Determination of characteristic muon precession and relaxation signals in FeAs and FeAs$_2$, possible impurity phases in pnictide superconductors

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We report muon-spin relaxation measurements of highly homogeneous samples of FeAs and FeAs$_2$, 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 FeAs$_2$ 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, 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$_x$ have already been synthesized: 1111 compounds where the La$^{3+}$ ion has been substituted for other rare-earths leading to a higher superconducting transition temperature, $T_c \sim 55$ K; 122 compounds related to the parent compound BaFe$_2$As$_2$ (e.g. Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$: $T_c = 38$ K), and LiFeAs where critical temperatures between 12 K and 18 K have been reported. Most 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 which could affect their measured properties. Previously determined Mössbauer results on the three most plausible pnictide impurity phases: FeAs, FeAs$_2$, and Fe$_2$As$_2$ 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. The $^{75}$As 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. 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 superconductor superconductors has been muon-spin relaxation ($\mu$SR) measuring both the superconducting and magnetic properties. 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.

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 BaFe$_2$As$_2$) 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 with and without 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. Temperature dependent relaxations have also been found in a number of other oxypnictide samples.

Such measurements of the magnetic properties could indeed 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 $\mu$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 FeAs$_2$, in order to more clearly interpret the results of previous reported $\mu$SR studies of magnetism in FeAs-based mate-
The proportions of the signal amplitudes are given in brackets.

For the compounds which show more than one precession frequency the proportions of the signal amplitudes are given in brackets.

Table I: Precession frequencies (T → 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 brackets.

| Sample          | Reference | Precession Frequencies (MHz) |
|-----------------|-----------|------------------------------|
| LaFeAsO         | Refs. 17, 24 | 23 (70-90%), 3 (10-30%)     |
| LaFeAsO₁₋ₓFₓ   | Ref. 15   | 22 – 24                      |
| LaFeAsO₀.₇F₀.₃₀ | Ref. 17   | 18, 10, 2                    |
| SmFeAsO        | Ref. 21   | 23.8                         |
| NdFeAsO        | Ref. 22   | ~ 24                         |
| CeFeAsO₀.₉₄F₀.₀₆ | Ref. 23 | 8                           |

| Sample          | Reference | Precession Frequencies (MHz) |
|-----------------|-----------|------------------------------|
| BaFe₂As₂        | Ref. 22   | 28.8 (80%), 7 (20%)          |
| Ba₀.₅₇K₀.₄₃Fe₂As₂ | Ref. 22 | 26                           |
| Ba₀.₅₇K₀.₄₃Fe₂As₂ | Ref. 23 | 18, 4                        |
| SrFe₂As₂        | Ref. 23   | 45                           |
| Sr₁₀₁₅Na₀.₅Fe₂As₂ | Ref. 23 | 37, 10                       |

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. FeAs has previously been shown not to order above 5 K by Mössbauer spectroscopy being diamagnetic. FeAs and FeAs₂ were prepared by similar methods. All manipulations were performed in an argon-filled glovebox. Fe (Alfa Aesar, 99.9998%) 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 hours at 500°C, then the samples were re-ground, re-sealed in fresh silica tubes and annealed at 800°C for a further 48 hours. The FeAs sample was found to be single phase by Powder X-ray Diffraction (PXRD), although a small amount of elemental arsenic had sublimed away from the solid in the reaction vessel. The FeAs sample was found to contain 1.9 mol % FeAs₂ as an impurity phase. Rietveld refinements (Fig. 1) against laboratory PXRD data for the FeAs (upper) and FeAs₂ (lower) samples used in the μSR 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 hours on a Rigaku Miniflex II diffractometer equipped with a secondary beam monochromator using CuKα radiation) and 0.02 for the FeAs₂ refinement (data collected in 3 hours on a PANalytical X-pert PRO diffractometer using Cu Kα₁ radiation.)

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 in the two detectors (N_F and N_B) as:

\[ A(t) = \frac{N_F(t) - \alpha N_B(t)}{N_F(t) + \alpha N_B(t)}, \]

where \( \alpha \) is an experimental calibration constant related to the relative efficiency of the detectors.

The muon spins are sensitive to both static and fluc-
FIG. 2: (Color online.) Muon asymmetry data for FeAs showing the spin precession signal evident at low-temperature, the paramagnetic signal at 80 K, and the rapid spin depolarization evident close to $T_N$. The low-temperature data are fitted to Eq. (2) and the 80 K data are fitted to Eq. (3).

FIG. 3: (Color online.) Muon asymmetry data for FeAs$_2$ showing the form of the spin relaxation over the measured temperature range. The lines are fits to Eq. (3) described in the text. Inset: Temperature dependence of the muon spin relaxation rate $\lambda$ defined in Eq. (3).

tuating local fields at their stopping positions inside the material, and these affect how the form of the muon decay asymmetry changes with time. In FeAs we see two distinct behaviors in different temperature ranges and therefore the data require a different parameterization in each temperature range. At low-temperature in FeAs we have long range magnetic order and quasistatic magnetic fields at the muon stopping sites with two well separated precession frequencies. The data are well described by the function:

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

The two terms in the sum are damped oscillations corresponding to muons precessing around quasistatic local fields at two magnetically inequivalent stopping sites. The $\lambda_i$ 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 third term is an exponential relaxation, of rate $\lambda_3$, due to fluctuations flipping the spins of muons having a non-zero spin component along the local magnetic field direction.

For the paramagnetic phase of FeAs the muon decay asymmetry was well described by a single exponential relaxation:

$$A(t) = A_0 e^{-\lambda t}. \quad (3)$$

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 $T_N$ we observe a well-defined muon spin precession at two frequencies. 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 $\lambda_1 = 52(6)$ 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 $\mu$SR spectra below $T_N$, leading us to believe that FeAs is completely ordered throughout its bulk in this temperature regime. Above $T_N$ the relaxation rate decreases with increasing temperature.

Examples of the muon decay asymmetry data recorded on the FeAs$_2$ sample are shown in Fig. 3. The data are well described by a single exponential relaxation [Eq. (3)] 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 $\mu$SR 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, twice that of FeAs. From this we must conclude that the local environments for implanted muons are relatively similar in FeAs and the 1111 compounds, but FeAs impurities are not producing this signal. The precession frequencies are significantly different from those in the 122 materials and they show magnetic transitions at $T > 140$ K. The 3 MHz signal reported in LaFeAsO is not due to FeAs, de-
spite the onset around 70 K reported in Ref.\textsuperscript{24}. In Sm-based oxypnictides a temperature dependent relaxation behavior was observed\textsuperscript{16,19} which followed a thermally activated behavior consistent with crystal field excitations to the first excited state of the Sm\textsuperscript{3+} ion. On the basis of Mössbauer measurements on nominally similar samples this has been argued to be due to FeAs impurities.\textsuperscript{25} 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.\textsuperscript{26} No such drop in the initial asymmetry was observed.\textsuperscript{27} The experiment of Ref.\textsuperscript{13} would have measured signals very similar to those in Fig.\textsuperscript{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 $\mu$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 FeAs\textsubscript{2}, although there is relatively little data taken around 100 K. FeAs\textsubscript{2} certainly does not show the same thermally activated temperature dependence observed in the Sm-oxypnictides\textsuperscript{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.\textsuperscript{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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