Antiferromagnetic spin excitations in single crystals of nonsuperconducting Li$_{1-x}$FeAs

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We use neutron scattering to determine spin excitations in single crystals of nonsuperconducting Li$_{1-x}$FeAs throughout the Brillouin zone. Although angle resolved photoemission experiments and local density approximation calculations suggest poor Fermi surface nesting conditions for antiferromagnetic (AF) order, spin excitations in Li$_{1-x}$FeAs occur at the AF wave vectors $Q = (1,0)$ at low energies, but move to wave vectors $Q = (\pm 0.5, \pm 0.5)$ near the zone boundary with a total magnetic bandwidth comparable to that of BaFe$_2$As$_2$. These results reveal that AF spin excitations still dominate the low-energy physics of these materials and suggest both itinerancy and strong electron-electron correlations are essential to understand the measured magnetic excitations.

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Understanding whether magnetism is responsible for superconductivity in FeAs-based materials continues to be one of the most important unresolved problems in modern condensed matter physics.1,2 For a typical iron arsenide such as LaFeAsO,4 band structure calculations predict the presence of the hole-like Fermi surfaces at the $\Gamma(0,0)$ point and electron-like Fermi surfaces at the $M(1,0)/(0,1)$ points in the Brillouin zone [Fig. 1(a)].5 As a consequence, Fermi surface nesting and quasiparticle excitations between the hole and electron pockets can give rise to static antiferromagnetic (AF) spin-density-wave order at the in-plane wave vector $Q = (1,0)$.6 Indeed, neutron scattering experiments have shown the presence of the $Q = (1,0)$ AF order in the parent compounds of iron arsenide superconductors, and doping to induce superconductivity suppresses the static AF order.7 In addition, angle-resolved photoemission measurements8 have confirmed the expected hole and electron pockets in superconducting iron arsenides, thus providing evidence for superconductivity arising from the sign-revised electron-hole interocket quasiparticle excitations.9–12

Of all the FeAs-based superconductors,1 LiFeAs is special since it has the highest transition temperature ($T_c = 18$ K) amongst the stoichiometric compounds.13–17 Furthermore, it does not have static AF order due to the poor Fermi surface nesting properties with shallow hole pockets near the $\Gamma(0,0)$.18 It has been suggested that the flat tops of the hole pockets in LiFeAs imply a large density of states near the Fermi surface, which should promote ferromagnetic (FM), instead of the usual AF, spin fluctuations for superconductivity.19 If this is indeed the case, AF spin fluctuations should not be fundamental to the superconductivity of FeAs-based materials and the superconducting pairing would not be in the spin singlet channel. A determination of the magnetic properties in LiFeAs is thus important to complete our understanding about the role of magnetism in the superconductivity of FeAs-based materials.

In this paper, we present inelastic neutron scattering measurements on single crystals of nonsuperconducting Li$_{1-x}$FeAs with $x = 0.06 \pm 0.01$, where there is no static AF order. As a function of increasing energy, spin excitations in Li$_{0.94}$FeAs have a spin gap below $\Delta \approx 13$ meV, are centered at the AF wave vector $Q = (1,0)$ for energies up to $\approx 80$ meV, and then split into two vertical bands of scattering before moving to the zone boundaries at the wave vectors $Q' = (\pm 1/2, \pm 1/2)$ near $E \approx 130$ meV. These $Q'$ vectors have been observed in the spin excitations of FeTe/Se compounds and imply the existence of a strong competition between FM and AF exchange couplings.20 While the dispersions of the low-energy spin excitations ($E \leq 80$ meV) in Li$_{0.94}$FeAs are similar to that of (Ba,Ca,Sr)Fe$_2$As$_2$,21–23 the high-energy spin excitations near the zone boundary are quite different from these materials, and cannot be modeled from a simple Heisenberg Hamiltonian with effective nearest ($J_{1u}$ and $J_{1b}$) and next nearest neighbor ($J_{2}$) exchange couplings.21,22 By integrating the local susceptibility $\chi''(\omega)$ in absolute units over the entire bandwidth of spin excitations, we find the spin fluctuating moment $m^2 = 2.1 \pm 0.6 \mu_B^2$, a value that is comparable with other pnictides. Therefore, spin excitations in Li$_{0.94}$FeAs are similar to other iron pnictides but are not directly associated with Fermi surface nesting from hole and electron pockets, contrary to expectations from local density approximation calculations.18,19

Our experiments were carried out on the ARCS time-of-flight chopper spectrometer at the Spallation Neutron Source, Oak Ridge National Laboratory. We also performed thermal triple-axis spectrometer measurements on the BT-7 triple-axis spectrometer at NIST Center for Neutron Research. Our single crystals were grown using the flux method and inductively coupled plasma analysis on the samples showed that the compositions of the crystals are Li$_{0.94(\pm 0.02)}$FeAs. Figure 1(b) shows zero-field-cooled (ZFC) and field-cooled (FC) susceptibility measurements on Li$_{0.94}$FeAs, which
local susceptibility. The solid line is a guide to the eye.

The nesting condition for the expected AF nesting wave vector \(Q_{\text{AFM}} = (1,0)\) is not favorable. 18 (b) Zero-field-cooled (ZFC) and field-cooled (FC) susceptibility measurements on Li\(_{0.94}\)FeAs. No superconductivity was observed due to Li deficiency. (c,d) The directions for BaFe\(_2\)As\(_2\) at 5 K.21 The filled circles show the measured values.

To study the spin excitations, we co-aligned 7.5 g of single crystals of Li\(_{0.94}\)FeAs (with a mosaic of 2\(^\circ\)) and loaded the samples inside a He refrigerator or cryostat. To facilitate easy comparison with spin wave measurements in BaFe\(_2\)As\(_2\),21 we define the wave vector \(Q\) at \((q_x, q_y, q_z)\) as \((H, K, L) = (q_x a/2\pi, q_y b/2\pi, q_z c/2\pi)\) reciprocal lattice units (r.l.u.), where \(a = b = 5.316\) Å, and \(c = 6.306\) Å. For both triple-axis and ARCS measurements, we aligned crystals in the \([H, 0, L]\) scattering zone. The ARCS data are normalized to absolute units using a vanadium standard. The incident beam energies were \(E_i = 80,140,250\) meV with \(E_i\) parallel to the \(c\) axis.

Before describing in detail the spin excitation dispersion curves and dynamic local susceptibility in Figs. 1(c)–1(e), we first discuss the triple-axis measurements on the static AF order and spin excitations. Figures 2(a) and 2(b) show elastic scattering along the \([H, 0, 3]\) and \([1, 0, L]\) directions across the expected AF peak position (1,0,3), respectively. In contrast to Na\(_{1-x}\)FeAs, where static AF order is clearly observed,24 there is no evidence for static AF order in this sample. To search for AF spin excitations, we carried out constant-\(Q\) scans at the AF wave vector \(Q = (1,0,3)\) and background (0,4,0,3) positions. The outcome in Fig. 2(c) shows a step-like increase in scattering above background for \(E > 13\) meV, clearly suggesting the presence of a large spin gap of \(\Delta = 13\) meV. To confirm there is indeed a spin gap, we carried out constant-energy scans along the \([H, 0, 3]\) direction at \(E = 9\) and 16 meV as shown in Fig. 2(d). While the scattering is featureless at \(E = 9\) meV, there is a clear peak centered at \(Q = (1,0,3)\) at \(E = 16\) meV. Figure 2(e) shows the temperature dependence of the imaginary part of the dynamic susceptibility \(\chi''(E)\) obtained by subtracting the background and correcting for the Bose population factor. Surprisingly, the spin gap has no observable temperature dependence between 2 K and 190 K, much different from the temperature dependence of the spin gaps in the (Ba,Str,Ca)Fe\(_2\)As\(_2\) family of materials.25–27 which disappear rapidly with increasing temperature. The weak temperature dependence of the dynamic susceptibility has

![FIG. 1.](image-url) (Color online) (a) Fermi surfaces from the spin-restricted local density approximation calculation for LiFeAs.18,19 There are two hole-like Fermi surfaces near the \(\Gamma(0,0)\) point with \(d_{xy}/d_{xz}\) character and one electron-like Fermi surface near the \(M(1,0)\) point. The nesting condition for the expected AF nesting wave vector \(Q_{\text{AFM}} = (1,0)\) is not favorable.18 (b) Zero-field-cooled (ZFC) and field-cooled (FC) susceptibility measurements on Li\(_{0.94}\)FeAs. No superconductivity was observed due to Li deficiency. (c) The dashed lines show spin wave dispersions along the \([H, 0]\) and \([1, K]\) directions for BaFe\(_2\)As\(_2\) at 5 K.21 The filled circles show the measured spin excitation dispersions along the \([H, 0]\) and \([1, K]\) directions for Li\(_{0.94}\)FeAs. While spin waves in BaFe\(_2\)As\(_2\) extend up to 200 meV along the \([1, K]\) direction, spin excitations in Li\(_{0.94}\)FeAs reach the zone boundary near \(Q = (1,0.5)\). (d) The energy dependence of the local susceptibility. The solid line is a guide to the eye.

![FIG. 2.](image-url) (Color online) Triple-axis measurements to search for static AF order and spin excitations in Li\(_{0.94}\)FeAs. (a) Elastic scattering along the \([H, 0, 3]\) and \([1, 0, L]\) directions at 2 K show no evidence of AF order at the expected position \(Q = (1,0,3)\). The arrows indicate Al sample holder scattering. (c) Constant-\(Q\) scans at the wave vectors \(Q = (1,0,3)\) (signal) and \(Q = (0,4,0,3)\) (background) positions at 2 K. A clear spin gap is seen at \(\Delta = 13\) meV. (d) Constant-energy scans at \(E = 9\), 16 meV along the \([H, 0, 3]\) direction. While the scan at \(E = 9\) meV is featureless, a clear peak is seen at \(E = 16\) meV confirming the spin gap. (e) Imaginary part of the dynamic susceptibility \(\chi''\) at 2 K and 190 K. The magnitude of the spin gap is unchanged between 2 and 190 K. (f) Temperature dependence of the dynamic susceptibility has almost temperature independent between 2 K and 190 K. Error bars where indicated represent one standard deviation.
been confirmed by constant-energy scans in Fig. 2(f), where \( \chi''(Q) \) at \( E = 16 \text{ meV} \) remains essentially unchanged from 2 K to 190 K.

Figure 3 summarizes the ARCS time-of-flight measurements on Li\(_{0.94}\)FeAs at 5 K. Since spin excitations in Li\(_{0.94}\)FeAs have no \( c \)-axis modulations, we show in Figs. 3(a)–3(h) two-dimensional constant-energy (\( E \)) images of the scattering in the \( (H,K) \) plane for \( E = 25 \pm 5, 45 \pm 5, 70 \pm 10, 90 \pm 10, 110 \pm 10, 130 \pm 10, 150 \pm 10, \) and \( 170 \pm 10 \text{ meV} \), respectively. For energies between \( 25 \pm 5 \leq E \leq 90 \pm 10 \text{ meV} \), spin excitations form transversely elongated ellipses centered around AF \( Q = (1,0) \). The intensity of spin excitations which decreases with increasing energy, which is remarkably similar to spin waves in BaFe\(_2\)As\(_2\).\(^{21}\) For energies above 90 meV, spin excitations split into two horizontal arcs that separate further with increasing energy. The excitations finally merge into \( Q = (m \pm 0.5,n \pm 0.5) \) \((m,n = 0,1,2)\) and become weaker above 150 meV in Figs. 3(g) and 3(h).

In order to determine the dispersion of spin excitations for Li\(_{0.94}\)FeAs, we show in Fig. 4 cuts through the two-dimensional images in Fig. 3 and compare with identical cuts for BaFe\(_2\)As\(_2\).\(^{21}\) Figures 4(a)–4(d) show constant-energy cuts along the \([H,0]\) direction for energies of \( E = 55 \pm 5, 75 \pm 5, 95 \pm 5, 135 \pm 5 \text{ meV} \), respectively, while the dashed lines show identical spin wave cuts for BaFe\(_2\)As\(_2\).\(^{21}\) Since both measurements were taken in absolute units, we can see that spin excitations in Li\(_{0.94}\)FeAs are similar to that of BaFe\(_2\)As\(_2\) per Fe below 95 meV.\(^{21}\) Figures 4(e)–4(h) show constant-energy cuts along the \([1,K]\) direction for identical energies as that of Figs. 4(a)–4(d). For energies above 95 meV, the strength of the spin excitations in Li\(_{0.94}\)FeAs is rapidly suppressed compared to that of BaFe\(_2\)As\(_2\) and become very weak above \( E = 135 \text{ meV} \). This can originate from an absence of magnetic scattering, or that the scattering is very broad as might occur for an itinerant electron system interacting with Stoner excitations. This is different from spin waves in BaFe\(_2\)As\(_2\), which extend up to 250 meV. Based on these constant-energy cuts, we show in Figs. 1(c) and 1(d) the comparison of spin excitation dispersions of Li\(_{0.94}\)FeAs (filled circles) with those of spin waves in BaFe\(_2\)As\(_2\) (dashed lines). They are similar for energies between 50–95 meV, while the spin excitations in Li\(_{0.94}\)FeAs are broader below 50 meV.

We have attempted, but failed, to use a simple Heisenberg Hamiltonian with effective nearest and next nearest neighbor exchange couplings to fit the observed spin excitation spectra.\(^{21,22}\) For all possible combinations of the \( J_{1a}, J_{1b}, \) and \( J_2 \), the expected zone boundary spin excitations are quite different from the observed spectra (see EPAPS information).\(^{28}\) If we include the next-next-nearest-neighbor exchange coupling...
J₁, the expected spectra near the zone boundary have some resemblance to the data in Fig. 3 although the low-energy excitations would be different. This means that the effective exchange couplings in Li₀.₈₄FeAs are extremely long-ranged, a hallmark that itinerant electrons are important for spin excitations in this material. Since the data close to the band top along the [1, K] direction are higher in energy than along the [H, 0] direction, we need J₁b < 0 to recover this feature in a J₁b-J₂-J₃ model. This means that effective exchange interactions in Li₀.₈₄FeAs may be similar to the (Ca,Sr,Ba)Fe₂As₂ iron pnictides in spite of their different zone boundary spectra.

Finally, we show in Fig. 1(e) the energy dependence of the local susceptibility, defined as χ′′(E) = ∫ χ′(q, E)dq/∫ dq, where the average is over the magnetic scattering signal χ′′(q, E) over the Brillouin zone [Fig. 3(b)]. The corresponding fluctuating moment ⟨m²⟩ = 2.1 ± 0.6 μ₀² per formula unit. We can use both pure local and itinerant spin models to sketch a basic physical picture based on the moment value. If we assume a quantum local spin model to describe the fluctuations, the moment value implies the spin value is about one. If we take a pure itinerant model, our result would suggest that at least three electrons per iron site occupy the states with energies up to the magnetic bandwidth (~150 meV) below the Fermi energy. This suggests that the bandwidths of the electron bands near the Fermi surface are narrow. In other words, the band renormalization factors are large and the electron-electron correlations must be strong.

In summary, we measured spin excitations in single crystals of Li₀.₈₄FeAs. Similar to other iron pnictides, the low energy excitations are still strongly AF. However, comparing to other iron pnictides, they have several distinct properties: (a) a larger spin gap, close to 13 meV that is essentially temperature independent below 190 K; (b) a comparable total magnetic moment; (c) different wave vectors at the zone boundary for high energy excitations. Moreover, the excitations cannot be described by magnetic models with only short range magnetic exchange couplings. Our results suggest the AF spin fluctuations are fundamental to the superconductivity of FeAs-based materials. FM fluctuations exist in Li₀.₈₄FeAs, but they only affect the high energy spin excitations.

We have become aware of a related work on powder samples of superconducting LiFeAs, where AF spin fluctuations have been reported.

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