Anisotropic upper critical field and possible Fulde-Ferrel-Larkin-Ovchinnikov state in the stoichiometric pnictide superconductor LiFeAs

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Measurements of the temperature and angular dependencies of the upper critical field \( H_c2 \) of a stoichiometric single crystal LiFeAs in pulsed magnetic fields up to 50 T were performed using a tunnel diode resonator. Complete \( H_c2(T) \) and \( H_c2(T) \) functions with \( H_c2(0) = 17 \pm 1 \) T, \( H_c2(0) = 26 \pm 1 \) T, and the anisotropy parameter \( \gamma \) decreasing from 2.5 at \( T_c \) to 1.5 at \( T \ll T_c \) were obtained. The results for both orientations are in excellent agreement with a theory of \( H_c2 \) for two-band \( s^\pm \) pairing in the clean limit. We show that \( H_c2(T) \) is mostly limited by the orbital pair breaking, whereas the shape of \( H_c2(T) \) indicates strong paramagnetic Pauli limiting and the inhomogeneous Fulde-Ferrel-Larkin-Ovchinnikov state below \( T_F \sim 5 \) K.

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There are only a few stoichiometric iron-based compounds (Fe-SCs) exhibiting ambient-pressure superconductivity without doping. Among them, LiFeAs is unique because of its relatively high \( T_c = 18 \) K,1 as compared to LaFePO \( (T_c \approx 5.6 \) K\) and KFe\(_2\)As\(_2\) \( (T_c = 3 \) K). The absence of doping-induced disorder leads to weak electron scattering, low resistivity, \( \rho(T_c) \approx 10 \mu\Omega \cdot cm \) (Ref. 4) and high resistivity ratio, \( \rho_{RRR} = \rho(300K)/\rho(T_c) > 30 \).\(^{4,5}\) These parameters differ significantly from those of most Fe-SCs for which superconductivity is induced by doping, for example, Ba(Fe\(_{1-x}\)Ti\(_x\))\(_2\)As\(_2\) (Refs. 6 and 7), (Ba\(_{1-x}\)K\(_x\))Fe\(_2\)As\(_2\) (Ref. 3), and BaFe\(_2\)As\(_2\) (Ref. 8). With the highest \( T_c \) among stoichiometric Fe-SCs, negative \( \partial H_c/\partial P \)\(^{9}\) tetragonal crystal structure,\(^1,5\) and the absence of antiferromagnetism,\(^9\) LiFeAs serves as a model of clean, nearly optimally doped Fe-SC.\(^4\) Because of very high \( H_c2 \) of Fe-SCs, they may also exhibit exotic behavior caused by strong magnetic fields, for example, the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state in which the Zeeman splitting results in oscillations of the order parameter along the field direction.\(^11\) Thus, measurements of \( H_c2(T) \) in stoichiometric LiFeAs single crystals can reveal manifestations of \( s^\pm \) pairing in the clean limit\(^12\) for which the FFLO state is least suppressed by doping-induced disorder\(^11\) as compared to other optimally doped Fe-SCs.

Measurements of the upper critical fields parallel \( (H_c2^{||}) \) and perpendicular \( (H_c2^{\perp}) \) to the crystallographic c axis in many Fe-Sc have shown several common trends.\(^6,7,13,14,27\) Close to \( T_c \) where \( H_c2 \) is limited by orbital pair breaking, the anisotropy parameter \( \gamma \) \( \equiv H_c2^{||}/H_c2^{\perp} \) ranges between 1.5 and 5,\(^{13,14,23,26}\) in agreement with the anisotropy of the normal state resistivity \( \rho_{\parallel}/\rho_{\perp} \)\(^{12}\) above \( T_c \). As \( T \) decreases, \( H_c2(T) \) becomes more isotropic,\(^18,20,27\) consistent with multiband pairing scenarios and the behavior of \( H_c2 \) in dirty MgB\(_2\)\(^{28}\) yet opposite to clean \( s^+ \) MgB\(_2\) single crystals.\(^29\) However, the more isotropic \( H_c2 \) at low \( T \) can also result from strong Pauli pair breaking for \( H \parallel ab \), since the observed \( H_c2 \) on many Fe-SCs significantly exceeds the BCS paramagnetic limit \( H_p[T] = 1.84T_c[K] \).\(^{17,18,25-27,30}\) Thus, measuring \( H_c2 \) in LiFeAs can probe the interplay of orbital and Pauli pair breaking in the clean \( s^\pm \) pairing limit at high magnetic fields. These measurements are also interesting because magnetic fluctuations may contain significant ferromagnetic contribution which may lead to triplet pairing.\(^31\) Experimentally, vortex properties of LiFeAs were found to be very similar to the supposedly triplet Sr\(_2\)Ru\(_2\)O\(_4\),\(^32\) although NMR studies suggest singlet pairing.\(^33\) Triplet superconductors can exhibit unusual responses to a magnetic field,\(^34\) and, indeed, candidate materials show pronounced anomalies, as observed in UP\(_3\) (Refs. 35 and 36) and Sr\(_3\)Ru\(_2\)O\(_4\) (Ref. 37). Surprisingly, our measurements show that normalized \( H_c2^{\perp} \) of LiFeAs matches quite closely that of Sr\(_3\)Ru\(_2\)O\(_4\).

We present the measurements of a complete \( H-T \) phase diagram of LiFeAs in pulsed magnetic fields up to 50 T and down to 0.6 K using a tunnel diode resonator (TDR) technique. We found that \( H_c2^{||} \) shows rapid saturation at low temperatures, consistent with strong Pauli pair breaking. A similar conclusion was reached from torque measurements.\(^38\) Our data can be described well by a theory of \( H_c2 \) for the multiband \( s^\pm \) pairing in the clean limit,\(^39\) which also suggests the FFLO state in LiFeAs for \( H \parallel c \) below 5 K. Previous measurements of \( H_c2 \) in LiFeAs were performed at relatively low fields,\(^3,40\) thus not allowing to reveal the spin-limited behavior at low \( T \). The only reported high-field measurements associate \( H_c2 \) with the disappearance of irreversibility in torque measurements.\(^38\) The authors supported this association by comparing with the specific heat data. However, in our opinion, the irreversibility field may underestimate the true \( H_c2(T) \) and have different temperature dependence due to depinning of vortices. It may also have significant (cusplike) angular variation, which would be particularly important for torque measurements that rely on the finite angle between magnetic moment and field. Related complications were discussed in high-\( T_c \) cuprates.\(^41\)

Single crystals of LiFeAs were grown in a sealed tungsten crucible using the Bridgeman method and placed in ampoules.
Immediately after opening, samples were covered with Apiezon N grease, which provides some degree of short-term protection. The samples were cleaved and cut inside the grease layer to minimize exposure to the air. The two studied samples had dimensions of 0.6 × 0.5 × 0.1 mm³ (sample A) and 0.9 × 0.8 × 0.2 mm³ (sample B). The superconducting transition temperature for both samples was $T_c = 17.6 ± 0.1$ K (more than 10% higher than $T_c = 15.5$ K of Ref. 38). (Full transition curves of samples from the same batch are presented in Ref. 4.) Dynamic magnetic susceptibility $\chi$ was measured with 190-MHz (sample A) and 16-MHz (sample B) TDR. The magnetic field was generated by a 50-T pulsed magnet with a 11-ms rise time at Clark University. A single-axis rotator with a 0.5° angular resolution was used to accurately align the sample with respect to the magnetic field [see inset in Fig. 2(a)]. The data have been taken for each orientation at temperatures down to 0.66 K. The normal-state data at 25 K have also been taken for both orientations and subtracted. Measured shift of the resonant frequency $\Delta f \propto \chi$ (Ref. 42), thus exhibits a kink at $H_c2$ where London penetration depth diverges and is governed by the normal-state skin depth. Thus, barring uncertainty due to fluctuations, it is probing a “true” upper critical field.

There are only two data points obtained from the second crystal (sample B). Due to lack of high-field magnet time, we could not finish the whole phase diagram for this sample. However, two data points were obtained at the lowest temperature of 0.66 K and are fully consistent with those from sample A. The transition temperature in zero field was nearly identical between the two samples (17.5 and 17.6 K, respectively). These two observations provide a strong confirmation of the reproducibility of the $H_c2(T)$ functions.

Figure 1 shows the change of the resonant frequency as a function of $H$ for sample A for two field orientations and two temperatures and also shows a graphical definition of $H_c2$. We note that we obtain the same values of $H_c2$ from pulse and conventional magnet measurements (up to 9 T) at higher temperatures. From many such traces, both $H_c2^\perp$ and $H_c2^\parallel$ were determined as shown in Fig. 1 and are plotted in Fig. 2. Only lowest temperature pulse field sweeps as well as an $H = 0$ temperature sweep were measured for sample B. The results practically coincide with the data for sample A.

Figure 2(a) compares our $H_c2$ data on samples A and B with the previous transport and torque measurements. Figure 2(a) also shows the behavior expected from the orbital Werthamer-Helfand-Hohenberg (WHH) theory with $H_{orb}(0) = 0.69 T_c d H_c2/d T |_{T_c}$, the single-gap BCS paramagnetic limit, $H_{BCS}^p = 1.84 T_c = 32.2$ T, as well as $H_{orb}^p = 34.7$ T and $H_{BCS}^p = 20.4$ T calculated with $\Delta_1(0)/T_c \approx 1.885$ and $\Delta_1(0)/T_c \approx 1.111$ reported for the same samples in Ref. 4. Clearly, the observed $H_c2(T)$ exhibits much stronger flattening at low temperature compared to the orbital WHH theory. The inset in Fig. 2(a) shows the dependence of $H_c2$ on the angle $\varphi$ between $H$ and the $ab$ plane at 0.66 K where $H_c2^\perp$ is defined at a maximum of $H_c2(\varphi) = H_c2^\perp + (H_c2^\parallel - H_c2^\perp) \cos \varphi$ depicted by the solid line.

We analyze our $H_c2(T)$ data using a two-band theory, which takes into account both orbital and paramagnetic pair breaking in the clean limit, and the possibility of the FFLO with the wave vector $Q(T, H)$. In this case the equation for $H_c2$ is given by

$$G_1 = \ln t + 2 e^2 \Re \sum_{n=0}^{\infty} \int_{q}^{\infty} du e^{-u^2} \times \left[ n + 1/2 - t \sqrt{b} \tan^{-1}\left( u \sqrt{b} \right) \right].$$

(2)

Here $Q(T, H)$ is determined by the condition that $H_{orb}(T, Q)$ is maximum, $a_1 = (\lambda_0 + \lambda_\perp)/2w$, $a_2 = (\lambda_0 - \lambda_\perp)/2w$, $\lambda_\perp = \lambda_{11} - \lambda_{22}$, $\lambda_0 = (\lambda^2 + 4 \lambda_{12} \lambda_{21})^{1/2}$, $w = \lambda_{11} \lambda_{22} - \lambda_{12} \lambda_{21}$, $\lambda = T/T_c$, and $G_2$ is obtained by replacing $\sqrt{b} \rightarrow \sqrt{t}b$ and $q \rightarrow q \sqrt{t}$ in $G_1$, where

$$b = \frac{\hbar^2 v_1^2 v_2^2 H}{8 \pi \phi_0 k_B^2 T_c^2 g_1}, \quad \alpha = \frac{4 \mu_0 \phi_0 g_1 k_B T_c}{\hbar^2 v_1^2},$$

(3)

$$q^2 = \frac{Q^2}{2 \phi_0 \epsilon_2 / 2 \pi H}, \quad \eta = \frac{\gamma_0^2}{v_1^2}, \quad s = \epsilon_2 / \epsilon_1.$$  

Here, $v_1$ is the in-plane Fermi velocity in band $l = 1, 2$, $\epsilon_l = m_{\perp}^{ab}/m_{\parallel}^{ab}$ is the mass anisotropy ratio, $\phi_0$ is the flux quantum, $\mu$ is the magnetic moment of a quasiparticle, $\lambda_{11}$ and $\lambda_{22}$ are the intraband pairing constants, $\lambda_{12}$ and $\lambda_{21}$ are the interband pairing constants, and $\alpha \approx 0.56 \mu_0 M$ where the Maki parameter $\alpha_M = \sqrt{2} H_{orb}^p / H_p$ quantifies the strength of the Zeeman pair breaking. The factors $g_1 = 1 + \lambda_{11} + |\lambda_{12}|$ and $g_2 = 1 + \lambda_{22} + |\lambda_{21}|$ describe the strong coupling Eliashberg corrections. For
the sake of simplicity, we consider here the case of $\epsilon_1 = \epsilon_2 = \epsilon$ for which $H_{c2}^{\parallel}$ is defined by Eqs. (1) and (2) with $g_1 = g_2$ and rescaled $q \rightarrow qe^{-3/4}$, $x \rightarrow x e^{-1/2}$, and $\sqrt{b} \rightarrow e^{1/4} \sqrt{b}$ in $G_1$ and $\sqrt{\eta b} \rightarrow e^{1/4} \sqrt{\eta b}$ in $G_2$.

Figure 2(b) shows the fit of the measured $H_c2(T)$ to Eq. (1) for $s^\pm$ pairing with $\lambda_{11} = \lambda_{22} = 0$, $\lambda_{12} = 20$, $\eta = 0.3$, $\alpha = 0.35$, and $\epsilon = 0.128$. Equation (1) describes $H_{c2}^{\parallel}(T)$, $H_{c2}^{\perp}(T)$ and $y_{HF}(T) = b_1(T) / \sqrt{\epsilon b_1(T)}$ where $b_1(T)$ and $b_2(T)$ are the solutions of Eq. (1) for $H \parallel c$ and $H \perp c$, very well. The fit parameters are also in good quantitative agreement with experiment. For instance, the Fermi velocity $v_1 = (g_1 k_B T_c / h) [8 \pi \phi_0 b_1(0) / H_{c2}^{\parallel}(0)]^{1/2}$ can be expressed from Eq. (4) in terms of material parameters and $b_2(0) = 0.314$ calculated from Eq. (1). For $T_c = 17.8$ K, $H_{c2}^{\parallel}(0) = 18.4$ T, and $g = 1.5$ for $\lambda_{12} = 0.5$, we obtain $v_1 = 1.12 \times 10^6$ cm/s, consistent with the ARPES results.

Several important conclusions follow from the results shown in Fig. 2(b). First, contrary to the single-band Ginzburg-Landau scaling, $\gamma_{HF}^{\parallel} = \epsilon^{-1/2}$, the anisotropy parameter $\gamma_{HF}(T)$ decreases as $T$ decreases. Not only is this behavior indicative of multiband pairing, but it also reflects the significant role of the Zeeman pair breaking in LiFeAs given that $\alpha_1 = \alpha / \sqrt{\epsilon} = 0.98$ for $H \parallel c$ or is close to the single-band FFLO instability threshold, $\alpha \approx 1.39$. In this case, $\gamma_{HF}(T)$ near $T_c$ is determined by the orbital breaking and the mass anisotropy $\epsilon$, but as $T$ decreases, the contribution of the isotropic Zeeman pair breaking increases, resulting in the decrease of $\gamma_{HF}(T)$. Another intriguing result is that the solution of Eq. (1) shows no FFLO instability for $H \parallel c$, but predicts the FFLO transition at $T < T_F \approx 5$ K for $H \parallel ab$. Similar to organic superconductors, this temperature is notably lower than $T_F = 0.56T_c^{\parallel}$ expected for a single band in the limit of no orbital pairing ($\alpha \rightarrow \infty$). The FFLO wave vector $Q(T) = 4\pi k_B T_c q(T) b_1^{1/2}(T) \sqrt{g_1}/h v_1$ appears spontaneously at $T = T_F = 5$ K where the FFLO period $\ell = 2\pi Q = h v_1/2k_B T_c q(T) b_1^{1/2}(T)$ diverges and then decreases as $T$ decreases, reaching $\ell(0) = \pi \eta_0/ g_1 q(0)b_1^{1/2}(0) \approx 9\eta_0$ at $T = 0$. Here $q(0) = 0.656$, $b(0) = 0.126$, and $\eta_0 = h v_1/2\pi k_B T_c \approx 7.3$ nm, giving $\ell(0) \approx 65.6$ nm for the parameters used above. The period $\ell(0)$ is much smaller than the mean free path, $\ell_{\text{mfp}} \approx 550$ nm, estimated from the Drude formula for an ellipsoidal Fermi surface with $\epsilon = 0.128$, $v_F = 112$ km/s, $m_{\text{eff}}$ equal to the free electron mass, and $\rho(T_c) = 10\mu \Omega$ cm. Notice that $\rho(T_c)$ may contain a significant contribution from inelastic scattering, so the mean free path for elastic impurity scattering which destroys the FFLO state is even larger than $\ell_{\text{mfp}}$. Therefore, the FFLO state predicted by our calculations may be a realistic possibility verifiable by specific heat, magnetic torque, and thermal conductivity measurements. Magnetic measurements have revealed a jump in the torque developing below $\sim 8$ K, consistent with the first order FFLO transition.

Finally, we compare LiFeAs with other superconductors, especially those for which $H_{c2}$ is clearly limited

FIG. 2. (Color online) (a) $H_c2(T)$ for $H \perp c$ (solid symbols) and $H \parallel c$ (open symbols). Blue circles and red squares correspond to samples A and B, respectively. For comparison we show the literature data from the resistivity measurements with midpoint criterion: (magenta) triangles, (green) rhombi, (brown) stars. Torque data are shown by (grey) pentagons. Dashed lines are the $WHH(\varphi)$ from Eq. (4) in terms of material parameters and $g = H_c2^{\parallel}(\varphi)$, $\lambda_{11}$, $\lambda_{22}$, and $\lambda_{12}$. The fit parameters of Eq. (1) for $H \parallel c$ and $H \perp c$, very well. The fit parameters are also in good quantitative agreement with experiment. For instance, the Fermi velocity $v_1 = (g_1 k_B T_c / h)[-8 \pi \phi_0 b_1(0)/H_{c2}^{\parallel}(0)]^{1/2}$ can be expressed from Eq. (4) in terms of material parameters and $b_1(0) = 0.314$ calculated from Eq. (1). For $T_c = 17.8$ K, $H_{c2}^{\parallel}(0) = 18.4$ T, and $g = 1.5$ for $\lambda_{12} = 0.5$, we obtain $v_1 = 1.12 \times 10^6$ cm/s, consistent with the ARPES results.

Several important conclusions follow from the results shown in Fig. 2(b). First, contrary to the single-band Ginzburg-Landau scaling, $\gamma_{HF}^{\parallel} = \epsilon^{-1/2}$, the anisotropy parameter $\gamma_{HF}(T)$
by either orbital or Zeeman pair breaking. Shown in Fig. 3 are the normalized $H_c^2(T)/T_c H_c^2$ as functions of $T/T_c$ for $\mathbf{H} \parallel ab$ where the Zeeman pair breaking is most pronounced. Here $H_c^2 = |d H_c^2/d T|_{T=0}$, and our data are shown by the thick solid black line, whereas the literature data are shown by symbols. The reference materials include LiFeAs;\(^{28}\) Pauli-limited\(^{27}\) organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br;\(^{33}\) heavy fermion CeCoIn$_5$;\(^{49}\) optimally doped iron pnictides, BaFe$_{1-x}$Co$_x$As$_2$ (Ref. 18) and Ba$_2$K$_{1-x}$FeAs$_2$;\(^{26}\) iron chalcogenide Fe(Se,Te);\(^{27}\) and conventional NbTi.\(^{50}\) Remarkably, scaled data obtained on crystals with different $T_c$ and by different measurements (this work and Ref. 38) are very similar, indicating an intrinsic behavior of LiFeAs, namely, that it is indeed closer to the Pauli-limited behavior and the FFLO state below 5 K for $H \perp c$.

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