energy for the optimally electron doped sample ($x = 0.028$) to a strong asymmetric line shape in the electron-overdoped regime ($x = 0.061$). Since STM measurements on the SC LiFeAs [see Fig. 1(b) in ref. 15] show strong asymmetric tunneling spectra consistent with that of the electron-overdoped NaFe$_{1-x}$Co$_x$As with $x = 0.061$, 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$_x$As [Fig. 1(a)]. This is also consistent with the fact that superfluid density in LiFeAs lies away from the Uemura plot for regular FeAs-based superconductors, but behaves more like an electron overdoped cuprates.

### III. CONCLUSIONS

In summary, we have shown that the stoichiometric LiFeAs is an electron-overdoped superconductor. Moreover, we find that small Li deficiencies in Li$_{1-x}$FeAs suppress superconductivity via an impurity scattering effect. Therefore, in spite of the absent static AF order and the shallow hole Fermi pockets near the $\Gamma(0,0)$ point, the fundamental SC mechanism in LiFeAs is similar to all other iron-based superconductors.

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