Two-dimensional magnetism in the pnictide superconductor parent material
SrFeAsF probed by muon-spin relaxation

P. J. Baker, I. Franke, T. Lancaster, S. J. Blundell, L. Kerslake, and S. J. Clarke

1Oxford University Department of Physics, Clarendon Laboratory,
Park Road, Oxford OX1 3PU, United Kingdom
2Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory,
South Parks Road, Oxford, OX1 3QR, United Kingdom
(Dated: November 27, 2008)

We report muon-spin relaxation measurements on SrFeAsF, which is the parent compound of a newly discovered iron-arsenic-fluoride based series of superconducting materials. We find that this material has very similar magnetic properties to LaFeAsO, such as separated magnetic and structural transitions \(T_N = 120 \text{ K}, T_c = 175 \text{ K}\), contrasting with SrFeAs2 where they are coincident. The muon oscillation frequencies fall away very sharply at \(T_N\), which suggests that the magnetic exchange between the layers is weaker than in comparable oxypnictide compounds. This is consistent with our specific heat measurements, which find that the entropy change \(\Delta S = 0.05 \text{ Jmol}^{-1}\text{K}^{-1}\) largely occurs at the structural transition and there is no anomaly at \(T_N\).

PACS numbers: 76.75.+i, 74.10.+v, 75.30.Fv, 75.50.Ee

Quasi-two-dimensional magnets on square lattices are the subject of considerable theoretical and experimental attention. This has primarily been due to the success of models of the spin-1/2 Heisenberg antiferromagnet in describing the physics of La\(_2\)CuO\(_4\), which is the prototypical parent compound of high-\(T_c\) cuprate superconductors. La\(_2\)CuO\(_4\) shows a tetragonal to orthorhombic structural transition at \(T_c \simeq 530 \text{ K}\) and Néel ordering at \(T_N \simeq 325 \text{ K}\). That \(T_N\) is far smaller than the antiferromagnetic exchange constant \(J \sim 1500 \text{ K}\) demonstrates that this compound has a remarkably large magnetic anisotropy, with weak coupling between the CuO\(_2\) layers. The magnetic parent compounds of FeAs-based superconductors such as LaFeAsO\(_{1-x}\)F\(_x\) have Fe atoms on a layered square lattice, and it is interesting to note that, like La\(_2\)CuO\(_4\), these have a tetragonal to orthorhombic structural distortion followed by antiferromagnetic ordering (e.g. Ref. [6]). Here we study the magnetic properties of a newly discovered parent compound to a series of furoopnictide superconductors, SrFeAsF\(_{1-x}\), where the fluoride ions should provide weaker magnetic exchange pathways between the FeAs layers than for LnFeAsO or AFe\(_2\)As\(_2\) compounds.

Doped fluoropnictide compounds based on CaFeAsF and SrFeAsF have recently been found to superconduct \(T_c \geq 22 \text{ K}\) \(^{10,11,12,13}\) with comparable transition temperatures to the previously discovered oxypnictide compounds based on LnFeAsO. These have similar FeAs layers to the oxypnictides, but divalent metal - fluoride layers replace the rare-earth - oxide layers. Fluoropnictides can be doped on the Fe site, as for CaFe\(_{0.9}\)Co\(_{0.1}\)AsF \((T_c = 22 \text{ K})\)\(^{10}\) or the divalent metal site, as for Sr\(_{0.5}\)Sm\(_{0.5}\)FeAsF \((T_c = 56 \text{ K})\)\(^{10}\) and several approaches have already been explored\(^9,10,11,12,13\). The magnetic, electronic, and structural properties of the parent compounds CaFeAsF and SrFeAsF, and also EuFeAsF, have already been investigated. All three show transitions evident in resistivity and dc magnetization measurements, at \(T_s = 120, 175, 155 \text{ K}\) respectively.\(^{7,8,9,12,13}\) In SrFeAsF the structural transition has been probed using X-ray diffraction, and changes in the magnetism using Mössbauer spectroscopy.\(^2\) The structural change varies smoothly below 175 K whereas the Mössbauer spectra became increasingly complicated as the temperature is reduced. It is also interesting that the sign of the Hall coefficient \(R_H\) in SrFeAsF is reported to be positive below \(T_s\), whereas it is negative in the undoped LaFeAsO and BaFe\(_2\)As\(_2\) parent compounds.\(^2\) This could result from a different electronic structure near the Fermi surface, which might have implications for both the magnetism of the undoped compound and the superconductivity that emerges when it is doped.

The magnetism of LnFeAsO compounds has already been intensively investigated by a wide range of techniques. Neutron diffraction measurements have been carried out on some of the undoped oxypnictides: LaFeAsO\(_{1-x}\)F\(_x\), NdFeAsO\(_{1-x}\)F\(_x\), PrFeAsO\(_{1-x}\)F\(_x\), and CeFeAsO\(_{1-x}\)F\(_x\). The results in each case indicate similar structural transitions at around \(T_s = 150 \text{ K}\), followed by long range, three-dimensional antiferromagnetic ordering of the iron spins with significantly reduced moments < 1 \(\mu_B/\text{Fe}\) at \(T_N\), around 20 K below \(T_s\), confirmed by other techniques.\(^{17,18}\) These features move to lower temperature with increasing doping and are absent in the superconducting phase for LaFeAsO\(_{1-x}\)F\(_x\) and CeFeAsO\(_{1-x}\)F\(_x\) although magnetism and superconductivity seem to coexist over a small doping range in SmFeAsO\(_{1-x}\)F\(_x\). In contrast, SrFeAs\(_2\) has coincident magnetic and structural ordering occurring in a first-order phase transition at \(T_o = 205 \text{ K}\).\(^{21}\) It seems that in general AFe\(_2\)As\(_2\) materials have more closely related structural and magnetic phase transitions, and more three-dimensional magnetism than the single layer FeAs materials. With the discovery of new fluororesenide parent materials it is important to compare the magnetic structures and the separation between \(T_s\) and \(T_N\) in the
oxide-arsenide and fluoro-arsenide materials. Here we address these comparisons in SrFeAsF using the techniques of muon-spin relaxation, which is a local probe of the magnetic fields inside the sample and their dynamics, and also specific heat measurements which examine the changes in entropy at the transitions.

The SrFeAsF sample was synthesized in a two step process similar to that described in Ref. 7. Stoichiometric quantities of sublimed strontium metal (Alfa 99.9 %), strontium fluoride powder (Alfa 99.9 %), iron powder (Alfa, 99.998 %), and arsenic pieces (Alfa, 99.9999 %; ground into powder) were ground together and sealed in a 9 mm diameter niobium tube. This was heated at 1°/min to 500°C and this temperature was maintained for 12 hours to ensure complete reaction of the volatile components before heating at 1°/min to 900°C. After 40 hours at 900°C the product was removed from the Nb tube, ground to a fine powder, pressed into a pellet, and placed into an alumina crucible which was then sealed in a pre-dried evacuated silica tube. This was heated at 1°C/min to 1000°C for 48 hours and then cooled at the natural rate of the furnace to room temperature. All manipulation was carried out in an argon-filled glove box. Analysis of the product by laboratory X-ray powder diffraction (PANalytical X-pert PRO) [Fig 1(a)] revealed that the sample consisted of about 97 % by mass SrFeAsF; SrF₂ was identified as a crystalline impurity phase, but no other crystalline binary or ternary impurity phases were identified. The refined room temperature lattice parameters of SrFeAsF were \( a = 4.00059(3) \, \text{Å}, c = 8.9647(1) \, \text{Å}, V = 143.478(4) \, \text{Å}^3 \) consistent with other reports. Measurement of the dc susceptibility was carried out in a Quantum Design MPMS5 instrument [Fig. 1(b)]. The magnetization of the sample as a function of field at 300 K showed no significant level of ferromagnetic impurity. Measurements as a function of temperature in an applied field of 1000 Oe revealed very similar behaviour to that reported previously.\(^7\) A broad feature at around 175 K is consistent with the closely associated antiferromagnetic ordering and structural phase transitions which occur in related compounds.\(^14,22,23\) Heat capacity measurements were carried out using a Quantum Design Physical Properties Measurement System (PPMS) using a standard relaxation time approach. A small part of the sample used for \( \mu \)SR measurements was attached to the sample platform using Apiezon N-grease. Measurements were corrected for the heat capacity of the sample platform and grease. Muon-rotation \( (\mu \)SR) experiments were performed using the General Purpose Surface-Muon Instrument (GPS) at the Swiss Muon Source (Paul Scherrer Institute, Switzerland). The measured parameter is the time-dependent muon decay asymmetry, \( A(t) \), recorded in positron detectors on opposite sides of the sample. Our sample was a pressed powder pellet of 1 cm diameter mounted inside a silver packet on a silver backing plate. This arrangement gives a time and temperature independent background to the signal which is straightforward to subtract.

The heat capacity measurements shown in Figure 1(c) show a clear feature at the structural transition and no anomalies or effects due to latent heat were evident at any other temperatures. Our data are in good agreement with those reported on this compound by Tegel et al.\(^7\) To separate the lattice and magnetic contributions to the heat capacity, we estimated the lattice background using the function:

\[
C(T) = \gamma T + A_D C_D(T, \theta_D) + A_E C_E(T, \theta_E),
\]

where \( \gamma \) is the Sommerfeld coefficient, and \( C_D \) and \( C_E \) are Debye and Einstein terms respectively. This was found...
to be an effective model for oxypnictides in Ref.\textsuperscript{23}. The parameters extracted from this fit (excluding data between 100 and 185 K) were $\gamma = 3.44(7)$ mJmol$^{-1}$K$^{-2}$, $A_D = 56.6(5)$ Jmol$^{-1}$K$^{-1}$, $\theta_D = 237(1)$ K, $A_E = 52.2(4)$ Jmol$^{-1}$K$^{-1}$, and $\theta_E = 407(3)$ K. These are comparable with the values determined for oxypnictide materials without rare-earth magnetic moments\textsuperscript{17,25}. The magnetic contribution is plotted in the inset to Figure I(c) showing that zero-field and 10 T measurements were effectively identical, and the integrated magnetic entropy is 0.5 Jmol$^{-1}$K$^{-1}$. While this is a small entropy change, it is twice the value observed in LaFeAsO, where features at both the structural and magnetic transitions are evident. SrFe$_2$As$_2$ has a far larger entropy change at the combined first-order structural and magnetic transition, $\sim 1$ Jmol$^{-1}$K$^{-1}$. The majority of the entropy change in SrFeAsF occurs close to $T_N = 175$ K, but it appears that another much broader feature at lower temperature also contributes. Since we find long-range magnetic ordering at $T_N = 120$ K using $\mu$SR (described below), it seems that the broad feature is likely to have a magnetic origin. The lack of a distinct anomaly in the specific heat (or in magnetization or resistivity data) suggests that the residue below the structural transition comes from the build up of 2D correlations within the FeAs planes. Gaining a rough estimate of the in-plane exchange constant $J \sim 250 - 300$ K from the position of the hump, and knowing $T_N = 120$ K, we can estimate the out-of-plane exchange constant $J_{\perp} \sim 0.05J$, consistent with the lack of any observed anomaly at $T_N$. This is a similar situation to that in La$_2$CuO$_4$\textsuperscript{22} though with a lower anisotropy in the exchange constants and a smaller separation between the structural and magnetic transitions.

In Figure 2 we present muon decay asymmetry data at temperatures of 10, 116, and 140 K. At low temperatures, up to around 75 K, two oscillations are clearly resolved but as we approach $T_N$ the broadening of each of the oscillations grows until they are both overdamped. This overdamped behavior is seen in the 116 K data set. Immediately above the magnetic ordering transition the muon decay asymmetry takes the exponential form expected for a paramagnet with electronic fluctuations faster than the characteristic time of the measurement. The data set at 140 K shown in Figure 2 is very similar to all those taken above the magnetic ordering temperature, and we saw no change in the relaxation signal when passing through $T_N = 175$ K.

Observing two precession frequencies in the magnetically ordered phase and finding that the temperature dependent relaxation is Gaussian (suggesting that the fluctuations of electronic moments are motionally narrowed), we were able to describe the raw asymmetry data using the fitting function:

$$A(t) = \sum_{i} A_i e^{-\lambda_i t} \cos(2\pi \nu_i t) + A_3 e^{-\sigma^2 t^2} + A_{bg} e^{-\Lambda t}. \quad (2)$$

The first two terms describe two damped oscillations, the third term describes the Gaussian relaxation for muon spins with their direction along that of the local field at their stopping site, which are depolarized by a random distribution of nuclear moments, and the final term describes the weak temperature-independent depolarization observed for muons stopping outside the sample. Above the magnetic ordering transition there is no oscil-
latory signal and we set $A_1 = A_2 = 0$. In many fluorine containing magnets a characteristic signal due to the formation of a bound state between a positive muon and one or more fluoride ions is observed above the magnetic ordering transition.\cite{22,23} No such signal is observed in SrFeAsF, probably because the magnetic ordering transition is at too high a temperature for the muons to be sufficiently well bound.

The parameters derived from fitting Eq. 2 to the raw data are shown in Figure 3. The two precession frequencies plotted in Figure 3(a) are well defined and at low-temperature appear to follow a conventional power law. Fitting the upper precession frequency to the function $\nu(T) = \nu(0)(1 - (T/T_N)^\beta)^\alpha$ leads to $T_N = 120.6(3)$ K, $\alpha = 3.1(3)$, and $\beta = 0.20(2)$. This is a much sharper magnetic transition than in LaFeAsO\cite{29,30} and this would suggest that the magnetism is more two-dimensional in this fluoropnictide. Also, $\beta$ is between the values expected for 2D Ising and 2D XY order parameters, though the sharp drop in the frequencies near to $T_N$ may mean that this fitting function is less effective in estimating the true critical parameters. The higher precession frequency tends to $\nu_1(0) = 22.22(5)$ MHz and, assuming the same power law, the lower precession frequency tends to $\nu_2(0) = 1.9(1)$ MHz. These frequencies are a little lower than in LaFeAsO\cite{29,30} but in a similar proportion. This suggests the magnetic structure is very similar to LaFeAsO and the ordered Fe moments $\mu_{Fe} \sim 0.3 \mu_B$\cite{14,21} Seeing the lower frequency signal persisting all the way to the magnetic ordering transition as Carlo et al.\cite{21} did in LaFeAsO suggests that this minority oscillation signal is intrinsic to the sample, and reflects the antiferromagnetic structure being sampled at a different site within the structure. It had previously been suggested that the some magnetic signals in these pnictide materials originated in FeAs impurities (e.g. Ref.\cite{17}) but we can discount this possibility for our SrFeAsF sample on the basis of $\mu$SR measurements on FeAs and FeAs$_2$, both of which give significantly different signals.\cite{21,23} In the ordered phase the higher frequency oscillation accounts for about 85% of the oscillating amplitude. This amplitude ratio for the two oscillating components is similar to the situation in LaFeAsO, as is the lower frequency signal becoming overdamped close to the magnetic ordering transition.\cite{29,30} The linewidths $\lambda_1$ and $\lambda_2$ [shown in Figure 3(b)] are both much smaller than the respective precession frequencies at low temperatures, giving rise to the clear oscillations seen in the 10 K data in Figure 2 and then grow towards the ordering transition giving the overdamped oscillations seen in the 116 K data.

Our results have shown that long ranged, three-dimensional antiferromagnetic ordering in SrFeAsF occurs, but with a greater separation between the structural and magnetic ordering transitions ($T_s - T_N \sim 50$ K) than in comparable oxypnictide compounds (e.g. LaFeAsO). While the $\mu$SR measurements show that the magnetic environment within the FeAs planes is very similar to that in oxypnictide compounds, we note that the magnetic ordering transition is not as clear in the magnetization and heat capacity measurements. The heat capacity and $\mu$SR measurements, in particular the lack of a heat capacity anomaly at $T_N$ and the low value of $\beta = 0.2$, both suggest far more two-dimensional magnetic interactions than in oxypnictide compounds, consistent with the increased separation $T_s - T_N$. This is also consistent with the expectation that the interplanar exchange mediated by a fluoride layer will be weaker than that mediated by an oxide layer.

Part of this work was performed at the Swiss Muon Source, Paul Scherrer Institute, Villigen, CH. We are grateful to Alex Amato for experimental assistance and to the EPSRC (UK) for financial support.

---

1. E. Manousakis, Rev. Mod. Phys. 73, 1 (1991).
2. M. A. Kastner et al., Rev. Mod. Phys. 70, 897 (1998).
3. P. Sengupta et al., Phys. Rev. B 68, 094423 (2003).
4. C. Yasuda et al., Phys. Rev. Lett. 94, 217201 (2005).
5. Y. Kamihara et al., J. Am. Chem. Soc. 130, 3296 (2008).
6. J. Zhao et al., Nature Materials 7, 953 (2008).
7. M. Tegel et al., arXiv:0810.2120 (unpublished).
8. F. Han et al., Phys. Rev. B 78, 100504(R) (2008).
9. S. Matsuishi et al., J. Am. Chem. Soc. 130, 14428 (2008).
10. G. Wu et al., arXiv:0811.0761 (unpublished).
11. S. Matsuishi et al., arXiv:0811.1147 (2008).
12. S. Matsuishi et al., J. Phys. Soc. Jpn. 77, 113709 (2008).
13. X. Zhu et al., arXiv:0810.2531 (unpublished).
14. C. de la Cruz et al., Nature 453, 899 (2008).
15. Y. Chen et al., Phys. Rev. B 78, 064515 (2008).
16. S. A. J. Kimber et al., Phys. Rev. B 78, 140503(R) (2008).
17. M. A. McGuire et al., Phys. Rev. B 78, 094517 (2008).
18. M. A. McGuire et al., arXiv:0811.0589 (unpublished).
19. H. Luetkens et al., arXiv:0806.3533 (2008).
20. A. J. Drew et al., arXiv:0807.4876 (unpublished).
21. C. Krellner et al., Phys. Rev. B 78, 100504(R) (2008).
22. M. Rotter et al., Phys. Rev. Lett. 101, 107006 (2008).
23. K. Sasmal et al., Phys. Rev. Lett. 101, 107007 (2008).
24. S. J. Blundell, Contemp. Phys. 40, 175 (1999).
25. P. J. Baker et al., arXiv:0811.2494 (unpublished).
26. K. Sun et al., Phys. Rev. B 43, 239 (1991).
27. J. H. Brewer et al., Phys. Rev. B 33, 7813 (1986).
28. T. Lancaster et al., Phys. Rev. Lett. 99, 267601 (2007).
29. H.-H. Klauss et al., Phys. Rev. Lett. 101, 077005 (2008).
30. J. P. Carlo et al., arXiv:0805.2186 (unpublished).
31. P. J. Baker et al., Phys. Rev. B (accepted) arXiv:0809.2522 (2008).