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

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We report muon-spin relaxation measurements on SrFeAsF, which is the parent compound of an 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 ($T_N = 122$ K, $T_s = 175$ K), contrasting with $SrFe_2As_2$ where they are coincident. The muon oscillation frequencies fall away very sharply at T_N [$\beta = 0.22(3)$], which suggests that the magnetic exchange between the layers is weaker than in comparable oxypnictide compounds. Our specific-heat measurements show that a small but distinct feature occurs at T_s. There is no anomaly evident at T_N as is typical for quasi-two-dimensional magnets. The magnetic entropy change between 100 and 185 K is $\Delta S = 0.5$ J mol^{-1} K^{-1}.

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Quasi-two-dimensional (quasi-2D) magnets on square lattices are the subject of considerable theoretical and experimental attention.[1–3] This has primarily been due to the success of models of the spin-1/2 Heisenberg antiferromagnet in describing the physics of La_2CuO_4, which is the prototypical parent compound of high-T_c cuprate superconductors. La_2CuO_4 shows a tetragonal to orthorhombic structural transition at around $T_o = 530$ K and Néel ordering at $T_N \simeq 325$ K. That T_N is far smaller than the antiferromagnetic exchange constant $J \sim 1500$ K demonstrates that this compound has a remarkably large anisotropy in the magnetic exchange constants, with weak coupling between the CuO_2 layers.[2] The magnetic parent compounds of FeAs based superconductors such as $LaFeAsO_{1-x}F_x$ (Ref. 4) have Fe atoms on a layered square lattice, and it is interesting to note that, like La_2CuO_4, these have a tetragonal to orthorhombic structural distortion followed by antiferromagnetic ordering (e.g., Ref. 5). Here we study the magnetic properties of a parent compound to a series of fluoropnictide superconductors, SrFeAsF,[6,7] where the fluoride ions should provide weaker magnetic exchange pathways between the FeAs layers than for *Ln*FeAsO or $A\mathrm{Fe}_2\mathrm{As}_2$ compounds.

Doped fluoropnictide compounds based on CaFeAsF and SrFeAsF have recently been found to superconduct[8–12] with comparable transition temperatures (T_c) to the previously discovered oxypnictide compounds based on *Ln*FeAsO. 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 $CaFe_{0.9}Co_{0.1}AsF$ ($T_c = 22$ K),[8] or the divalent metal site, as for $Sr_{0.5}Sm_{0.5}FeAsF$ ($T_c = 56$ K),[9] and a number of these possibilities have already been explored.[8–12] 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, and 155 K, respectively.[6–8,11,12] In SrFeAsF the structural transition has been probed using x-ray diffraction and the changes in the magnetism using Mössbauer spectroscopy.[6] 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 $BaFe_2As_2$ parent compounds.[7] 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 already been carried out on some of the undoped oxypnictides: LaFeAsO,[13] NdFeAsO,[14] PrFeAsO,[15] and CeFeAsO.[5] The results in each case indicate similar structural transitions at $T_s \simeq 150$ K, followed by long-range, three-dimensional antiferromagnetic ordering of the iron spins, with significantly reduced moments, $< \mu_B$ per Fe, at T_N around 20 K below T_s, as confirmed by other techniques.[16,17] These features move to lower temperature with increasing doping and are absent in the superconducting phase for $LaFeAsO_{1-x}F_x$ (Ref. 18) and $CeFeAsO_{1-x}F_x$,[5] although magnetism and superconductivity seem to coexist over a small doping range in $SmFeAsO_{1-x}F_x$.[19] In contrast, $SrFe_2As_2$ has coincident magnetic and structural ordering occurring in a first-order phase transition at $T_o = 205$ K.[20] It seems that in general $A\mathrm{Fe}_2\mathrm{As}_2$ 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 other fluoroarsenide parent materials it is important to compare the magnetic structures and the separation between T_s and T_N in the oxide-arsenide and fluoroarsenide materials. Here we address this in SrFeAsF using muon-spin relaxation (μSR), which is a local probe of magnetic fields and their dynamics, and specific-heat measurements that examine the changes in entropy at the transitions.

The SrFeAsF sample was synthesized in a two-step process similar to that described in Ref. 6. Stoichiometric quantities of sublimed strontium metal (Alfa, 99.9%), strontium fluoride powder (Alfa, 99.9%), iron powder (Alfa, 99.998%),

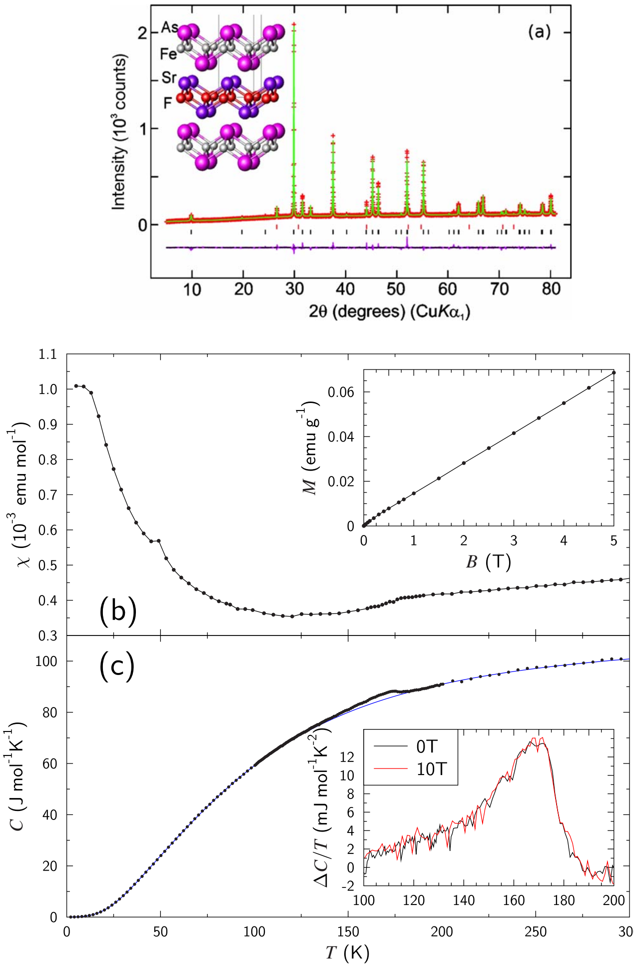

FIG. 1. (Color online) (a) Rietveld refinement against powder x-ray diffraction data; $\chi^2=1.98$ and a weighted pattern R-factor, wRp=0.044. The inset shows the structure. (b) dc magnetization measurements vs temperature in a field of 0.1 T. The small feature at about 50 K is probably due to a small amount of adsorbed O_2 apparent because of the small sample moment. (Inset) Magnetization vs field at 300 K. (c) Heat capacity $C(T)$ showing the peak at T_s which is highlighted in the inset. The line shows the lattice heat capacity fit discussed in the text.

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 °C/min to 500 °C and this temperature was maintained for 12 h to ensure complete reaction of the volatile components before heating at 1 °C/min to 900 °C. After 40 h 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 predried evacuated silica tube. This was heated at 1 °C/min to 1000 °C for 48 h 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; SrF_2 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 $a=4.000\,59(3)$ Å, $c=8.9647(1)$ Å, and $V=143.478(4)$ Å^3 consistent with other reports.[6] Measurement of the dc susceptibility was carried out in a Quantum Design MPMS5 instrument. Measurement of the magnetic moment 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 behavior to that reported previously.[6] A broad feature at around 175 K is consistent with the closely associated antiferromagnetic ordering and structural phase transitions which occur in related compounds.[13,21,22] 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 μSR measurements was attached to the sample platform using Apiezon N grease. Measurements were corrected for the heat capacity of the sample platform and grease. μSR experiments[23] were performed using the General Purpose Surface-Muon Instrument (GPS) at the Swiss Muon Source. 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 data shown in Fig. 1(c) show a clear feature at the structural transition T_s and no anomalies at any other temperatures. Our data are in good agreement with those reported on this compound by Tegel *et al.*[6] To separate the lattice and magnetic contributions to the heat capacity, we estimated the lattice background using the function

$$C(T) = \gamma T + C_{\mathrm{D}}(T,\theta_{\mathrm{D}}) + C_{\mathrm{E}}(T,\theta_{\mathrm{E}}), \tag{1}$$

where γ is the Sommerfeld coefficient and C_{D} and C_{E} are the Debye and Einstein terms, respectively. This was found to be an effective model for oxypnictides in Ref. 24. The parameters extracted from this fit (excluding data between 100 and 185 K) were $\gamma=3.44(7)$ mJ mol^{-1} K^{-2}, $A_{\mathrm{D}}=56.6(5)$ J mol^{-1} K^{-1}, $\theta_{\mathrm{D}}=237(1)$ K, $A_{\mathrm{E}}=52.2(4)$ J mol^{-1} K^{-1}, and $\theta_{\mathrm{E}}=407(3)$ K. These are comparable with the values determined for oxypnictide materials without rare-earth magnetic moments.[16,24] The magnetic contribution is plotted in the inset to Fig. 1(c) showing that zero-field and 10 T measurements were effectively identical, and the magnetic entropy change between 100 and 185 K is 0.5 J mol^{-1} K^{-1}. This is twice as large as the value observed in LaFeAsO around the distinct structural and magnetic transitions[16] but smaller than for $SrFe_2As_2$ (~1 J mol^{-1} K^{-1}) where the structural and magnetic transitions are coincident.[20]

The small change in entropy close to the transitions and the lack of an anomaly at T_{N} suggest either that two-dimensional correlations build up within the FeAs planes or that we are observing the ordering of itinerant electrons. Two-dimensional correlations building up above T_{N} would produce a hump in the heat capacity consistent with the form observed below T_s. Simulations of localized spin-1/2 Heisenberg models as a function of the in-plane (J) and out-of-

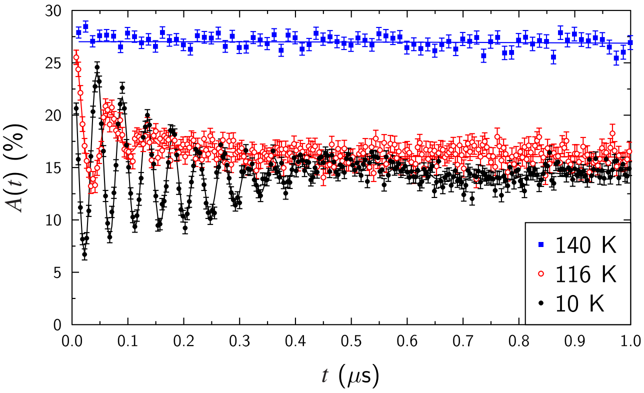

FIG. 2. (Color online) Muon asymmetry data for SrFeAsF showing the spin precession signal evident at low temperature, the greater damping of the oscillations close to T_N, and the paramagnetic signal at 140 K. The data are fitted to Eq. (2) with the parameters shown in Fig. 3.

plane ($J_\perp$) exchange constants[3] show no anomaly at T_N for $J_\perp/J \lesssim 0.05$, giving an approximate upper bound for this ratio in SrFeAsF. However, SrFeAsF is evidently a bad metal[6,7] and therefore this localized moment description can only be approximate. Itinerancy should lead to the BCS-type contribution from the spin-density wave (SDW) transition at $T_s = 175$ K dominating the form of the data, as we observe, although the form of the residue shows that the magnetic contribution cannot be neglected. That the contribution to the heat capacity from the structural transition is far larger than that from the magnetic ordering is similar to the situation in La_2CuO_4,[25] although with a lower anisotropy in the exchange constants and a smaller separation between the structural and magnetic transitions.

In Fig. 2 we present muon decay asymmetry data at temperatures of 10, 116, and 140 K. Observing two precession frequencies in the magnetically ordered phase, we were able to describe the asymmetry data using the fitting function

$$A(t) = \sum_{i=1,2} A_i e^{-\lambda_i t} \cos(2\pi\nu_i t) + A_3 e^{-\lambda_3 t} + A_{\mathrm{bg}} e^{-\Lambda t}. \qquad (2)$$

Terms 1 and 2 describe the two damped oscillations, term 3 describes the exponential relaxation of muon spins aligned along the local-field direction at their stopping sites, and the final term describes the weak temperature-independent depolarization observed for muons stopping outside the sample. After preliminary fitting showed that the oscillation frequencies remained in proportion for all temperatures, we constrained $\nu_2 = 0.09\nu_1$ in the final analysis. The data set at 140 K shown in Fig. 2 is very similar to all those taken above the magnetic ordering temperature, and we saw no change in the exponentially relaxing signal when passing through $T_s = 175$ K. In the paramagnetic phase of many fluorine containing magnets a characteristic signal due to the formation of a bound state of a positive muon and one or more fluoride ions is observed.[26,27] In SrFeAsF no such signal is observed, probably because the magnetic ordering temperature is too high for the muons to be sufficiently well bound.

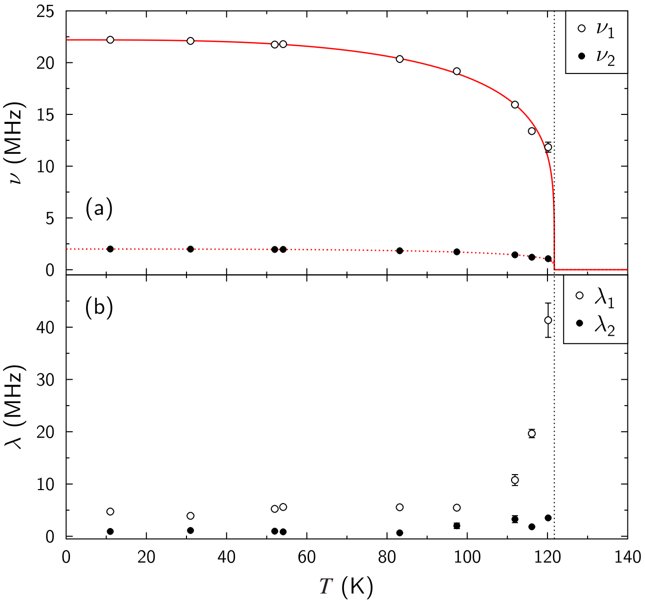

FIG. 3. (Color online) Parameters extracted from fitting raw asymmetry data using Eq. (2) described in the text. (a) Oscillation frequencies ν_1 and $\nu_2 = 0.09\nu_1$ with lines drawn showing the power-law function described in the text. (b) Linewidths of the two oscillating components λ_1 and λ_2.

The parameters derived from fitting Eq. (2) to the raw data are shown in Fig. 3. Fitting the upper precession frequency to the function $\nu(T) = \nu(0)[1-(T/T_N)^\alpha]^\beta$ leads to $T_N = 122(1)$ K, $\alpha = 3.0(3)$, and $\beta = 0.22(3)$. The magnetic transition appears rather sharper than in LaFeAsO,[28,29] suggesting that the magnetism is more two dimensional in this fluoropnictide. β is quite close to the value expected for a system with a 2D *XY* order parameter, 0.23.[30] However, understanding the origin of such a critical parameter in quasi-2D systems is far from trivial as competition between interactions such as the coupling between layers and the strength of the crystal field leads to a range of β values between $\sim 0.1 \leq \beta \leq 0.25$. Further work investigating the other critical parameters of this compound would be needed to give a more definite assignment of the universality class.

The higher oscillation frequency tends to $\nu_1(0) = 22.20(5)$ MHz, which is slightly lower than in LaFeAsO (Refs. 28 and 29) but with the two frequencies in a similar proportion. Seeing the lower-frequency signal persisting all the way to the magnetic ordering transition as Carlo *et al.*[29] had done in LaFeAsO suggests that this minority oscillation signal is intrinsic to the sample and reflects the antiferromagnetic structure sampled at a different site within the structure. It had previously been suggested that the magnetic signals in these pnictide materials were originating in FeAs impurities (e.g., Ref. 16), but we can discount this possibility on the basis of μSR measurements on FeAs and $FeAs_2$, which both give significantly different signals.[31] 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.[28,29] The linewidths λ_1 and

λ_2 [Fig. 3(b)] are both far smaller than the respective precession frequencies at low temperatures, giving rise to the clear oscillations seen in the 10 K data in Fig. 2, and then grow toward the ordering transition giving the overdamped oscillations seen in the 116 K data.

Our results have shown that long-range, 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 μSR 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 μSR measurements, in particular the lack of a heat-capacity anomaly at T_N and the low value of $\beta = 0.22$, both suggest far more two-dimensional magnetic interactions. This is consistent with the expectation that the interplanar exchange mediated by a fluoride layer will be weaker than that mediated by an oxide layer.

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