FAST TRACK COMMUNICATION

Anomalous superconducting state in LiFeAs implied by the $^{75}$As Knight shift measurement

S-H Baek¹, L Harnagea¹, S Wurmehl¹, B Büchner¹,² and H-J Grafe¹

¹ IFW-Dresden, Institute for Solid State Research, PF 270116, D-01171 Dresden, Germany
² Institut für Festkörperphysik, Technische Universität Dresden, D-01062 Dresden, Germany

E-mail: sbaek.fu@gmail.com

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Abstract

$^{75}$As NMR investigation of a single crystal of superconducting LiFeAs is presented. The Knight shift and the in situ ac susceptibility measurements as a function of temperature and external field are indicative of two superconducting (SC) transition temperatures, each of which is associated with its own upper critical field. Strikingly, the Knight shift maintains its normal state value over a temperature range in the SC state before it drops abruptly, being consistent with spin-singlet pairing. Together with our previous NMR study, the anomalous SC state featuring the constant Knight shift is attributed to the extremely sensitive SC properties of LiFeAs, probably stemming from its proximity to a critical instability.

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It is commonly argued that superconductivity in iron pnictides is driven by the antiferromagnetic (AFM) spin fluctuations which are associated with nesting between the hole and electron Fermi surface pockets, although the SC gap symmetry seems to vary among the materials from nodal to nodeless [1–3]. An exception to this general picture is LiFeAs, which is superconducting as is, without any signature of nesting and static magnetism, yet with rather high $T_c \sim 18$ K [4–6].

While the absence of nesting and static magnetism in LiFeAs [5] might support a non-magnetic origin for the SC pairing, such as phonons [7] or orbital fluctuations [8], AFM spin fluctuations remain a strong candidate responsible for the SC pairing [9–12], e.g., by recovering the nesting condition via magnetic response shifting [13]. If this is indeed the case, it would strengthen the belief that AFM spin fluctuations are fundamental to the superconductivity of iron pnictides. On the other hand, spin-triplet pairing which is driven by ferromagnetic spin fluctuations originating from strong Hund coupling has also been suggested [14], accompanied by some experimental support [15–18]. Such debates about the pairing mechanism in LiFeAs may imply that the nature of superconductivity in this material is different from other iron-pnictide families, and it has been suggested that the close proximity of the system to a strong magnetic instability may effect the unusual sensitivity of the SC properties [17, 14].

In an effort to confirm the underlying instability and to uncover its nature, we carried out $^{75}$As nuclear magnetic resonance (NMR) in a single crystal of LiFeAs chosen from a different batch to that used in our previous NMR study [17], focusing on the low temperature range near and below $T_c \sim 18$ K. While the in situ ac susceptibility and the NMR signal intensity confirm the bulk $T_c$, the Knight shift remains constant down to a temperature at which it drops sharply. Although the constant Knight shift behavior in the SC state is not easily reproducible in other single crystals, our data suggest that an anomalous superconducting state...
In the literature [20–24], the superconducting transition temperature for each field was determined from the sharp drop of $K_{\parallel}$ as denoted by arrows.

where the Knight shift does not change could be stabilized. We discuss that LiFeAs is very close to a critical instability which affects the SC state, particularly near the region of the normal/superconducting boundary.

The single crystal of LiFeAs was grown by a self-flux method as described in [4]. Due to the sensitivity of the sample to air and moisture, the sample was carefully sealed into a quartz tube filled with Ar gas for NMR measurements. The sealed sample was mounted on a goniometer for accurate alignment of the sample along the external field. $^{75}$As $(I = 3/2)$ nuclear magnetic resonance (NMR) experiments were performed in the range of temperature 3.6–25 K and external field 0–16 T. We also carried out $^{75}$As nuclear quadrupole resonance (NQR) to determine the quadrupole frequency $\nu_Q$. The NQR spectrum shows a width of 75 kHz at 20 K, which is much narrower than $\sim$170 kHz in a powder sample [19] and thus indicates a sign of good chemical homogeneity for the sample.

The Knight shift $K$, i.e., the local static spin susceptibility, was measured from the $^{75}$As NMR central line at various external fields applied parallel and perpendicular to the crystallographic c axis. The large quadrupole frequency $\nu_Q = 21.08$ MHz of $^{75}$As $(I = 3/2)$, which is almost $T$-independent in the low temperature range investigated, shifts the central transition of $^{75}$As by the second order quadrupole effect given by $\Delta \nu = 3\nu_Q^2/16\omega_0^2 (1 - \cos^2\theta)(1 - 3\cos^2\theta)$ for $I = 3/2$ where $\omega_0$ is the unshifted Larmor frequency and $\theta$ is the angle between the external field $H$ and the $c$ axis. The Knight shift shown in figure 1 was obtained by subtracting $\Delta \nu$ from the total shift of the central line. The SC transition temperature $T_c$ was identified from a sudden drop of $K$ for a given external field $H$, which indicates spin-singlet Cooper pairing. Whereas this behavior seems consistent with previous NMR studies for this compound [19, 9], we find that values for $T_c$, particularly for $H \parallel c$, are much lower than values reported in the literature [20–24]. At 8.5 T for $H \parallel c$, for example, $K$ does not drop down even at 3.6 K, indicating that $T_c \leq 3.5$ K is significantly lower than the expected value ($\sim$10 K) [20–24].

In order to confirm the transition temperature, we measured the in situ $ac$ susceptibility $\chi_{ac}$ using a NMR radio frequency (rf) circuit. In the SC state, the Meissner effect induces the change of impedance and thus the tuning frequency of the rf circuit. Therefore, the onset of superconductivity could be detected by monitoring $\chi_{ac}$ as a function of temperature. Figure 2 shows $\chi_{ac}(T)$ measured at various external fields $H$. Here we define $T_c$ as the temperature where $\chi_{ac}$ reaches 10% of the full drop to the low temperature plateau for each field, and it is denoted by down arrows. Clearly $T_c$ detected by $\chi_{ac}$ is much higher than that obtained by Knight shift measurements for each field (up arrows). Note that, at 8.5 T parallel to the $c$ axis, a clear onset was observed at 11 K by $\chi_{ac}$, which is compatible with values reported thus far [20–24], in stark contrast to the absence of the Knight shift anomaly down to 3.6 K. It may be worthwhile to note that $\chi_{ac}$ displays a small but noticeable anomalous change in its slope at $T_c$ obtained by $K$.

As the two experimental methods seem to distinguish different onset temperatures for the SC transition, here we define the two onset temperatures obtained by $\chi_{ac}$ and $K$ as $T_{c\chi}$ and $T_{K\parallel}$, respectively. While a sharp drop of $K$ is usually a good indication of spin-singlet superconductivity, $\chi_{ac}$ alone is not sufficient in general to verify a bulk $T_c$, because other non-superconducting effects might alter the temperature dependence of $\chi_{ac}$. To check the validity of $T_{c\chi}$, we carefully examined the temperature evolution of the $^{75}$As spectra. In the SC state, the signal intensity should decrease due to supercurrents which reduce the sample volume that can be penetrated by the rf field, and therefore this could be another good probe for detecting the onset of bulk superconductivity. Figure 3 shows the $^{75}$As NMR spectra as a function of temperature measured at 8.5 T, where the Boltzmann correction was made by multiplying $T$ for each
Therefore, we conclude that results measured in other samples by different groups [22–24].

Figure 3. Temperature dependence of $^{75}$As NMR central line at $H = 8.5$ T for (a) $H \perp c$ and (b) $H \parallel c$. (c) Signal intensity and Knight shift versus temperature at 8.5 T. The temperature dependence of signal intensity for both $H \perp c$ and $H \parallel c$ agrees well with that for $\chi_{ac}$, indicating that $T_{c}^{ac}$ represents the onset of screening due to superconductivity. The Knight shift, however, reveals $T_{c}^{ac}$ which is significantly lower than $T_{c}^{ac}$. $K_{c}$ was offset vertically for comparison.

Figure 4. $H$–$T$ phase diagram for LiFeAs. The two onset temperatures $T_{c}^{ac}$ and $T_{c}^{ac}$ were obtained by ac susceptibility and the Knight shift, respectively. Data from [24, 18] are shown for comparison. The onset temperatures of paramagnetic irreversibility from Li et al. fall between the $T_{c}^{ac}$ and $T_{c}^{ac}$ line, while $T_{c}(H \parallel c)$ in [18] determined from resistivity (not shown for clarity) almost coincides with $T_{c}^{ac}(H)$. Note that shades of blue and red are applicable only to the case of $H \perp c$ and thus some care is needed to compare the data for $H \parallel c$.

Further analysis of the Knight shift, the signal intensity, and the ac susceptibility obtained at various external fields reveals quite different field dependences for $T_{c}^{ac}$ and $T_{c}^{ac}$. (For raw $^{75}$As spectra at external fields other than 8.5 T, see supplemental material available at stacks.iop.org/JPhysCM/25/162204/mmedia.) The resulting $H$–$T$ phase diagram is presented in figure 4. We find that the $H$-dependence of $T_{c}^{ac}$ is in qualitative agreement with other studies [21, 24, 22]. For example, the data from Khim et al. [24] are compatible with $T_{c}^{ac}$ data for the $H$-dependence as well as with the anisotropy.

In contrast, the $H$-dependence of $T_{c}^{ac}$ is very different from that of $T_{c}^{ac}$, other than for its much lower values. For $H \perp c$, while $T_{c}^{ac}$ exhibits almost a linear $H$-dependence up to 16 T, $T_{c}^{ac}$ does not decrease linearly with increasing $H$. Consequently, the difference $T_{c}^{ac} - T_{c}^{ac}$ becomes larger at higher fields. This trend is more pronounced for $H \parallel c$. Note that the estimated $H$-dependence of $T_{c}^{ac}$ for $H \parallel c$ (dashed line in figure 4) agrees with the absence of $T_{c}^{ac}$ at 8.5 T down to 3.6 K.

Our experimental results naturally raise important questions. Does $K$, i.e., the intrinsic spin susceptibility, remain unchanged across $T_{c}^{ac}$ but drop below $T_{c}^{ac}$? Do the two seemingly distinguishable SC states above and below $T_{c}^{ac}$ occur in a single phase? It should be emphasized that only one phase must be present in the normal state above $T_{c}^{ac}$, because NMR and NQR spectra exhibit very sharp single lines, and their signal intensities are well conserved at all temperatures investigated. Although inhomogeneous superconductivity is extremely unlikely due to bulk superconductivity in our single crystals, here we discuss the possibility that the two SC transitions result from phase segregation in bulk form below $T_{c}^{ac}$, i.e., a partial volume fraction of the sample (region I).
becomes superconducting at $T_{c}^{ac}$ first, and the rest of the sample (region II) remains normal down to $T_{c}^{ac}$ but undergoes the SC transition at $T_{c}^{ac}$.

If phase segregation takes place at $T_{c}^{ac}$, the otherwise single spectrum would be segregated into two parts arising from the SC region I and the normal region II, respectively. In this case, the unchanged Knight shift of the ‘total’ spectrum between $T_{c}^{ac}$ and $T_{c}^{ac}$ could be realized only either (i) if the SC transition in region I is extremely sharp so that the decreasing Knight shift is not detected, or (ii) if triplet superconductivity occurs in region I so that $K$ for region I is still the same as that for the normal region II. The consequence of case (i) should be an almost discontinuous change of the signal intensity just below $T_{c}^{ac}$. On the contrary, we find that the $T$-dependence of the signal intensity shows a gradual change over a temperature range (see figure 3(c)), ruling out this scenario. Similarly, case (ii) is also ruled out as follows. Since singlet superconductivity occurs at $T_{c}^{ac}$, we should have two different SC pairing states below $T_{c}^{ac}$. Since $K$ from region II decreases while $K$ from region I remains constant, two NMR lines or a noticeable broadening below $T_{c}^{ac}$ should be observed. As shown in figure 3(a), however, the well-defined single line at all temperatures is inconsistent with this scenario. Also by close inspection of the $T$-dependence of the $^{75}$As spectrum at other external fields (available at stacks.iop.org/JPhysCM/25/162204/mmedia), the phase segregation scenario turns out to be highly improbable. Hence, we reach the remarkable conclusion that $K$ is indeed a constant in the SC state between $T_{c}^{ac}$ and $T_{c}^{ac}$, suggesting that the anomalous SC state may change at $T_{c}^{ac}$ to a somewhat ‘normal’ SC state with singlet-pairing symmetry.

A priori, the unchanged Knight shift through $T_{c}^{ac}$ contrasts with spin-singlet pairing, because it implies that the spin degree of freedom for electrons does not vanish in the SC state. Surprisingly, another signature of the possible unusual SC state in LiFeAs was also verified independently in a different single crystal by recent magnetometry measurements [18] which report a paramagnetic (PM) response within the SC state at high fields. The onset temperature of PM irreversibility $T_{irr}$ as a function of $H \parallel c$ is located between the $T_{c}^{ac}$ and $T_{c}^{ac}$ lines (see figure 4), whereas $T_{c}$ determined from resistivity is well consistent with $T_{c}^{ac}(H \parallel c)$. The anomalous PM response in the SC state, which is ascribed to the triplet component induced by high fields [18], is indeed in excellent agreement with the non-vanishing spin susceptibility in the SC state revealed by the constant Knight shift. Note that, since $T_{irr}$ is a crossover temperature rather than a measure of the actual transition, $T_{irr} < T_{c}^{ac}$ is very reasonable. Therefore, combining our NMR results and [18], we interpret that both the constant Knight shift and the PM response observed in a similar region of the phase diagram are signs of spin-triplet pairing that could perhaps be stabilized under certain conditions. This may be a realization of the theoretical prediction that a spin triplet could occur in iron pnictides, depending on various parameters such as Hund coupling and onsite Coulomb repulsion [29, 30, 14].

Interestingly, PM irreversibility at high fields was not reproduced in other samples, this being attributed to the extreme sensitivity of the samples [18] which was already proposed in our previous NMR study [17]. Such a difficult reproducibility of the constant Knight shift behavior as well as of the PM response in [18], together with the extreme sensitivity of the SC properties demonstrated in our previous NMR study [17], suggests that the triplet-like anomalous SC state is unstable in nature, being susceptible to even minute off-stoichiometry. This is also consistent with the large variation of $T_{c}$ from 15.5 to 18 K which has been found in a recent transport study [31], although all the measured samples show the lowest residual–resistivity ratios and thus appear to be of high quality.

Here we argue that the peculiar sensitivity of LiFeAs could be a natural consequence of its close proximity to a critical instability, near which the unusual SC state could emerge. Hence, as long as the off-stoichiometry is small (i.e., the sample quality is pure enough), the effect of the instability would persist especially at high temperatures/fields causing $T_{c}(H = 0)$ and $H_{c2}(T = 0)$ to be very much sample-dependent, whether or not the unusual SC state is actually stabilized. Note that this picture indeed accounts well for the non-trivial large variation of $T_{c}$ and $H_{c2}$ reported so far in LiFeAs [21–24, 31] and the persisting 2D superconducting fluctuations up to 1.47 $T_{c}$ [31]. Furthermore, given the possible realization of an anomalous SC state which differs from the usual spin-singlet state, contradicting experimental results regarding the pairing symmetries in LiFeAs [16, 32, 33] may be reconciled with each other, in terms of the closeness to a critical ferromagnetic instability.

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Note added in proof. After completion of this manuscript, we became aware of a theoretical work [34], which shows a possible transition from triplet to singlet SC states, greatly supporting our NMR results.

References

[1] Lumsden M D and Christianson A D 2010 Magnetism in Fe-based superconductors J. Phys.: Condens. Matter 22 203203
[2] Stewart G R 2011 Superconductivity in iron compounds Rev. Mod. Phys. 83 1589–652
[3] Chubukov A 2012 Pairing mechanism in Fe-based superconductors Ann. Rev. Condens. Mater. Phys. 3 57
[4] Morozov I et al 2010 Single crystal growth and characterization of superconducting LiFeAs Cryst. Growth Des. 10 4428–32
[5] Borisenko S V et al 2010 Superconductivity without nesting in LiFeAs Phys. Rev. Lett. 105 067002
[6] Pitcher M J et al 2010 Compositional control of the superconducting properties of LiFeAs J. Am. Chem. Soc. 132 10467–76
[7] Kordyuk A A, Zabolotnyy V B, Evtushinsky D V, Kim T K, Morozov I V, Kulic M L, Follath R, Behr G, Buechner B and Borisenko S V 2011 Angle-resolved photoemission spectroscopy of superconducting LiFeAs: evidence for strong electron–phonon coupling Phys. Rev. B 83 134513
[8] Kontani H and Onari S 2010 Orbital-fluctuation-mediated superconductivity in iron pnictides: analysis of the five-orbital Hubbard–Holstein model Phys. Rev. Lett. 104 157001

[9] Jeglić P et al 2010 75As nuclear magnetic resonance study of antiferromagnetic fluctuations in the normal state of LiFeAs Phys. Rev. B 81 140511

[10] Platt C, Thomale R and Hanke W 2011 Superconducting state of the iron pnictide LiFeAs: a combined density-functional and functional-renormalization-group study Phys. Rev. B 84 235121

[11] Taylor A E, Pitcher M J, Ewings R A, Perring T G, Brydon P M R, Daghofer M, Timm C and van den Brink J 2011 Theory of magnetism and triplet superconductivity in iron pnictides: analysis of the superconducting LiFeAs single crystals Phys. Rev. B 84 094509

[12] Hajiri T, Ito T, Niwa R, Matsunami M, Min B H, Kwon Y S and Kimura S 2012 Three-dimensional electronic structure and interband nesting in the stoichiometric superconductor LiFeAs Phys. Rev. B 85 094502

[13] Qureshi N et al 2012 Inelastic neutron-scattering measurements of incommensurate magnetic excitations on superconducting LiFeAs single crystals Phys. Rev. Lett. 108 117001

[14] Brydon P M R, Daghofer M, Timm C and van den Brink J 2011 Theory of magnetism and triplet superconductivity in LiFeAs Phys. Rev. B 83 060501

[15] Pramanik A K, Harnagea L, Nacke C, Wolter A U B, Wurmehl S, Kataev V and Büchner B 2011 Fishtail effect and vortex dynamics in LiFeAs single crystals Phys. Rev. B 83 094502

[16] Hänke T, Sykora S, Schlegel R, Baumann D, Harnagea L, Wurmehl S, Daghofer M, Büchner B, van den Brink J and Hess C 2012 Probing the unconventional superconducting state of LiFeAs by quasiparticle interference Phys. Rev. Lett. 108 127001

[17] Baek S-H, Grafe H-J, Hammerath F, Fuchs M, Rudisch C, Harnagea L, Aswartham S, Wurmehl S, van den Brink J and Büchner B 2012 75As NQR–NQR study in superconducting LiFeAs Eur. Phys. J. B 85 159

[18] Li G, Urbano R R, Goswami P, Tarantini C, Lv B, Kuhns P, Reyes A P, Chu C W and Balicas L 2013 Anomalous hysteresis as evidence for a magnetic-field-induced chiral superconducting state in LiFeAs Phys. Rev. B 87 024512

[19] Li Z, Ooe Y, Wang X-C, Liu Q-Q, Jin C-Q, Ichida M and Zheng G-Q 2010 75As NQR and NMR studies of superconductivity and electron correlations in iron arsenide LiFeAs J. Phys. Soc. Japan 79 083702

[20] Lee B, Khim S, Kim J S, Stewart G R and Kim K H 2010 Single-crystal growth and superconducting properties of LiFeAs Europhys. Lett. 91 67002

[21] Heyer O, Lorenz T, Zabolotnyy V B, Evtushinsky D V, Boriseno S V, Morozov I, Harnagea L, Wurmehl S, Hess C and Büchner B 2011 Resistivity and Hall effect of LiFeAs: evidence for electron–electron scattering Phys. Rev. B 84 064512

[22] Kurita N, Kitagawa K, Matsubayashi K, Kismarachardja A, Choi E-S, Brooks J S, Uwatoko Y, Uji S and Terashima T 2011 Determination of the upper critical field of a single crystal LiFeAs: the magnetic torque study up to 35 Tesla J. Phys. Soc. Japan 80 013706

[23] Cho K, Kim H, Tanatar M A, Song Y J, Kwon Y S, Coniglio W A, Agosta C C, Gurevich A and Prozorov R 2011 Anisotropic upper critical field and possible Fulde–Ferrel–Larkin–Ovchinnikov state in the stoichiometric pnictide superconductor LiFeAs Phys. Rev. B 83 060502

[24] Khim S, Lee B, Kim J W, Choi E S, Stewart G R and Kim K H 2011 Pauli-limiting effects in the upper critical fields of a clean LiFeAs single crystal Phys. Rev. B 84 104502

[25] Stockert U, Abdel-Hafiez M, Evtushinsky D V, Zabolotnyy V B, Wotier A U B, Wurmehl S, Morozov I, Klingeler R, Borisenko S V and Büchner B 2011 Specific heat and angle-resolved photoemission spectroscopy study of the superconducting gaps in LiFeAs Phys. Rev. B 83 224512

[26] Borisenko S V, Zabolotnyy V B, Kordyuk A A, Evtushinsky D V, Kim T K, Morozov I V, Follath R and Büchner B 2012 One-sign order parameter in iron based superconductor Symmetry 4 251–64

[27] Lankau A, Keopernik K, Borisenko S, Zabolotnyy V, Büchner B, van den Brink J and Eschrig H 2010 Absence of surface states for LiFeAs investigated using density functional calculations Phys. Rev. B 82 184518

[28] Knolle J et al 2012 Incommensurate magnetic fluctuations and fermi surface topology in LiFeAs Phys. Rev. B 86 174519

[29] Daghofer M, Moreo A, Riera J A, Arrigoni E, Scalapino D J and Dagotto E 2008 Model for the magnetic order and pairing channels in Fe pnictide superconductors Phys. Rev. Lett. 101 237004

[30] Nicholson A, Ge W, Zhang X, Riera J, Daghofer M, Oleš A M, Martins G B, Moreo A and Dagotto E 2011 Competing pairing symmetries in a generalized two-orbital model for the pnictide superconductors Phys. Rev. Lett. 106 217002

[31] Ruiller-Albenque F, Colson D, Forget A and Alloul H 2012 Multiorbital effects on the transport and the superconducting fluctuations in LiFeAs Phys. Rev. Lett. 109 187005

[32] Hashimoto K, Kasahara S, Katsumata R, Mizukami Y, Yamashita M, Ikeda H, Terashima T, Carrington A, Matsuda Y and Shibata T 2012 Nodal versus nodeless behaviors of the order parameters of LiFeP and LiFeAs superconductors from magnetic penetration-depth measurements Phys. Rev. Lett. 108 047003

[33] Jang D-J, Hong J B, Kwon Y S, Park T, Gofryk K, Ronning F, Thompson J D and Bang Y 2012 Evidence for s+ -wave pairing symmetry in LiFeAs from its low-temperature specific heat Phys. Rev. B 85 180505

[34] Aperis A and Varelogiannis G 2013 arXiv:1303.2231