As-75 nuclear magnetic resonance study of antiferromagnetic fluctuations in the normal state of LiFeAs

Citation for published version:

Digital Object Identifier (DOI):
10.1103/PhysRevB.81.140511

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Physical Review B: Condensed Matter and Materials Physics

Publisher Rights Statement:
Copyright 2010 The American Physical Society. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Physical Society.

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
75As nuclear magnetic resonance study of antiferromagnetic fluctuations in the normal state of LiFeAs

1Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
2Institute of Mathematics, Physics and Mechanics, Jadranska 19, 1000 Ljubljana, Slovenia
3Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany
4School of Chemistry, University of Edinburgh, West Mains Road, EH9 3JJ Edinburgh, United Kingdom
5Department of Chemistry and TCSUH, University of Houston, Houston, Texas 77204-5002, USA
6Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia

Received 16 December 2009; published 30 April 2010

We present a detailed study of 75As nuclear magnetic resonance Knight shift and spin-lattice relaxation rate in the normal state of stoichiometric polycrystalline LiFeAs. Our analysis of the Korringa relation suggests that LiFeAs exhibits strong antiferromagnetic fluctuations, if transferred hyperfine coupling is a dominant interaction between 75As nuclei and Fe electronic spins, whereas for an on-site hyperfine coupling scenario, these are weaker, but still present to account for our experimental observations. Density-functional calculations of electric field gradient correctly reproduce the experimental values for both 75As and 7Li sites.

DOI: 10.1103/PhysRevB.81.140511

PACS number(s): 74.70.–b, 76.30.–v, 76.60.–k

Following the discovery of superconductivity in LaFeAsO1−xFex,1 nuclear magnetic resonance (NMR) provided one of the earliest evidences for unconventional pairing in the superconducting (SC) state,2–4 multigap superconductivity,5–7 pseudogap (PG) behavior in the normal state,2,5,8 and antiferromagnetic (AFM) ordering of Fe2+ spins in the undoped parent compounds of Fe-As superconductors.3,9,10 Although the SC pairing mechanism is still under debate, it is commonly believed that AFM fluctuations play an important role in promotion of high-temperature superconductivity in this family. This is indicated by the presence of the AFM phase next to the SC ground state in the phase diagrams of REFeAsO (Ref. 11) (“1111,” RE=rare earth) and AFe2As2 (Ref. 12) (“122,” A=alkaline-earth metal) compounds.

Recently, LiFeAs, the so-called “111” member of the Fe-As superconductors, has been reported13 to undergo a transition to the SC state at Tc=18 K without additional doping and apparent AFM ordering or accompanying structural phase transition. Its structure is a simplified analog of the “1111” or “122” members: FeAs layers comprised of edge-sharing FeAs4 tetrahedra are separated by double layers of Li ions. However, the tetrahedra are deformed and the Fe-Fe distance is considerably shorter compared to other Fe-As superconductors. Moreover, Tc linearly decreases with increasing pressure, similar as in overdoped K1−xFe2As2,14 although the charge amount of −1 per FeAs unit would rather compare LiFeAs to undoped SrFe2As2.14 LiFeAs is also claimed to be a weakly to moderately,15 or moderately to strongly16 correlated system. These conflicting results raise an important question about the significance of AFM fluctuations and the placement of LiFeAs in the general Fe-As superconductor phase diagram.

Here we employ 75As NMR to quantitatively account for the extent of spin correlations in the normal state of LiFeAs and compare it to a typical “122” member. We find that the spin-lattice relaxation rate T1−1 is enhanced, compared to the values calculated for the noninteracting electron scenario. The quantitative comparison with cuprates and organic superconductors17 indicates that AFM correlations may also play an important role in the LiFeAs superconductor.

Stoichiometric polycrystalline LiFeAs was synthesized from high-temperature reactions as described in detail in Ref. 13. For magnetic resonance experiments the LiFeAs sample was sealed into the quartz tube under vacuum to avoid contamination with moisture during the measurements. To check the quality of our polycrystalline LiFeAs samples, we performed electron paramagnetic resonance measurements in the vicinity of SC transition. A nonresonant microwave absorption effect18 occurs sharply below 21 K [Fig. 1(a)], demonstrating the onset of SC state at Tc~20 K in agreement with Ref. 13 and demonstrating the high quality of our sample. 75As (I=3/2) NMR frequency-sweep spectra were measured in a magnetic field of 9.4 T with a two-pulse sequence β−τ−β−τ−echo, a pulse length τp=5 μs, interpulse delay τ=100 μs, and repetition time 100 ms at room temperature. The reference frequency of ν 75As =68.48 MHz was determined from a NaAsF6 standard. The 75As T−1 was measured with inversion-recovery technique.

The band-structure calculations were performed within the local-density approximation (LDA), as described in detail in Refs. 10 and 19. As basis set Li/2s2p3d+3s3p, Fe(3s3p/4s4p3d+5s5p), and As(3s3p/4s4p3d+5s5p) were chosen for semicore/valence+ polarization states. A well-converged k mesh with 1183 k points in the irreducible part of the Brillouin zone was used. The structural parameters were taken from Ref. 13. The calculated Vzz component of the electric field gradient (EFG) tensor is converted into the experimentally measured quadrupole splitting νQ using the relation νQ=3eVzzQ/(2h(2J−1)) with the quadrupole moment Q and nuclear spin I given in Table I.

Representative 75As NMR spectra of the central (−1/2−1/2) and the satellite (±1/2→±1/2) transitions for the polycrystalline LiFeAs sample are shown in Fig. 1(b) for...
temperatures between room temperature and $T_c$. Over the entire temperature range the line shape remains characteristic for an axially symmetric EFG tensor, in accordance with the $^{75}$As site symmetry 4$mm$, indicating the absence of a structural phase transition, as encountered in the undoped “1111” and “122” members of the Fe-As superconductors family. Analysis of the splitting between both singularities belonging to the satellite transitions reveals only a moderate temperature dependence of $Q_0$, which monotonically decreases from 21.35 MHz at room temperature reaching 20.87 MHz at low temperatures [inset to Fig. 1(c)]. There is no indication of AFM ordering down to $T_c$, which would be seen as an abrupt broadening of the NMR line shape due to the appearance of internal magnetic fields.3,10

In Fig. 2(a) we show the $^7$Li ($I=3/2$) NMR spectrum measured at 300 K. Contrary to the $^{75}$As resonance the shift of the $^7$Li NMR line is small and negative [Fig. 2(a)]. However, the value of $-61(5)$ ppm cannot be attributed to the pure orbital shift (typical values are an order of magnitude smaller), which may indicate an incomplete charge transfer

![Graph](image)

**TABLE I.** Comparison between calculated and experimental $Q_0$’s for $^{75}$As and $^7$Li sites. Quadrupole moments $Q$ are taken from Ref. 20.

| Site | $I$ | $Q_{\text{calc}}$ (fm$^2$) | $V_{zz}^{\text{calc}}$ (V/m$^2$) | $\nu_0^{\text{calc}}$ (MHz) | $|\nu_0^{\text{exp}}|$ (MHz) |
|------|-----|-----------------------------|-------------------------|-----------------------------|-------------------------|
| $^{75}$As | 3/2 | 31.4 | $-5.82 \times 10^{21}$ | $-22.1$ | 21.35 |
| $^7$Li | 3/2 | $-4.01$ | $-0.11 \times 10^{21}$ | $0.054$ | 0.034 |

FIG. 2. (Color online) (a) Experimental (solid red line) and calculated (dotted black line) $^7$Li NMR spectra at 300 K and magnetic field 4.7 T [$\nu_{\text{ref}}$($\text{LiCl}$) = 77.7247 MHz] of LiFeAs polycrystalline sample. (b) $^7$Li echo amplitude as a function of interpulse delay $\tau$ measured at 300 K (see text for details). (c) The calculated $V_z$, at the Fe (green diamonds), Li (red circles), and Fe (blue squares) sites as a function of $\Delta z$ (see text for details), together with experimental data for Li (black circle) and As (black diamond). The minimum in energy regarding the As $z$ position is marked by the black arrow. The inset shows the Li values on a smaller scale.
is somewhere in between these two limits with properties analogous to those of optimally doped Fe-As superconductors. It seems that this can explain the relatively high $T_c$, its decrease with the applied pressure and the absence of AFM ordering.

In order to quantitatively verify the presence of AFM fluctuations in the normal state of LiFeAs, we turn to the analysis of the Korringa relation for $^{75}$As,

$$T_1 TK_s^2 = \frac{\hbar}{4 \pi k_B} \frac{\gamma_s^2}{\gamma_n^2} \beta,$$

where $\gamma_s$ and $\gamma_n$ are the electron and nuclear gyromagnetic ratios, respectively. The phenomenological parameter $\beta$, called the Korringa factor, characterizes the extent of spin correlations. In case $^{75}$As couples to the noninteracting Fe 3d electrons (i.e., Fermi gas) via the on-site Fermi contact interaction, the Korringa factor is $\beta = \beta_0 = 1$. Strong ferromagnetic fluctuations increase the value of $\beta$ while AFM fluctuations decrease it. However, it has been recently proposed for the Fe-As superconductors that the $^{75}$As nuclei are coupled to the localized Fe electronic spins via the isotropic transferred hyperfine coupling. According to Millis et al., this renormalizes the noninteracting $\beta_0$ value. Namely, $T_1^{-1}$ due to the $\mathbf{q}$-dependent spin fluctuations is obtained from Moriya’s expression

$$\frac{1}{T_1} \propto \sum_\mathbf{q} |A(\mathbf{q})|^2 \frac{\chi(\mathbf{q}, \omega_n)}{\omega_n},$$

where $\chi(\mathbf{q}, \omega_n)$ is the imaginary part of the electron spin susceptibility at the wave vector $\mathbf{q}$ and at the nuclear Larmor frequency $\omega_n$. In case $^{75}$As nucleus is coupled to the localized Fe electronic spins via isotropic transferred hyperfine coupling, we have $|A(\mathbf{q})|^2 \propto \cos^2 \frac{\alpha}{2} \cos^2 \frac{\alpha}{2}$, where $\alpha$ is the distance between two neighboring Fe$^{3+}$ spins. For noninteracting spins, $\chi(\mathbf{q}, \omega_n)$ has no strong singularities in the $\mathbf{q}$ space, and can be taken out of the summation (integrals) in Eq. (2). Compared to the on-site scenario, we get an extra factor $\int d\mathbf{q} \int d\omega_n = \int d\mathbf{q} \int d\omega_n \cos^2 \frac{\alpha}{2} \cos^2 \frac{\alpha}{2} = 4$, which renormalizes the noninteracting $\beta_0$ value to $\beta_0 = 4$. From here we proceed as usual: in case $\beta > 4$ ferromagnetic fluctuations are predicted, whereas AFM fluctuations should lead to $\beta < 4$.

For instance, in cuprates, a prototypical example of a system where AFM fluctuations are important, $\beta$ is reduced by a factor of 15, compared to the noninteracting electron scenario with transferred hyperfine coupling. A similar factor is found in some organic superconductors.

The experimentally extracted Korringa factor $\beta$ for $^{75}$As in LiFeAs is displayed in Fig. 3(c). It amounts to $\sim 0.7$ at room temperature and then monotonically reduces to $\sim 0.1$ approaching $T_c$. We stress that the absolute values of $\beta$ depend on our choice of $K_{\text{orb}}$. For $K_{\text{orb}} = 0.13\%$ and $K_{\text{orb}} = 0.17\%$ the low-temperature value of $\beta$ changes to 0.17 and 0.03, respectively. Regardless of this uncertainty, the analysis above demonstrates the enhancement of $T_1^{-1}$ at low temperatures with respect to noninteracting electron limits in both scenarios considered above, and demonstrates the strength of AFM fluctuations in LiFeAs. For comparison we...
add β values for SrFe$_2$As$_2$, (Ref. 27) to Fig. 3. In this case, β is systematically larger by a factor of ~1.6 compared to LiFeAs, and above 250 K β is larger than β$_0$. In case of the hyperfine transferred coupling scenario, the experimental β should be compared to β$_{\text{ref}}$ rather than to β$_0$. Then, the enhancement of T$_c$ in LiFeAs for a factor as large as 40 ± 20 at low temperatures suggests strong AFM fluctuations, as recently predicted by quantum chemical calculations. However, our LDA calculations, which correctly predict $\nu_Q$ for both $^{75}\text{As}$ and $^7\text{Li}$ sites without taking into account strong electronic correlations, speak against well-defined localized moments at the Fe sites as assumed in the transferred hyperfine coupling scenario. In this case, the correct reference valid for the on-site coupling is β$_{\text{ref}}$=1 and the enhancement of T$_c$ in LiFeAs is reduced to a factor of 10 ± 5 speaking for weaker AFM fluctuations. It is not clear at the moment how strongly β is enhanced since cross terms between different bands in the LiFeAs multiband structure can influence the Fermi contact and the transferred coupling mechanisms. The ambiguity in the analysis above opens three important issues, which will have to be addressed in future studies: (i) is the coupling of $^{75}\text{As}$ to itinerant electrons in LiFeAs really onsite while it is transferred in “122” members? (ii) If this is the case, is it related to structural differences of the FeAs layer between the two families? And, (iii) should LiFeAs really be treated as a strongly correlated system?

In summary, NMR and band-structure investigations were employed to investigate the normal-state properties of the LiFeAs superconductor. The presence of a PG in the uniform spin susceptibility measured by the $^{75}\text{As}$ Knight shift is overshadowed by AFM fluctuations in the T$_c$ measurements. Although the precise determination of the strength of AFM fluctuations should be a subject of further investigations, we believe that LiFeAs is the simplest Fe-As superconductor where correlation effects might be important and should be considered in future studies.

We acknowledge stimulating discussions with P. Prelovšek, I. Sega, and D. Mihailović. This work was supported in part by the Slovenian Research Agency. A.M.G. and B.L. acknowledge the NSF (Grant No. CHE-0616805) and the R. A. Welch Foundation (Grant No. E-1297) for support.

21 Among interactions that are quadratic in $^7\text{Li}$ spin operators and can thus lead to oscillations, quadrupole interaction is expected to be dominant with respect to the Ruderman-Kittel-Kasuya-Yosida interaction. The latter is relevant only for heavy nuclei [C. Froidevaux and M. Weger, Phys. Rev. Lett. 12, 123 (1964)].
27 Knight shift (with reasonable $g_{\text{iso}}=0.20$) and $(T/T_1)^{-1}$ values obtained from our measurements on polycrystalline SrFe$_2$As$_2$, agree well with those reported in single-crystal study [K. Kitagawa, N. Katayama, K. Ohgushi, and M. Takigawa, J. Phys. Soc. Jpn. 78, 063706 (2009)].