Enhancement of Superfluid Stiffness, Suppression of Superconducting $T_c$ and Field-induced Magnetism in 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 suggest 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 $\rho_s$ 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 oxypnic- tide SCs [5] containing FeAs layers show a wide range of $T_c$ [6, 7, 8, 9, 10] and those studied so far have shown behavior broadly consistent with Uemura scaling [11, 12, 13, 14, 15, 16, 17, 18, 19], as observed for hole-doped cuprates. In this Letter we test this relation- ship for LiFeAs [20, 21, 22], a newly discovered variant of pnictide SC without the lanthanide-oxide layer. In LiFeAs the Fe–Fe separation in the FeAs layers are significantly shorter than in previously studied pnictide SC compounds. This produces additional frustrating magnetic interactions which may 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 $a = 0.378\ \text{nm}$ and $c = 0.635\ \text{nm}$ 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 the spin-density wave (SDW) state appears to be notably absent from this system.

Transverse field muon spin rotation (TF-\(\mu\)SR) is a method of accurately measuring the internal magnetic field distribution within the vortex lattice (VL) of a type-II SC [25]. Spin polarized positrons (gyromagnetic ratio $\gamma_{\mu}/2\pi = 135.5$ MHzT$^{-1}$, lifetime $\tau_{\mu} = 2.2$ $\mu$s) 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:

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

where $\phi$ is a phase offset associated with the emitted positron detector geometry. The function $p(B)$ allows the extraction of the in-plane penetration depth $\lambda_{ab}$ 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 references [21] and [22] and the presence of superconductivity was confirmed by SQUID magnetometry. Two samples were selected for the \(\mu\)SR studies. Sample 1 with $T_c = 16$ K and lattice parameters $a=3.774(1)\ \text{Å}$, $c=6.353(1)\ \text{Å}$ and $V=90.5(1)\ \text{Å}^3$ was prepared by heat-
ing a 1:1:1 ratio of the elements in a sealed tantalum tube at 750 °C for 24 hours, a method similar to that described by Tapp et al. [22]. 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 $\mu$SR are not generally sensitive to low level impurity phases and we note also that common impurity phases found in pnictide SCs, such as FeAs and FeAs$_2$, give very different $\mu$SR signals [26] from those which we will describe below. Both samples are stoichiometric and have equal cell parameters within experimental uncertainty; we attribute the differences in $T_c$ to very small differences in Li occupation which are not readily detectable using structural or bulk analytical probes. Muon-spin rotation measurements were made on the GPS instrument at the Swiss Muon Source, Paul Scherrer Institut, CH.

In TF-$\mu$SR 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 sites. This leads to a roughly Gaussian relaxation $P_z(t) \propto \exp\left[-(\sigma_n t)^2/2\right] \cos(\gamma_\mu B_0 t + \phi)$. 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

$$\sigma^2 = \sigma_{VL}^2 + \sigma_n^2$$  \hspace{1cm} (2)

and the corresponding field width due to the VL is $B_{\text{rms}} = \sigma_{VL}/\gamma_\mu$. The data fitting procedure also takes into account the small fraction 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 $B_{\text{rms}}$ 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, $B_{\text{rms}}$ increases monotonically on cooling below the $T_c$. The increasing width does not appear to be saturating at low temperatures and consequently cannot be described by a simple two-fluid or $s$-wave BCS model.

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

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

Equation 3 is valid in the London limit at fields well above $B_{c1}$ and well below $B_{c2}$ where $B_{\text{rms}}$ 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 $B_{\text{rms}}$ in the Ginzburg-Landau (GL) model for an anisotropic SC [28] to fit our field dependent data.
At lower fields it follows the GL dependence for the experimentally larger penetration depth, however above 0.1 T the data obtained for sample 1 is seen to be only very weakly field dependent (Fig. 2a), 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, suggesting a field-induced magnetic contribution which can be fitted by adding an additional term $\sigma_M$ to Eq. 4, where $\sigma_M$ follows a $B_0^2$ power law. After allowing for this field induced magnetism, the $\lambda_{ab}$ value in this second sample is obtained to be 244(2) nm.

The original calculation is for normal field configuration and an extension to the polycrystalline case was made under the assumption that the length scales $\lambda$ and $\xi$ 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 for sample 1 is as for (a) but for a field of 600 mT.

At 600 mT, however, significant additional broadening becomes apparent on both sides of the main peak. Panel (c) is for the 600 mT data in (c) with the 40 mT data in (a). The latter 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).

The observation of the departure from GL behavior [Fig. 2(b)] and shifts in spectral weight [Fig. 4(c)] for sample 2 at high field may be suggestive of 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$_2$-xSr$_x$CuO$_4$ (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 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 sample 1 may be due to the greater proximity to the SDW state driven by some small change in Li-site occupancy. This is suggestive that the SC state in LiFeAs may be extremely close to a magnetic instability.

The extracted values of $\lambda_{ab}$ 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. 6. In a region where standard Uemura scaling applies there will be a linear relation between $\rho_s$ 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...
the other FeAs SCs. Alternatively one may regard observed transition temperatures and the behaviour of samples have a superfluid stiffness that is enhanced over the behaviour of the LiFeAs system obtained here, in contrast to the other pnictide superconductors, which sit closer to the $T_c$ expected for h-doped cuprates. The symbol size represents the typical estimated uncertainty of the data points.

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$^{11}$, Nd$^{13}$ and Sm$^{12,15}$ and the Ba$_x$K$_{1-x}$Fe$_2$As$_2$ family$^{18,19}$. The data taken from the previous reports has 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 behaviour of the LiFeAs system obtained here, in contrast to the other pnictide superconductors, which sit closer to the trend for h-doped cuprates. The symbol size represents the typical estimated uncertainty of the data points.

any trend line that would describe the LaFeAsO$_4$,NdFeAsO$_{1-x}$F$_x$ and Ba$_x$K$_{1-x}$Fe$_2$As$_2$ 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 behaviour 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 Fe–As–Fe exchange interactions, we may speculate that this mechanism may be frustrated by the increasing role played by direct Fe–Fe interactions in LiFeAs. The Fe–As–Fe exchange is also expected to be modified by the compression of the FeAs$_4$ tetrahedra and consequent changes to the Fe–As–Fe bond angles in the LiFeAs structure. Associated changes in the electronic structure will also increases the electronic bandwidth$^{32}$ 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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