

Characteristic muon precession and relaxation signals in FeAs and FeAs₂: Possible impurity phases in pnictide superconductors

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We report muon-spin relaxation measurements of highly homogeneous samples of FeAs and FeAs₂, both previously found as impurity phases in some samples of recently synthesized pnictide superconductors. We observe well-defined muon precession in the FeAs sample with two precession frequencies of 38.2(3) and 22.7(9) MHz at 7.5 K, with the majority of the amplitude corresponding to the lower frequency component. In FeAs₂ we confirm previous measurements showing that no long-ranged magnetic order occurs above 2 K and measure the muon-spin relaxation rate, which increases on cooling. Our results exclude the possibility that previous muon-spin relaxation measurements of pnictide superconductors have been measuring the effect of these possible impurities.

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With the recent discovery of high-temperature superconductivity in pnictide compounds containing FeAs layers,¹ considerable research activity has been devoted to studying both their superconducting and magnetic properties. A rich variety of compounds related to the original LaFeAsO_{1-x}F_x has already been synthesized: 1111 compounds²⁻⁴ where other rare-earth ions have been substituted for the La³⁺ ion leading to a higher superconducting transition temperature $T_c \sim 55$ K, 122 compounds^{5,6} related to the parent compound BaFe₂As₂ (e.g., Ba_{0.6}K_{0.4}Fe₂As₂; $T_c = 38$ K), and LiFeAs where critical temperatures between 12 and 18 K have been reported.⁷⁻⁹ Most of these materials show some competition between superconductivity and magnetism as variables such as pressure or doping are changed. As these new materials have been characterized, it has become apparent that some samples contain significant concentrations of magnetic impurities^{10,11} which could affect their measured properties. Previously determined Mössbauer results¹² on the three most plausible pnictide impurity phases FeAs, FeAs₂, and Fe₂As have been compared to spectra from a series of FeAs-based superconductors, suggesting that the impurity concentration could be up to 50% in some samples.¹⁰ The ⁷⁵As NMR results on SmFeAsO_{1-x}F_x showed a resonance line at 265 MHz that was attributed to the presence of the binary phase FeAs, possibly on a nanoscopic scale.¹¹ It is therefore important that the properties of possible impurity phases are known, so that the quality of existing and future results can be accurately assessed.

Among the techniques already applied to the pnictide superconductors has been muon-spin relaxation (μ SR),^{13,14} measuring both the superconducting and magnetic properties.¹⁵⁻²⁵ Two sorts of magnetic effects have been reported: static Fe magnetism, usually in the parent compound or lightly doped samples, and fluctuating magnetism in more strongly doped samples. The presence of lanthanide moments can also play a role at lower temperatures.^{16,19}

Static Fe magnetism leads to muon precession below the magnetic ordering temperature T_N , which is typically 150 K in the parent compounds (i.e., LaFeAsO and BaFe₂As₂) and

falls with doping. The precession frequencies reported for the 1111 and 122 compounds already measured are shown in Table I. In the absence of long-range magnetic order, fluctuating Fe moments lead to muon-spin relaxation without coherent precession. Results on superconducting Sm-containing oxypnictides with¹⁶ and without¹⁹ F doping have shown a significant thermally activated change in the zero-field muon-spin relaxation rate which has been argued to be intrinsic to the samples. This has been disputed following NMR measurements on notionally similar compositions in which FeAs impurity concentrations of up to 50% were found.¹⁰ Temperature dependent relaxations have also been found in a number of other oxypnictide samples.^{17,20}

Such measurements of the magnetic properties could in-

TABLE I. Precession frequencies ($T \rightarrow 0$) reported in samples of 1111 and 122 FeAs-based superconductors. For the compounds which show more than one precession frequency the proportions of the signal amplitudes are given in parentheses.

| Sample | Reference | Precession Frequencies (MHz) |
|--|-----------|------------------------------|
| 1111 | | |
| LaFeAsO | 17 and 24 | 23 (70%–90%), 3 (10%–30%) |
| LaFeAsO _{1-x} F _x | 15 | 22–24 |
| LaFeAsO _{0.97} F _{0.03} | 17 | 18, 10, 2 |
| SmFeAsO | 21 | 23.8 |
| NdFeAsO | 22 | ~24 |
| CeFeAsO _{0.94} F _{0.06} | 23 | 8 |
| 122 | | |
| BaFe ₂ As ₂ | 22 | 28.8 (80%), 7 (20%) |
| Ba _{0.55} K _{0.45} Fe ₂ As ₂ | 22 | 26 |
| Ba _{0.5} K _{0.5} Fe ₂ As ₂ | 23 | 18, 4 |
| SrFe ₂ As ₂ | 23 and 25 | 45; 44 (70%), 13 (30%) |
| Sr _{0.5} Na _{0.5} Fe ₂ As ₂ | 23 | 37, 10 |

deed be strongly affected by the presence of magnetic impurity phases, and therefore it is important to isolate possible impurity phases and measure their properties in isolation. The μ SR technique allows the values of magnetic fields at muon stopping sites to be determined very precisely. Also, the amplitude of a signal resulting from a particular phase is proportional to its volume fraction in the sample since the muon decay asymmetry is a sum over a large number of muons stopped in different places within the sample. It is therefore possible to make a direct comparison between the muon-spin relaxation in pure samples of the proposed impurity phases and the signal resulting from impurity phases in an FeAs-based superconducting or magnetic sample. In this Brief Report we study the form of the muon-spin relaxation in the two principal impurity phases, FeAs and FeAs₂,²⁶ in order to more clearly interpret the results of previous reported μ SR studies of magnetism in FeAs-based materials.

FeAs is known to have a Néel temperature around $T_N=77$ K and displays helimagnetic order, as is common for compounds with the MnP structure.^{27,28} FeAs₂ has previously been shown not to order above 5 K by Mössbauer spectroscopy,¹² being diamagnetic.²⁹ FeAs and FeAs₂ were prepared by similar methods. All manipulations were performed in an argon-filled glovebox. Fe (Alfa Aesar, 99.998%) and As (Alfa Aesar, 99.9999%) were mixed in the appropriate molar ratios and sealed in evacuated silica tubes. These vessels were heated for 48 h at 500 °C, then the samples were reground, resealed in fresh silica tubes, and annealed at 800 °C for a further 48 h. The FeAs₂ sample was found to be single phase by powder x-ray diffraction (PXRD). The FeAs sample was found to contain 1.9 mol % FeAs₂ as an impurity phase. Rietveld refinements (Fig. 1) against laboratory PXRD data produce lattice parameters consistent with previous reports^{27,29} and do not suggest any nonstoichiometry. The samples are contaminated by very small amounts of ferromagnetic impurity phases but at levels below the sensitivity of laboratory PXRD; this will not only affect the μ SR data (because muons are a volume probe) but also mimics the trace impurities that are likely to be present in pnictide samples which are prepared in similar ways.

Muon-spin rotation (μ SR) experiments were performed on the General Purpose Surface Muon Instrument (GPS) at the Swiss Muon Source (Paul Scherrer Institute, Switzerland). In our μ SR experiments¹³ spin-polarized positive muons (gyromagnetic ratio $\gamma_\mu/2\pi=135.5$ MHz T⁻¹ and lifetime $\tau_\mu=2.2$ μ s) were implanted into the samples, where they stop quickly without significant loss of spin polarization. Each of the powder samples was mounted inside a silver packet on a flypast sample holder to reduce the background from muons stopping outside the sample. To measure the time evolution of the muon-spin polarization, emitted decay positrons were collected in detectors placed forward (F) and backward (B) relative to the initial muon-spin direction (antiparallel to the beam momentum). The muon decay asymmetry is defined in terms of the count rates (after the subtraction of a time-independent background) in the two detectors (N_F and N_B) as

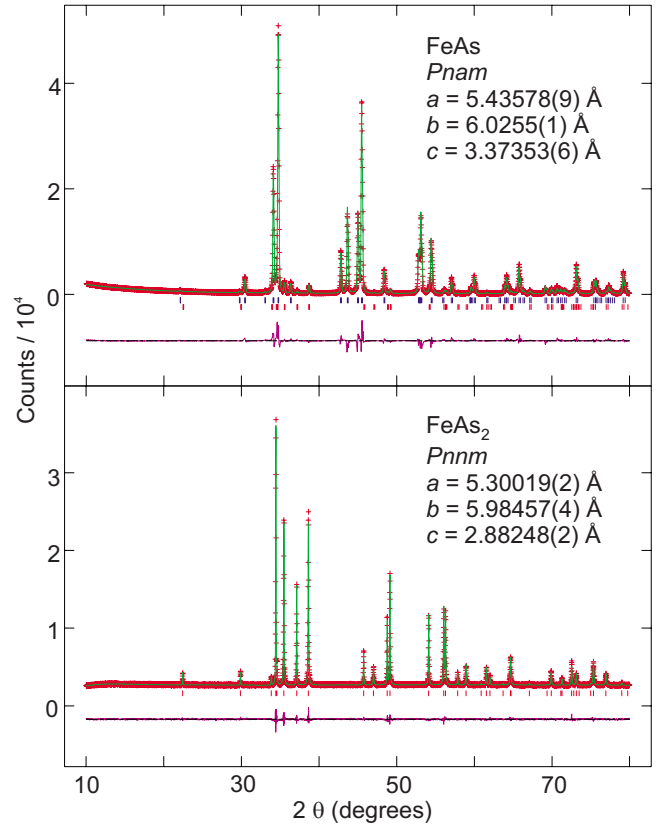


FIG. 1. (Color online) Rietveld refinements against laboratory PXRD data for the FeAs (upper) and FeAs₂ (lower) samples used in the μ SR experiments. Data (red points), fit (green line), and difference (purple line) are shown. In the case of FeAs tick marks are for 2 mol % FeAs₂ (lower) and the FeAs majority phase (upper). Space groups and refined lattice parameters are included in the plots. Weighted profile R factors are 0.11 for the FeAs refinement (data collected in 18 h on a Rigaku Miniflex II diffractometer equipped with a secondary beam monochromator using Cu $K\alpha$ radiation) and 0.02 for the FeAs₂ refinement (data collected in 3 h on a PANalytical X-pert PRO diffractometer using Cu $K\alpha_1$ radiation).

$$A(t) = \frac{N_F(t) - \alpha N_B(t)}{N_F(t) + \alpha N_B(t)}, \quad (1)$$

where α is an experimental calibration constant related to the relative efficiency of the detectors.

The muon spins are sensitive to both static and fluctuating local fields at their stopping positions inside the material, and these affect the time dependence of the muon decay asymmetry. In FeAs we see three distinct behaviors in different temperature ranges, and therefore the data require a different parametrization in each temperature range. These temperature regions are shown in Fig. 2. At temperatures well below T_N (region A) we observe coherent muon oscillation at two magnetically inequivalent stopping sites giving two well-defined frequencies. Muons with their spins parallel to the local field are depolarized by fluctuations flipping their spins leading to an exponential relaxation. We describe the muon depolarization in temperature region A using Eq. (2). Closer to T_N (region B) the muon oscillations cease to be coherent

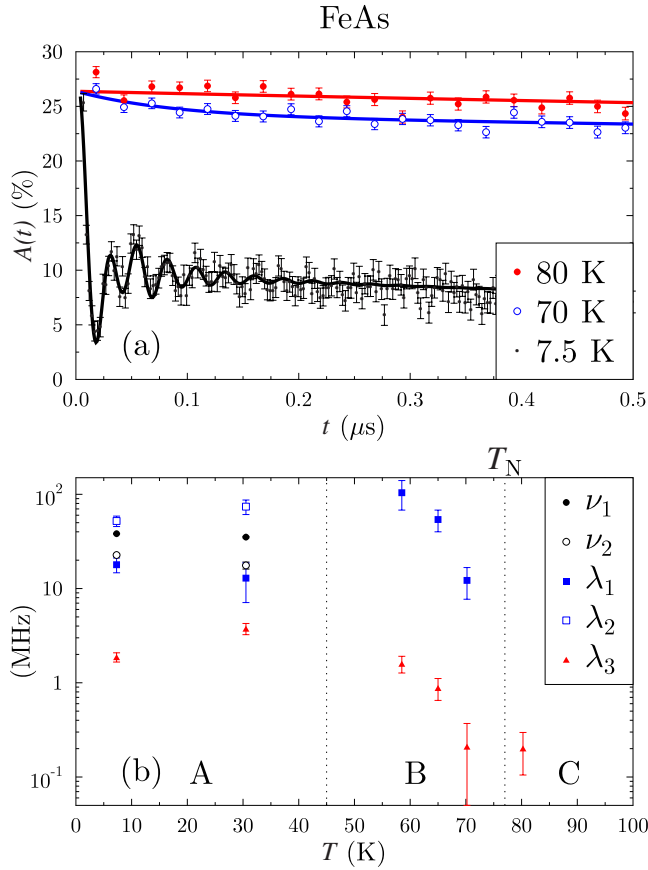


FIG. 2. (Color online) (a) Muon asymmetry data for FeAs showing the spin precession signal evident at low temperature, the rapid spin depolarization evident close to T_N , and the paramagnetic signal at 80 K. The data are fitted to Eqs. (2)–(4), respectively, with the parameters shown in panel (b). (b) Parameters derived from fitting Eqs. (2)–(4) to the raw data as described in the text.

and we observe a rapid depolarization instead of the oscillations, with the data well described by Eq. (3). In the paramagnetic phase above T_N (region C) the decay asymmetry was well described by a single exponential relaxation given by Eq. (4),

$$A(t) = \sum_{i=1,2} A_i e^{-\lambda_i t} \cos(2\pi\nu_i t) + A_3 e^{-\lambda_3 t}, \quad (2)$$

$$A(t) = A_1 e^{-\lambda_1 t} + A_3 e^{-\lambda_3 t}, \quad (3)$$

$$A(t) = A_3 e^{-\lambda_3 t}. \quad (4)$$

The λ_i parameters describe damping rates and $\nu_i = \gamma_\mu B_i / 2\pi$ are the precession frequencies proportional to the magnitude of the magnetic field at each stopping site.

The muon decay asymmetry data recorded for FeAs at temperatures of 7.5, 70, and 80 K are shown in Fig. 2. At temperatures well below T_N (in region A) we observe a well-defined muon-spin precession at two frequencies, accounting for 2/3 of the relaxing amplitude as would be expected from polycrystalline averaging. At 7.5 K the dominant frequency is $\nu_1 = 22.7(9)$ MHz, accounting for around 70% of the precession signal. This frequency is strongly damped with λ_1

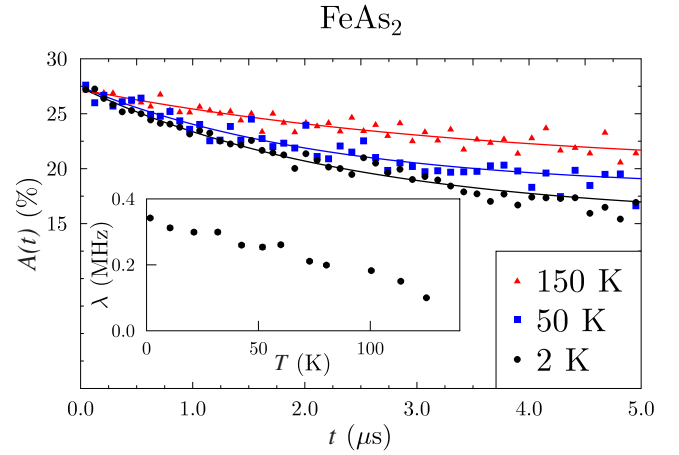


FIG. 3. (Color online) Muon asymmetry data for FeAs₂ showing the form of the spin relaxation over the measured temperature range. The lines are fits to Eq. (4) described in the text. Inset: temperature dependence of the muon-spin-relaxation rate λ_3 defined in Eq. (4).

$= 52(6)$ MHz. The remaining 30% of the signal has a precession frequency of $\nu_2 = 38.2(3)$ MHz with a damping rate of $\lambda_2 = 18(3)$ MHz. The exponentially relaxing part of the signal has a relaxation rate of $\lambda_3 = 1.9(2)$ MHz. This form of the relaxation is evident up to close to T_N with similar amplitudes as the temperature increases, but the damping of the precession signals increases. Above 60 K the precession is overdamped and we can no longer resolve the precession frequencies. We find no evidence of any additional components in the μSR spectra below T_N , leading us to believe that FeAs is completely ordered throughout its bulk below T_N . Above T_N the relaxation rate decreases with increasing temperature.

Examples of the muon decay asymmetry data recorded on the FeAs₂ sample are shown in Fig. 3. The data are well described by a single exponential relaxation [Eq. (4)] at all temperatures, but the relaxation rate increases on cooling to around 0.35 MHz at 2 K.

We can now compare our results to those summarized in the introduction and Table I. None of the samples previously measured using μSR show both the combination of frequencies we have measured or the relative amplitudes we have measured for FeAs. The 23 MHz signal we observe is similar to that in the 1111 compounds but they have no higher frequency signal and a much lower damping rate. The 23 MHz signal in the 1111 compounds also persists all the way up to $T_N \sim 150$ K, which is twice that of FeAs. From this we must conclude that the local environments for implanted muons are similar in FeAs and the 1111 compounds, but FeAs impurities are not producing this signal. The FeAs oscillation frequencies are significantly different from those in the 122 materials and they show magnetic transitions at $T > 140$ K. The 3 MHz signal reported^{17,24} in LaFeAsO is not due to FeAs despite the onset around 70 K reported in Ref. 24. In Sm-based oxypnictides a temperature-dependent relaxation behavior was observed^{16,19} which followed a thermally activated behavior consistent with crystal-field excitations to the first-excited state of the Sm^{3+} ion. On the basis of Mössbauer

measurements on nominally similar samples, this has been argued to be due to FeAs impurities.¹⁰ Our measurements on FeAs strongly exclude this possibility. Since the measurements on F-doped samples were performed at a pulsed muon source at which the pulse length places an upper limit on the measurable precession frequency, any FeAs impurities would have given a drop in the initial muon asymmetry $A(0)$ of 0.15% per 1% of impurity present.³⁰ No such drop in the initial asymmetry was observed.¹⁶ The experiment of Ref. 19 would have measured signals very similar to those in Fig. 2 had any FeAs been present in the samples, which they did not. From this comparison we conclude that none of the FeAs-based superconductors previously measured using μ SR were sufficiently contaminated with FeAs inclusions so as to give results directly due to such an impurity.

The situation in those 1111 compounds where a temperature-dependent relaxation rate is reported is more

complicated to relate to impurity phases. None of the samples show the same temperature-dependent relaxation rate as FeAs₂, although there is relatively little data taken around 100 K. FeAs₂ certainly does not show the same thermally activated temperature dependence observed in the Sm oxypnictides,^{16,19} nor is it showing any significant changes in the relaxation rate in the lower-temperature region where features have been found in other oxypnictides.^{17,20} That the values of the relaxation rates in the impurity phases are similar to those in the oxypnictides is more likely to be related to the similarity of the muon's local environment in the superconductors to that in the magnetic systems we consider here.

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