Enhanced superfluid stiffness, lowered superconducting transition temperature, and field-induced magnetic state of the pnictide superconductor LiFeAs

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Transverse-field muon-spin rotation measurements performed on two samples of LiFeAs demonstrate that the superfluid stiffness of the superconducting condensate in relation to its superconducting transition temperature is enhanced compared to other pnictide superconductors. Evidence is seen for a field-induced magnetic state in a sample with a significantly suppressed superconducting transition temperature. The results in this system highlight the role of direct Fe-Fe interactions in frustrating pairing mediated by antiferromagnetic fluctuations and indicate that, in common with other pnictide superconductors, the system is close to a magnetic instability.

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The relationship between critical temperature T_c and superfluid stiffness ρ_s in a superconductor (SC) provides important information concerning the balance between the strength of the pairing and the efficiency of electromagnetic screening. In many SCs these two parameters are related by Uemura scaling,[1,2] though deviations from this are found for overdoped cuprates[3] and organic SCs.[4] The recently discovered oxypnictide SCs (Ref. 5) containing FeAs layers show a wide range of T_c,[6–10] and those studied so far have shown behavior broadly consistent with Uemura scaling,[11–19] as observed for hole-doped cuprates. In this Brief Report we test this relationship for LiFeAs,[20–22] a recently discovered variant of pnictide SC where Li replaces the lanthanide-oxide layer. In LiFeAs the closest Fe-Fe separation in the FeAs layers is significantly shorter than in previously studied pnictide SC compounds. This produces additional frustrating magnetic interactions which are expected to weaken the strength of the antiferromagnetic coupling through Fe-As bonds, which has been suggested to mediate the superconducting pairing.[23] We find that this produces a departure from the previously observed scaling behavior which can provide some insight into the nature of the pairing in this family of compounds.

LiFeAs crystallizes in a tetragonal space group ($P4/nmm$) with $a=0.378$ nm and $c=0.635$ nm and contains FeAs layers, based on edge-sharing tetrahedral $FeAs_4$ units, interspersed with layers containing Li ions. The tetrahedra are compressed in the basal plane relative to those in LaFeAsO and $SrFeAs_2$. This implies that although the Fe-As bond distance 0.2414 nm in LiFeAs is similar to the other compounds, the Fe-Fe distance of 0.268 nm is considerably shorter. Superconductivity can be obtained at up to 18 K in this compound, though differences have been observed even between samples with similar cell volumes, probably connected with slight compositional variation, as described previously for compositions close to LiFeAs.[24] In contrast with the oxypnictides, no further doping is necessary to induce superconductivity, and from studies to date the spin-density wave (SDW) state has appeared to be notably absent.

Transverse-field (TF) muon-spin rotation (SR) (TF-μSR) is a method for accurately measuring the internal magnetic field distribution within the vortex lattice (VL) of a type-II SC.[25] Spin-polarized positive muons (gyromagnetic ratio $\gamma_\mu/2\pi=135.5$ MHz T^{-1}; lifetime $\tau_\mu=2.2$ μs) are implanted into the bulk of the sample at random positions on the length scale of the VL. A magnetic field $B_{c1}<B_0<B_{c2}$ is applied perpendicular to the initial muon-spin direction and the muons precess around the total local magnetic field at their stopping site. This gives a method of randomly sampling the magnetic field distribution using the time evolution of the muon-spin polarization $P_x(t)$, which is related to the distribution of local magnetic fields in the sample $p(B)$ via

$$P_x(t) = \int_0^\infty p(B)\cos(\gamma_\mu Bt + \phi)dB, \qquad (1)$$

where ϕ is a phase offset associated with the emitted positron detector geometry. The function $p(B)$ allows the extraction of the in-plane penetration depth λ_{ab} and hence the superfluid stiffness $\rho_s \propto \lambda_{ab}^{-2}$.

Powder samples of LiFeAs were prepared from high-purity elemental reagents (>99.9%) by the methods described in Refs. 21 and 22, and the presence of superconductivity was confirmed by superconducting quantum interference device (SQUID) magnetometry. Two samples were selected for the μSR studies which were made on the GPS instrument at the Swiss Muon Source located at the Paul Scherrer Institut in Switzerland. Sample 1 with $T_c=16$ K, and lattice parameters $a=3.774(1)$ Å, $c=6.353(1)$ Å, and $V=90.5(1)$ Å^3, was prepared by heating a 1:1:1 ratio of the elements in a sealed tantalum tube at 750 °C for 24 h, a method similar to that described by Tapp *et al.*;[22] the susceptibility was very similar to that of sample 1 in Ref. 21. Sample 2 with $T_c\sim 12$ K, and a broader superconducting transition than that observed for other reported samples, was the same as sample 2 in Ref. 21 ($a=3.774(1)$ Å, $c=6.354(2)$ Å, and $V=90.5(1)$ Å^3). Laboratory powder x-ray diffraction indicated that the samples were at least 98% phase pure. Measurements using μSR are not generally sensitive to low level impurity phases, and we

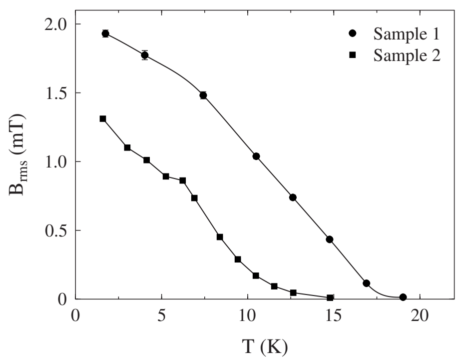

FIG. 1. The temperature dependence of the superconducting contribution to the field width of the μSR line shape measured in a transverse field of 40 mT for the two samples of LiFeAs. The curves are a guide to the eyes.

note also that common impurity phases found in pnictide SCs, such as FeAs and $FeAs_2$, give very different μSR signals[26] from those which we will describe below. Both samples have equal cell parameters and are stoichiometric within experimental uncertainty. However differences in Li occupation of less than 5% are not readily detectable using structural or bulk analytical probes. Noting that for $LaFeAsO_{1-x}F_x$ a change in the doping x of order 2% shifts T_c from zero to its maximal value,[5] we attribute the difference in T_c between our two Li_xFeAs samples to a variation in x at a level of $\sim 1\%$.

In TF-μSR measurements performed above T_c, one might expect $p(B)=\delta(B-B_0)$. However, broadening of $p(B)$ is caused by the contribution from randomly oriented nuclear moments near the muon stopping

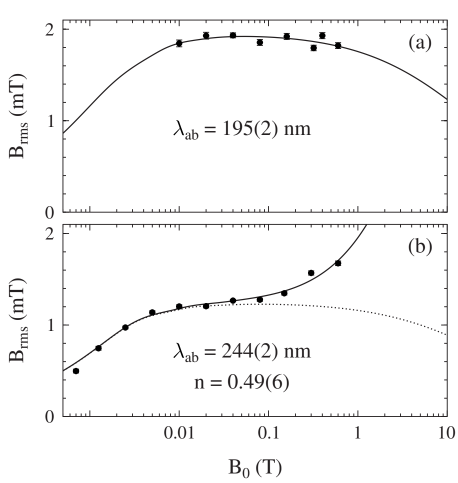

FIG. 2. (a) The magnetic field dependence of the superconducting contribution to the μSR line width for sample 1 measured at 1.6 K. The field dependence is very weak and the *ab* penetration depth can easily be extracted from the data by fitting to the field dependence of the GL model (solid curve). (b) The field dependence for sample 2 (with lower T_c). The low field behavior can again be fitted to the GL model, but a marked deviation sets in at fields above 0.1 T, and the overall fit (solid line) needs to include a field-induced magnetic contribution $\sigma_M \propto B^n$ in addition to the VL contribution (dotted line).

sites. This leads to a roughly Gaussian relaxation $P_x(t) \propto \exp[-(\sigma_n t)^2/2]\cos(\gamma_\mu B_0 t+\phi)$. Below T_c the spectrum $p(B)$ broadens considerably due to the dephasing contribution from the VL. The additional broadening is fitted well by a further Gaussian damping term so that the overall damping is

$$\sigma^2 = \sigma_{VL}^2 + \sigma_n^2 \tag{2}$$

and the corresponding field width due to the VL is $B_{rms}=\sigma_{VL}/\gamma_\mu$. The data fitting procedure also takes into account the small fraction (<20%) of the signal coming from muons stopping in the silver sample support which gives a weakly relaxing background component. The resulting temperature-dependent contribution to the field width B_{rms} due to the superconducting VL is shown in Fig. 1 for the two samples in an applied transverse field of $B_0=40$ mT. In both samples, B_{rms} increases monotonically upon cooling below T_c. A simple two-fluid or *s*-wave BCS model would saturate below $\sim T_c/3$ whereas our data do not, requiring either a more complex *s*-wave model or a clean-limit *d*-wave model to explain the continued approximately linear increase at low temperatures.

The *ab* plane penetration depth λ_{ab} and corresponding superfluid stiffness can be derived from B_{rms} for a powder sample using the relation[27]

$$B_{rms} = \frac{\sigma_{VL}}{\gamma_\mu} = (0.00371)^{1/2}\frac{\phi_0}{(3^{1/4}\lambda_{ab})^2}. \tag{3}$$

Equation (3) is valid in the London limit at fields well above B_{c1} and well below B_{c2} where B_{rms} is independent of applied field. A more sophisticated approach allows for the field dependence that occurs for realistic sample parameters, and we use a recent calculation of the field-dependent B_{rms} in the Ginzburg-Landau (GL) model for an anisotropic SC (Ref. 28) to fit our field-dependent data (Fig. 2). The original calculation is for normal field configuration, and an extension to the polycrystalline case was made under the assumption that the length scales λ and ξ diverge following $1/\cos\theta$ as the field orientation approaches the plane at $\theta=0$ (high anisotropy limit), with the corresponding contribution to the overall width scaling as $\cos\theta$. The data obtained for sample 1 are seen to be only very weakly field dependent [Fig. 2(a)], indicating that the measured field range is well separated from B_{c1} and B_{c2} and a best fit[29] yields $\lambda_{ab}=195(2)$ nm. In contrast, sample 2 behaves rather differently [Fig. 2(b)]. At lower fields it follows the GL dependence for the expected longer penetration depth, however above ~ 0.1 T a significant increase in the width with applied field is apparent, indicating a field-induced magnetic contribution which can be fitted by adding an additional term σ_M^2 to Eq. (2), where σ_M follows a B_0^n power law. After allowing for this field-induced magnetism, the λ_{ab} value in this second sample is obtained to be 244(2) nm.

Figure 3(a) shows the SC field distribution in sample 1 at 40 mT obtained from a Fourier transform. A broadened VL powder distribution [Fig. 3(b)] along with a narrow background peak can account for most of the profile, although there is some additional spectral weight on the low field side.

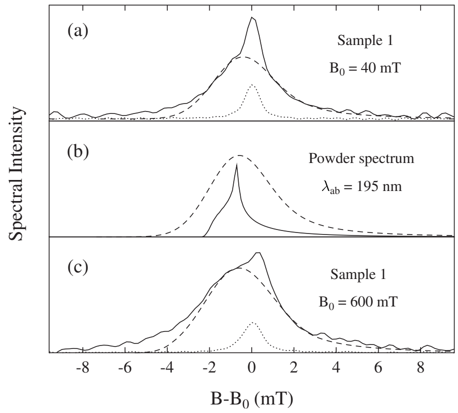

FIG. 3. (a) Spectral distribution of the internal field in sample 1 at 40 mT obtained by Fourier transformation. The dotted line is the normal state and the solid line is the SC state. The dashed line represents a Gaussian broadened powder profile detailed in (b), where the unbroadened powder profile is shown as the solid curve. Panel (c) is as for (a) but for a field of 600 mT.

The profile remains similar when the field is raised to 600 mT [Fig. 3(c)]. The same spectral analysis for sample 2 is shown in Fig. 4. The profile at 40 mT is qualitatively similar to that seen in sample 1 but with the additional weight on the low field side being relatively larger. At 600 mT, however, significant additional broadening becomes apparent on both sides of the peak.

The observation of the departure from GL behavior [Fig. 2(b)] and shift in spectral weight [Fig. 4(c)] for sample 2 at high field provides evidence for field-induced magnetism. The superconducting state in pnictides is known to be proximate to SDW order, but no SDW state has been observed directly in the LiFeAs system. Field-induced magnetism has been investigated in cuprate SCs, particularly following neutron studies of $La_{2-x}Sr_xCuO_4$ (LSCO),[30] the results of which have been interpreted as microscopic phase coexistence of SDW and SC states, driven by coupling of the two order parameters.[31] Such an approach predicts an induced SDW

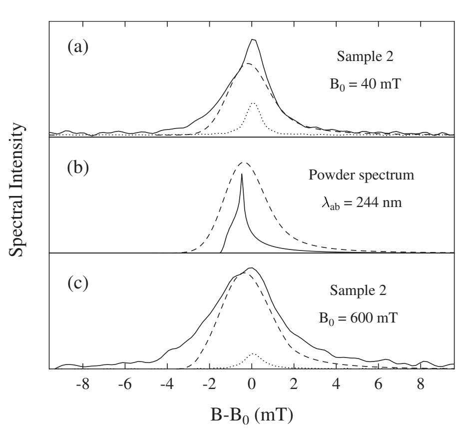

FIG. 4. As Fig. 3 but for sample 2 which shows evidence of field-induced magnetism. The VL linewidth is narrower here than for sample 1, and the additional field-induced broadening is clearly seen on both sides of the main peak when comparing the 600 mT data in (c) with the 40 mT data in (a).

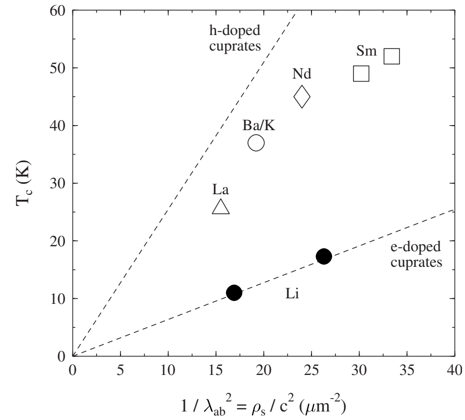

FIG. 5. An Uemura plot of the superconducting transition temperature T_c versus the low temperature superfluid stiffness. Data obtained here for the two LiFeAs samples are compared with previously reported data for doped members of the $LnFeAsO_{1-x}F_x$ family: Ln=La (Ref. 11), Nd (Ref. 13) and Sm Refs. 12 and 15, and the $Ba_xK_{1-x}Fe_2As_2$ family (Refs. 18 and 19). The data taken from the previous reports have been restricted to the highest T_c sample in each study. The lower dashed line indicates the trend line for electron-doped cuprates, which closely corresponds to the behavior of the LiFeAs system obtained here, in contrast to the other pnictide superconductors, which sit closer to the trend for hole-doped cuprates. The symbol size represents the typical estimated uncertainty of the data points.

moment which scales roughly as $B_0^{1/2}$ for $B_0 \ll B_{c2}$,[31] in agreement with our fitted $n=0.49(6)$. That the field-induced broadening shows up in sample 2 and not in sample 1 is most likely due to the greater proximity to the SDW state driven by a small change in Li-site occupancy.

The extracted values of λ_{ab} allow us to place these materials on an Uemura plot, as shown in Fig. 5, alongside values obtained from reported data on other FeAs-based SCs using Eq. (3). In a region where standard Uemura scaling applies there will be a linear relation between ρ_s and T_c. However, from Fig. 5 it can be seen that no single scaling line can be used for all of the data. The data appear to split into two groups with the trend for the LiFeAs samples being lower than any trend line that would describe the $LnFeAsO_xF_y$ and $Ba_xK_{1-x}Fe_2As_2$ data. This indicates that the LiFeAs samples have a superfluid stiffness that is enhanced over the values that might be expected on the basis of their observed transition temperatures and the behavior of the other FeAs SCs. Alternatively one may regard T_c for a given strength of superfluid condensate as being suppressed in the LiFeAs case, particularly when compared to the magnetic lanthanides $NdFeAsO_{1-x}F_x$ and $SmFeAsO_{1-x}F_x$. This implies that although the superconducting state in the FeAs layers is reasonably robust (the superfluid is stiff) the strength of the pairing is significantly suppressed for LiFeAs. If the pairing is mediated by antiferromagnetic fluctuations originating from the indirect Fe-As-Fe exchange interactions, one would expect that this mechanism would be frustrated by the increasing role played by direct Fe-Fe interactions in LiFeAs. Deviation from perfect tetrahedral structure for the $FeAs_4$ units is known to suppress T_c in pnictide superconductors,[32] and the significant compression of the $FeAs_4$ tetrahedra in the LiFeAs structure is also expected to strongly modify the Fe-As-Fe exchange coupling. Associated changes in the electronic structure will also increase the electronic bandwidth[33] and hence contribute to a reduction in the effective pairing strength. The increased bandwidth also leads to a reduced effective mass m^* so that the superfluid stiffness n_s/m^* is then expected to become enhanced relative to T_c, as we have observed experimentally in this study.

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