The upper critical field and its anisotropy in LiFeAs

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(Dated: January 18, 2011)

The discovery of superconductivity in iron pnictides has attracted world-wide interests in searching for new type of high Tc superconductors and unveiling their unconventional nature of superconductivity. Until now, several series of iron-based superconductors have been found, which possess a similar layered crystal structure to those of the high Tc cuprates. Resembling the cuprates and heavy fermions, superconductivity in most of the iron pnictides/chalcogenides seems to be closely tied up with magnetism; superconductivity appears while antiferromagnetism is suppressed by hole (or electron) doping or by application of external pressure. In particular, the layered crystal structure and the high superconducting transition temperatures of the iron pnictides/chalcogenides initially suggested a strong analogy with the cuprates, providing an alternative to study the puzzles of high Tc superconductivity. However, significant discrepancies have been observed between the iron-based superconductors and other layered superconductors. For example, d-wave superconductivity was realized in the high Tc cuprates, but an s±-type order parameter has been proposed for the iron pnictides/chalcogenides superconductors. Upper critical field is another important superconducting parameter. A large upper critical field has been identified in both iron pnictides/chalcogenides and the cuprates, but the former shows a rather weak effect of anisotropy. In particular, nearly isotropic upper critical field μ₀Hc2(Tc) has been observed in the 122- and 11-type iron pnictides/chalcogenides, remarkably different from any other layered superconductors. LiFeAs, a much cleaner compound with a large ratio of room temperature resistivity to residual resistivity (RRR∼40), seems to be very unique among the iron pnictide superconductors. Bearing a nearly identical structure of (Fe₂As₂)²⁻ and also a similar electronic structure to other iron pnictides, LiFeAs, however, shows simple metallic behavior prior to entering the superconducting state, lacking evidence of structural/magnetic transitions. Moreover, the stoichiometric compound LiFeAs becomes superconducting at ambient pressure and without introducing additional charge carriers via doping. Nevertheless, LiFeAs still demonstrates a relatively high Tc (Tc ≃ 18 K), being comparable with those iron pnictides/chalcogenides which parent compounds undergo a magnetic/structural transition. Unfortunately, LiFeAs is extremely air sensitive and many of its superconducting properties remain mysterious because of the restrictions of accessible experimental methods. In LiFeAs the extrapolation of μ₀Hc2 near Tc to zero temperature gives a rather large value of μ₀Hc2(0)(~ 80 T). In order to fully track the field dependence of superconductivity, a strong magnetic field is desired. Here we report the first resistivity measurement of LiFeAs in a pulsed magnetic field down to 1.4K, from which the temperature-magnetic field phase diagram is well established. The upper critical field μ₀Hc2 is determined to be 15 T and 24.2 T at T = 1.4K for H || c and H || ab, respectively. In comparison with other series of iron pnictide superconductors, the upper critical field shows a moderate anisotropic effect and its value of μ₀Hc2(0) is largely reduced.

I. INTRODUCTION

The discovery of superconductivity in iron pnictides has attracted world-wide interests in searching for new type of high Tc superconductors and unveiling their unconventional nature of superconductivity. Until now, several series of iron-based superconductors have been found, which possess a similar layered crystal structure to those of the high Tc cuprates. Resembling the cuprates and heavy fermions, superconductivity in most of the iron pnictides/chalcogenides seems to be closely tied up with magnetism; superconductivity appears while antiferromagnetism is suppressed by hole (or electron) doping or by application of external pressure. In particular, the layered crystal structure and the high superconducting transition temperatures of the iron pnictides/chalcogenides initially suggested a strong analogy with the cuprates, providing an alternative to study the puzzles of high Tc superconductivity. However, significant discrepancies have been observed between the iron-based superconductors and other layered superconductors. For example, d-wave superconductivity was realized in the high Tc cuprates, but an s±-type order parameter has been proposed for the iron pnictides/chalcogenides superconductors. Upper critical field is another important superconducting parameter. A large upper critical field has been identified in both iron pnictides/chalcogenides and the cuprates, but the former shows a rather weak effect of anisotropy. In particular, nearly isotropic upper critical field μ₀Hc2(Tc) has been observed in the 122- and 11-type iron pnictides/chalcogenides, remarkably different from any other layered superconductors. LiFeAs, a much cleaner compound with a large ratio of room temperature resistivity to residual resistivity (RRR∼40), seems to be very unique among the iron pnictide superconductors. Bearing a nearly identical structure of (Fe₂As₂)²⁻ and also a similar electronic structure to other iron pnictides, LiFeAs, however, shows simple metallic behavior prior to entering the superconducting state, lacking evidence of structural/magnetic transitions. Moreover, the stoichiometric compound LiFeAs becomes superconducting at ambient pressure and without introducing additional charge carriers via doping. Nevertheless, LiFeAs still demonstrates a relatively high Tc (Tc ≃ 18 K), being comparable with those iron pnictides/chalcogenides which parent compounds undergo a magnetic/structural transition. Unfortunately, LiFeAs is extremely air sensitive and many of its superconducting properties remain mysterious because of the restrictions of accessible experimental methods. In LiFeAs the extrapolation of μ₀Hc2 near Tc to zero temperature gives a rather large value of μ₀Hc2(0)(~ 80 T). In order to fully track the field dependence of superconductivity, a strong magnetic field is desired. Here we report the first resistivity measurement of LiFeAs in a pulsed magnetic field down to 1.4K, from which the temperature-magnetic field phase diagram is well established. The upper critical field μ₀Hc2 is determined to be 15 T and 24.2 T at T = 1.4K for H || c and H || ab, respectively. In comparison with other series of iron pnictide superconductors, the upper critical field shows a moderate anisotropic effect and its value of μ₀Hc2(0) is largely reduced.

II. EXPERIMENTAL METHODS

High-quality single crystals of LiFeAs have been grown by a self-flux technique. The precursor of Li₃As was synthesized from Li piece and As chips that were sealed in a Nb tube under Ar atmosphere and then treated at 650°C for 15 hours in a sealed quartz tube. The Li₃As, Fe and As powders were mixed in the ratio of Li:Fe:As=1:0.8:1. The powder mixture was then pressed into a pallet in an alumina oxide tube. To prevent the vaporized Li from attacking the quartz tube at high tem-
perature, the sample pallet was subsequently sealed in a Nb tube and a quartz tube under vacuum. The sealed quartz tube was heated at 800°C for 10h before heating up to 1100 °C at which it was held for another 10h. Finally, it was cooled down to 800°C with a rate of 5°C per hour. Crystals with a size up to 4mm×3mm×0.5mm were obtained. The whole preparation work were carried out in a glove box protected with high purity Ar gas. The obtained single crystals were first characterized by x-ray diffraction with a Mac Science diffractometer and ac susceptibility measurements using the Oxford cryogenic system (Maglab-Exa-12) prior to the transport measurements in a pulsed magnetic field at Los Alamos.

Electrical resistivity was measured using a typical four-contact method in pulsed fields of up to 40T and at temperatures down to 1.4K in a Helium-4 cryostat. Note that the applied electrical current was always along the ab-plane. In order to minimize the inductive self-heating caused by the fast change of magnetic field, small crystals with typical sizes 2mm×0.5mm×0.1mm were cleaved off along the c-direction from the as-grown samples. In order to avoid oxidizing the samples, special cares were paid to protect the samples from exposing to air while preparing for the electrical contacts. Data were recorded using a 10 MHz digitizer and 100 kHz alternating current, and analyzed using a custom low-noise digital lock-in technique. Temperature dependence of the electrical resistivity at zero field was measured with a Lakeshore resistance bridge.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 presents the temperature dependence of the electrical resistivity $\rho(T)$ at zero magnetic field for LiFeAs. Obviously, LiFeAs shows simple metallic behavior upon cooling down from room temperature, followed by a sharp superconducting transition at $T_c \approx 17.5$ K, which is in consistence with the reports in literature.\cite{10,12} Note that the weak kink in the resistivity $\rho(T)$ around 75K is attributed to the change of cooling rate. No evidence of structural/magnetic transition has been observed in LiFeAs. In order to demonstrate the superconducting transition in detail, we plot the low temperature electrical resistivity and magnetic susceptibility in the inset of Fig.1, which were measured with samples cut from the same batch. As frequently observed in superconductors, the bulk $T_c$ determined from the magnetic susceptibility is slightly lower. The observations of a large RRR ($\approx 15$) and a narrow superconducting transition indicate high quality of the samples investigated here. Since LiFeAs is a good metal with low resistivity, measurements of its electrical resistivity in a pulsed magnetic field is rather challenging. Nevertheless, we have succeeded in obtaining a good set of resistivity data up to a magnetic field of 40T after many failures. Fig. 2 shows the field dependence of the electrical resistivity $\rho(\mu_0 H)$ of LiFeAs at variant temperatures, in which the magnetic field is applied along (a) the c-axis and (b) the ab-plane, respectively. One can see that a relatively sharp superconducting transition survives down to very low temperatures, even though the signals become more noisy upon cooling down, in particular for the case of $H \parallel ab$. Obviously, the superconducting transition is eventually suppressed upon applying a magnetic field, but the critical field required to suppress superconductivity is much larger for

![FIG. 1: Temperature dependence of the electrical resistivity $\rho(T)$ for LiFeAs at zero field. The lower inset shows the magnetic susceptibility $\chi(T)$.

FIG. 2: Magnetic field dependence of the electrical resistivity at variant temperatures for LiFeAs: (a) $H \parallel c$; (b) $H \parallel ab$.](image-url)
\( H \parallel ab \). Furthermore, the normal state of LiFeAs remains metallic upon suppressing superconductivity in a sufficiently high magnetic field, being different from those of the 122- and 11-type compounds\(^7,8\).

\[
\mu_0 H_{c2}^{\alpha}(0)[T] = 1.86 T_c[K].
\]  

(2)

For conventional superconductors, \( \mu_0 H_{c2}^{\alpha}(0) \) is usually much larger than \( \mu_0 H_{c2}^{\alpha \parallel H}(0) \) and, therefore, their upper critical field is mainly restricted by the orbital pair-breaking mechanism. In our case, the initial slope of \( \mu_0 H_{c2} \) at \( T_c \), i.e., \( -d \mu_0 H_{c2}/dT|_{T=T_c} \), is determined as 3.3 T/K and 1.2 T/K for \( H \parallel ab \) and \( H \parallel c \), respectively. Thus the values of \( \mu_0 H_{c2}^{\alpha \parallel H}(0) \) are accordingly derived as 39.8T for \( H \parallel ab \) and 14.5T for \( H \parallel c \); the latter is close to the experimental value of \( \mu_0 H_{c2} \lesssim 15T \) at \( T=1.4K \), indicating an orbitally limited critical field for \( H \parallel c \). On the other hand, Eq. 2 yields \( \mu_0 H_{c2}^{\alpha \parallel H}(0) = 32.6T \). The experimentally derived value of \( \mu_0 H_{c2}(0) \sim 25T \) for \( H \parallel ab \) is, therefore, well below the corresponding values of \( \mu_0 H_{c2}^{\alpha \parallel H}(0) \) and \( \mu_0 H_{c2}^{\alpha \parallel c}(0) \). The solid lines in Fig. 3 present the WHH fits to the experimental data of \( \mu_0 H_{c2}(T_c) \), in which both the spin-paramagnetic and orbital pair-breaking effects were considered\(^9\). The parameter \( \lambda_{so} \) describes the strength of the spin-orbit scattering. The fits give the Maki parameter \( \alpha = 0 \) and 1.74 for field along the c-axis and the ab-plane, respectively. The former further confirms the orbitally limited critical field for \( H \parallel c \). However, the resulted fitting parameters \( \alpha = 1.74, \lambda_{so} = 0.3 \) indicate that the upper critical field is likely spin-paramagnetically limited for \( H \parallel ab \) even though we still could not exclude the possibility of the orbital effect due to its multi-band effect. As shown in Fig. 3 (see the dotted line and the solid line for \( H \parallel ab \)), the spin-paramagnetic effect might lower the upper critical field, and therefore, reduce the anisotropy of \( \mu_0 H_{c2} \) at low temperatures. For comparison, Fig. 4 plots the

\[
\mu_0 H_{c2}^{\alpha \parallel H}(0)[T] = -0.69 T_c(dH_{c2}/dT)|_{T=T_c}[K].
\]  

(1)

On the other hand, superconductivity is suppressed while the magnetic energy associated with the Pauli spin susceptibility in the normal state exceeds the condensation energy in the superconducting state as a result of Zeeman effect. In this case, the Pauli-limited upper critical field for weakly coupled superconductors can be written as\(^17,18\).
available upper critical fields for LiFeAs, independently determined from measurements of the electrical resistivity (this work), the magnetic torque and the resonant frequencies based on a tunnel-diode oscillator. One can see that the experimental results obtained from the above three methods are similar in general; the visible discrepancy might result from the exact determination of $T_c$. Nevertheless, the electrical resistivity studied here provides the most direct approach for determining the upper critical field.

![Graph](image)

**TABLE I: The derived superconducting parameters for LiFeAs**

| Field | $T_c$ (K) | $\mu_0H_{c2}(1.4\text{K})$ (T) | $\mu_0H_{c2}(T)$ | $\mu_0H_{orb}^s(T)$ | $\mu_0H_{orb}^p(T)$ | $\alpha$ | $\lambda_{20}$ | $\xi$(nm) |
|-------|-----------|-------------------------------|-------------------|---------------------|-------------------|--------|-------------|---------|
| $H \parallel c$ | 17.5 | 1.2 | 15 | 14.5 | 32.6 | 0 | 0 | 1.7 |
| $H \parallel ab$ | 17.5 | 3.3 | 24.2 | 39.8 | 32.6 | 1.74 | 0.3 | 4.8 |

In summary, we have determined the complete temperature-magnetic field phase diagram for the superconductor LiFeAs by means of measuring the electrical resistivity in a field up to 40T. The upper critical field of LiFeAs is derived as $\mu_0H_{c2}(1.4K)=15T$ and 24.2T for field applied along the $c$-axis and the $ab$-plane, respectively. The anisotropic parameter $\gamma$ decreases with decreasing temperature and shows a weak anisotropic effect at low temperatures. These findings indicate that weak anisotropy of $\mu_0H_{c2}$ seems to be a common feature of the iron-based superconductors, in spite of the layered nature of their crystal structure.

**V. ACKNOWLEDGEMENTS**

This work was supported by the National Science Foundation of China (No.10874146 and No. 10934005), the National Basic Research Program of China (973 program) under grant No. 2011CBA00103 and 2009CB929104, the PCSIRT of the Ministry of Education of China, Zhejiang Provincial Natural Science Foundation of China and the Fundamental Research Funds for the Central Universities. Work at NHMFL-LANL is performed under the auspices of the National Science Foundation, Department of Energy and State of Florida.

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