Crossover between magnetism and superconductivity in LaFeAsO with low H-doping level

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Received 11 April 2014, revised 12 May 2014
Accepted for publication 21 May 2014
Published 24 June 2014

Abstract

By making a systematic study of the hydrogen-doped LaFeAsO system by means of dc resistivity, dc magnetometry, and muon-spin spectroscopy, we addressed the question of universality of the phase diagram of rare-earth-1111 pnictides. In many respects, the behaviour of LaFeAsO$_{1-x}$H$_x$ resembles that of its widely studied F-doped counterpart, with H$^+$ realizing a similar (or better) electron doping in the LaO planes. In an $x = 0.01$ sample we found a long-range spin-density wave (SDW) order with $T_N = 119$ K, while at $x = 0.05$ the SDW establishes only at 38 K and, below $T_c = 10$ K, it coexists at a nanoscopic scale with bulk superconductivity. Unlike the abrupt magnetic-superconducting transition found in the La-1111 compound, the presence of a crossover region makes the H-doped system qualitatively similar to other Sm-1111, Ce-1111, and Nd-1111 families.

Keywords: superconductivity phase diagrams, doped pnictides, muon spin spectroscopy, LaFeAsO

(Received 11 April 2014, revised 12 May 2014, accepted 21 May 2014)

1. Introduction

The complexity of high-temperature superconductors, reflecting their quantum-correlated nature, has intrigued scientists over the years. In this respect the discovery of superconductivity below $T_c = 26$ K in LaO$_{1-x}$F$_x$FeAs [1] marked the beginning of a new era, that of iron-based compounds, which could be tested against the long-known cuprates. In both cases the doping of charges into the FeAs or CuO$_2$ layers, respectively, plays a key role for the appearance of superconductivity. The similar dependence of $T_c$ on the carrier doping is reflected in the superconducting domes of Fe-based materials, qualitatively similar to those of many unconventional superconductors.

Generally, in the phase diagrams of all the Ln-1111 family members (Ln being a lanthanoid) the static magnetism of the parent compounds is suppressed by carrier doping (or pressure) favouring the superconducting state. Depending on the rare earth Ln, the way in which this suppression effectively occurs gives rise to different kinds of phase transitions. In the case of La, an abrupt transition from the magnetic (M) to the superconducting (SC) phase takes place [2]. On the other hand, an M-SC coexistence in the form of a mesoscopic phase separation was found in F-doped La-1111 samples with $x = 0.06$ at ambient pressure [3] and, with $x = 0.055$, under hydrostatic pressure [4]. Similarly, for a whole series of other rare-earth metals (e.g., Ln = Ce [5], Sm [6], Nd [7]) the
transition is of a second-order type, with the M and SC phases nanoscopically coexisting over a finite range of F doping. This picture changes slightly in the case of substitutions in the FeAs planes: here the nanoscopic coexistence of reentrant magnetism with SC has been found in Ln-1111 (Ln = La, Nd, Sm) [8, 9] and in Ce-1111 [10] for Ru and Co substitutions, respectively. Nevertheless, if one considers only substitutions in the LnO planes, it remains unclear what makes La so peculiar, i.e., whether the strict separation of the M and SC phases is an intrinsic feature of this compound.

For a long time the low solubility limit of fluorine in 1111 systems (x < 0.15–0.20) has prevented their overdoped SC region from being explored. A clever way to circumvent this—at first sight unsurmountable—problem is to make use of the high solubility of hydrogen [11]. Although counterintuitive, neutron powder diffraction and DFT calculations have found not only that hydrogen substitutes for oxygen in the LnO layers but also, and most importantly, that it adopts a −1 charge state. Hence, to all appearances H− acts as if it were F−, while providing access to a very extended doping range (0 < x < 0.5) in (Ce, Sm)FeAsO1−(H). That hydrogen in its H− form substitutes for O2− and supplies electrons to the Tµ0.05, was measured by means of dc resistivity, magnetometry and µSR measurements on the same family reported the discovery of a second antiferromagnetic phase, where iron spins form an antiferromagnetic collinear structure at very high doping level (x > 0.4). Interestingly, this stripe-type magnetic order coexists with superconductivity up to x = 0.45 [13].

The availability of LaFeAsO1−xHx and a comparison with the well-known LaFeAsO1−xF2 family allowed us to address an initial question: is the abrupt M-SC transition in LaFeAsO1−xHx, for x = 0.01 (a) and x = 0.05 (b). The insets show the maximum in dq/dT (T) (a) and the drop in q(T) near Tc(b).

2. Experimental details

2.1. Sample preparation and characterization

Two polycrystalline LaFeAsO1−xHx samples with nominal H content x(H) = 0.01, 0.05 were synthesized by means of solid-state, high-pressure reaction, using La2O3, LaAs, LaH2, FeAs and Fe2As as starting materials, as reported in detail in [12, 15]. The sample with x(H) = 0.01 consisted of a single disc-shaped pellet (diameter 5.8 mm, average thickness 1.8 mm), whereas the sample with x(H) = 0.05 comprised a mosaic of pellets, whose biggest piece was a flat disc (diameter 5.7 mm, average thickness 1.3 mm). Room temperature, powder x-ray diffraction measurements using Cu Kα1 radiation were employed to assess the phase purity and to determine the structural parameters of the synthesized samples (see table 1). The main impurity consisted of unreacted La2O3, whose content never exceeded 2 wt%. To evaluate the exact hydrogen content in the synthesized samples we carried out thermal desorption spectroscopy measurements, whereas the chemical composition (excluding hydrogen) was determined by using a wavelength-dispersive-type electron-probe microanalyser.

2.2. Resistivity and magnetization measurements

The resistivity of the LaFeAsO1−xHx samples was measured by means of a standard four-point method, with the temperature dependences ρ(T) shown in figure 1. Upon cooling, the x(H) = 0.01 sample shows the typical transport features of underdoped iron-based oxypnictides: a low-temperature resistivity in the mΩ cm range and an inflection point (the arrow in figure 1), defined as the point of maximum of the first derivative, dρ/dT, generally attributed to a spin-density wave (SDW) transition [16]. At very low temperatures (T < 20 K) we were
able to detect also a small drop in resistivity. A similar feature has also been found in high-quality LaFeAsO single crystals, where it was ascribed to a change of the magnetic structure of the iron atoms from an antiferromagnetic to a ferromagnetic arrangement along the c axis [17]. The overall temperature behaviour closely reproduces the results reported in [12] for a nominally equivalent sample. In the $x = 0.05$ case the peak in $d\rho/dT$ disappears. The resistivity decreases almost linearly down to 75 K, while below this temperature a weak localization takes place, just before the superconducting transition at about 10 K, as defined by a zero-resistivity criterion. Both of these features are in good agreement with existing experimental data for an $x = 0.04$ sample [12].

To characterize in more detail the superconducting state of the $x = 0.05$ sample, we carried out dc magnetization measurements by means of a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The susceptibility versus temperature curves were measured from 2 to 20 K at $\mu_0 H = 1 \text{ mT}$, both in zero-field-cooled (ZFC) and in field-cooled (FC) conditions. In addition, dc isothermal magnetization measurements were performed at selected temperatures. The experimental results shown in figure 2 can be summarized as follows:

(a) The shielding fraction as inferred from the ZFC susceptibility data shown in figure 2(a) (after subtracting a ferromagnetic offset) provides an apparent shielding fraction of about 8%. This value, however, can be considered only as a lower bound for the superconducting volume fraction, since the attainment of the percolation threshold (i.e., zero resistivity below $T_c$) itself indicates that the superconducting phase occupies at least 20–30% of the sample volume [18].

(b) The isothermal magnetization curves at 5, 30 and 300 K indicate the presence of ferromagnetic impurities that mask the intrinsic diamagnetic response of the sample. In particular, the first-magnetization curve at 5 K does not show a diamagnetic (i.e., superconducting) slope (see the inset in figure 2(b)). Instead, its initially constant behaviour results from the interplay of two opposite contributions, namely, a diamagnetic contribution from the superconducting phase and a ferromagnetic one from the above-mentioned impurities.

Apart from the extrinsic effects of diluted ferromagnetic impurities, these experimental results closely resemble those relating to ruthenocuprates (see, e.g., [19, 20] and references therein), where superconductivity develops well within a magnetically ordered phase. Also in our case, we found a low-$T$ magnetic order in the FeAs planes (detected via $\mu$SR measurements—see section 3), which coexists with a superconducting phase. Typical internal magnetic fields in the SDW state of pnictides are about 20–40 mT [6, 7, 21], i.e., significantly higher than $H_{c1}$, the first critical SC field ($\mu_0 H_{c1} \sim 6 \text{ mT}$ at 1.8 K in LaFeAsO$_{1-x}$F$_x$ polycrystalline samples) [22]. In these conditions, a spontaneous vortex phase can easily develop, hence preventing any meaningful ZFC measurements at temperatures below the onset of the magnetic order.

2.3. Muon-spin spectroscopy

The muon-spin spectroscopy measurements were carried out at the GPS instrument of the SuS facility at the Paul Scherrer Institute, Switzerland. We performed ZF, LF and TF experiments. By means of the former one can detect spontaneous magnetic order, as well as distinguishing between short-range and long-range order [5, 23]. The latter, however, are typically used to distinguish between static and dynamic magnetism (on the $\mu$SR timescale) [23, 24]. TF measurements were performed only on the $x = 0.05$ sample, to study its superconducting properties.

In all of our experiments the relatively large sample thickness (about 1.5 mm) and the use of a veto counter, which ensured that the signal was acquired only from muons stopped in the sample, significantly improved the signal-to-noise ratio. Below we summarize the main experimental results for the $x = 0.01$ and 0.05 samples.

2.3.1. $\mu$SR in the $x = 0.01$ case. Figure 3 shows a selection of ZF spectra for the $x = 0.01$ sample. The most prominent feature is the presence of highly damped oscillations, indicative of several different precession frequencies, reflecting the different local fields probed by the implanted muons. To
distinguish between these contributions we fitted the time-dependent $\mu$SR asymmetries with the following model:

$$\frac{A^{\mu\text{SR}}(t)}{A^{\mu\text{SR}}(0)} = [1 - V_M(T)] g(t) + \sum_{i=1}^{N} w_i \left[ a_i f_i(\gamma_i B(t)) D_{T}(t) + a_i D_{L}(t) \right], \quad (1)$$

where $A^{\mu\text{SR}}(0)$ is the high-temperature value of the initial asymmetry, $V_M$ is the magnetic volume fraction, $g(t)$ the time-dependent relaxation in the paramagnetic state, and $\gamma_i \approx 2\pi \times 135.53$ MHz $\text{T}^{-1}$ the muon gyromagnetic ratio. In the magnetically ordered state a nonzero $V_M$ fraction of muons probes a local magnetic field $B_i$ at the implantation site $i$, $a_i$ and $g(t)$ in equation (1) refer to muons probing local magnetic fields in the transverse ($T$) and longitudinal ($L$) directions with respect to the initial spin polarization. The coherent precession of muons is taken into account by the $f_i(t)$ function, whereas $D_{T}(t)$ and $D_{L}(t)$ represent how this precession is damped. The former decay reflects the static distribution of local magnetic fields, whereas the latter is due to dynamical relaxation processes. Finally, the sum over $i$ generalizes equation (1) to the case of several inequivalent crystallographic implantation sites, whose populations $w_i$ satisfy the normalization condition $\sum_{i=1}^{N} w_i = 1$.

In the specific case of the $x = 0.01$ sample we find that (i) the high-temperature paramagnetic phase is best described by means of an exponential relaxation function $g(t) = e^{-t / \tau}$, which suggests the presence of fast-fluctuating nuclear magnetic moments; (ii) for the magnetically ordered phase ($T < T_N$) three distinct precession frequencies can reproduce the time-dependent asymmetry. The considerable damping of the time-dependent asymmetry signal cannot be fully taken into account by damped cosine functions. For this reason the $f_i(t)$ ($i = 1, 2, 3$) term was identified with a zeroth-order Bessel function. We recall that the Bessel function is generally the fingerprint of incommensurate long-range magnetic order [23, 25]. The respective transverse Gaussian relaxation widths $\sigma_T$ and the longitudinal relaxation rates $\lambda_L$ are fitted by means of equation (1).

Figure 5, however, shows the temperature dependence of the internal magnetic fields $B_{\mu}$, their respective transverse Gaussian relaxation widths $\sigma_T$ and the longitudinal relaxation rates $\lambda_L$. The dashed lines are guides for the eyes.

2.3.2. $\mu$SR in the $x(H) = 0.05$ case. The most representative ZF spectra for the $x = 0.05$ case are plotted in figure 6. Two main features are evident: a rather large relaxation present also at high temperatures, and a significantly damped signal with no coherent precessions below about 60 K. In this case, the time-dependent asymmetry was still fitted by means of...
equation (1), but with some differences with respect to the choices adopted for the sample \(x = 0.01\), as follows.

(i) For the high-temperature paramagnetic phase, the \(g(t)\) term is best described by a Lorentzian Kubo–Toyabe (KT) model, more suitable for fitting large relaxation rates due to homogeneously diluted ferromagnetic impurities (see below).

(ii) A very strong damping below about 60 K indicates the onset of a magnetic order. Since the time-dependent asymmetry does not oscillate, the product \(f(t)D_x(t)\) was modelled with a decaying exponential.

Only two distinct transverse components could be detected, whereas it was not possible to distinguish those corresponding to the longitudinal relaxation. As before, such components were merged into a single slowly decaying Lorentzian exponential. The parameters resulting from the fits using equation (1) are summarized in figure 7 and table 2. Figure 5 reports again the temperature dependence of the magnetic volume fraction. Also in this case, the average magnetic ordering temperature was deduced from a fit with an error-function-like model (see table 2). In contrast to the case for the \(x = 0.01\) sample, the \(x = 0.05\) sample shows a very broad magnetic transition and seems to fully order only at the lowest temperature. Moreover, no additional linear terms were necessary for the fit.

3. Discussion

3.1. Low versus intermediate \(H\) doping

The \(x = 0.01\) sample: Normally, the signature of a magnetically ordered phase in ZF-\(\mu\)SR experiments is an oscillating signal representing the fingerprint of a coherent muon-spin precession around the local field at the implantation site. This is the case for all the parent compounds (\(x = 0\)) of the Ln-1111 iron pnictides, as well as for our lightly doped \(x = 0.01\) sample (see figure 4). As in the case of the Ce-1111 family [5], even tiny amounts of doping are sufficient for changing the commensurate AF order of the parent compound into an incommensurate one, as suggested by the Bessel fit of the time-dependent asymmetry [23, 25]. In contrast to the case for the parent compounds, where two distinct frequencies, reflecting muons implanted in the FeAs and LaO planes, were predicted [26] and found experimentally [2, 26], in our case we detect three different precessions at about 145, 68,
and 15 mT (corresponding to 18.3, 13.1 and 1.9 MHz) with relative weights \( w_1, w_2, \) and \( w_3 \) of 0.69, 0.20, and 0.11, respectively (see table 2). As generally accepted for the Ln-1111 family [26], muons implanted in the FeAs planes represent the most populated site. By the same token, our \( B_{125} \) and \( B_{135} \) fields are most probably attributable to muons stopping in FeAs and LaO planes, respectively. These assumptions are in very good agreement with results from a 3% fluorine-doped LaFeAsO sample [14], indicating that 3% F and 1% H substitutions correspond to similar effective doping levels. This analogy is further reinforced by considering that the Néel temperature of the \( x(H) = 0.01 \) sample, resulting from fits of the dependence on \( T \) of the magnetic volume fraction, fully agrees with that of the fluorine-doped sample [14]. At the same time, the presence of a third frequency (\( B_{132} \)), surviving down to almost \( T_N \), is somewhat unexpected. In fact, this seems to imply, contrary to theoretical predictions [26], a third muon implantation site. Most probably, inhomogeneities in the local doping might reduce the field probed at the standard implantation sites and significantly broaden magnetic transitions, as confirmed by an \(~\sim 10-15\%\) fraction of sample volume whose magnetization never saturates below \( T_N \), giving rise to a rather unusual linear increase in \( V_{\mu} \) with decreasing temperature (see figure 5).

In conclusion, given the similar behaviours of the \( x(H) = 0.01 \) and \( x(F) = 0.03 \) systems (the latter being a nominal content), it seems that the O–H substitution dopes the Ln-1111 system more effectively with electrons.

The \( x = 0.05 \) sample: At intermediate dopings a short-range magnetic order, evidenced by a fast-decaying non-oscillating asymmetry signal, is usually found either in F-doped [5, 6] or in Fe-substituted samples (e.g., for Fe–Ru substitution [9, 27]). This seems to be the case also for the \( x = 0.05 \) sample, whose \( \mu\)SR relaxation data reported in figure 6 belong to two distinct temperature regimes: below and above \( T_S \), respectively. In the low-\( T \) regime, the short-range magnetism implies a fast dephasing of muon spins, resulting in a sharp drop of the asymmetry. The large dephasing is due to local fields with widths \( \Delta B_N = \lambda_T / T_N \) of about 22 and 4 mT at the lowest temperature. Since the relative weights are \( w_1 = 0.74 \) and \( w_2 = 0.24 \), their ratio recalls those generally accepted for the muon populations implanted in the FeAs and LnO planes of the 1111 family.

To verify the static nature (on the \( \mu\)SR timescale) of the local fields we performed a longitudinal-field (LF) spin-decoupling experiment at 5 K. An external magnetic field of increasing magnitude \( B_1 \) is applied along the initial muon-spin direction. As long as \( B_1 \) is lower than or of the same order as the internal static fields, it has a negligible influence on the muon polarization. However, when \( B_1 \) exceeds the typical internal field value, it ‘quenches’ the muon spins along the field direction and determines the full recovery of the longitudinal fraction. This is not the case for strongly fluctuating internal fields, where the effect of the external field is barely noticeable. Figure 8 shows the time-dependent asymmetry at different applied longitudinal fields. Clearly, an applied field above about 50 mT is sufficient for fully recovering the total muon-spin polarization. This is confirmed by the results shown in figure 9, where the initial longitudinal asymmetry \( \lambda_L \) and the transverse relaxation rates \( \lambda_T \) are plotted as a function of \( B_1 \). The saturation of the former and the disappearance of the latter unambiguously confirm the static nature of the internal fields in the low-\( T \), magnetically ordered phase of the \( x = 0.05 \) sample.

Above \( T_N \) the asymmetry behaviour does not depend on temperature and its time evolution is well described by a Lorentzian Kubo–Toyabe model, generally indicative of the presence of diluted ferromagnetic impurities [28]. To confirm this hypothesis, another series of LF decoupling experiments was carried out at \( T = 240 \) K. Figure 10 shows the time-dependent asymmetry at different applied fields, with all the data sets fitted using the above-mentioned field-dependent model. The prompt recovery of the full asymmetry in a relatively small applied field (50 mT) confirms the above picture. 

\textit{A posteriori}, this result justifies also the macroscopic magnetization behaviour as evidenced by dc magnetization measurements (see section 2.2).

3.2. Flux pinning and the superconducting volume fraction

Transport and dc susceptibility measurements show that the \( x = 0.05 \) sample is a superconductor with \( T_c = 10 \) K
Figure 10. LF-µSR time-domain spectra measured at $T = 240$ K for the $x = 0.05$ sample. The continuous lines represent numerical fits with a Lorentzian Kubo–Toyabe model.

(see table 2) and a superconducting volume fraction $V_{\text{SC}}$ of at least 20–30%. However, estimation of the true $V_{\text{SC}}$ from macroscopic data is notoriously difficult in complex systems having a magnetically ordered phase [19] with $T_N > T_c$ and, occasionally, also diluted magnetic impurities. In our case, things are even more complicated, since $H_{c1}$ is lower than the internal magnetic field, due both to the ordered Fe$^{3+}$ moments in the SDW phase and to the remanent magnetization from the diluted ferromagnetic impurities.

In such a situation even a conventional microscopic approach would still be faced with difficulties. Nevertheless, by the use of the so-called ‘TF-µSR pinning technique’ [29], we were able to overcome the difficulties related to the $V_{\text{SC}}$ determination, and find truly bulk superconductivity in the $x = 0.05$ sample. TF-µSR measurements were carried out by applying a magnetic field perpendicular to the muon momentum $p_\mu$. In this geometry, the flux-pinning experiment consisted in field cooling the sample in an external field $B_{\text{ext}} = 100$ mT, and then, while keeping the temperature fixed at 5 K (i.e., below $T_c$), in subsequently increasing the field by ~25% to 125 mT. This approach allowed us to study the SC vortex lattice by observing the changes in the respective µSR spectra.

To understand the outcome of the pinning experiment, it is useful to consider first what happens well above $T_N$. Figure 11(a) displays the fast Fourier transform (FFT) of the muon asymmetry data at 240 K in a 50 mT TF configuration. The amplitude of the real FFT signal is proportional to the local-field distribution $P(B)$, which in our case is characterized by a main Lorentzian peak, shifted by about –4.3 mT, and a small shoulder, centred at the applied-field value. This picture is confirmed by a fit of the time-dependent asymmetry with the model:

$$\frac{A_{\text{TF}}(t)}{A_{\text{int}}(0)} = \sum_{i=1}^{N} a_i \cos(\gamma_i B_i t) \exp(-\lambda_i t).$$

Only two components ($N = 2$) were required for the fit, of which one was at zero shift ($B_i - B_{\text{int}} = 0$) and with a relative weight of 3%, in good agreement with x-ray diffraction results, that indicate the presence of 2% of non-magnetic La$_2$O$_3$ (see table 1). The absence of other fit components not only confirms that the sample is in a single phase, but also that the ferromagnetic impurities can be considered as homogeneously diluted nanoscopic inclusions, whose amount is below the detection threshold of x-ray diffraction. The unexpected diamagnetic shift of the main component (see figure 11(a)) can be accounted for by considering the local magnetic field as seen by the implanted muons:

$$B_\mu = B_{\text{ext}} + B_{\text{kmag}} + B_e + B_{\text{demag}} + B_{\text{id}}.$$  

(3)

The ferromagnetic impurities can be considered as homogeneously diluted magnetic moments mostly aligned along $B_{\text{ext}}$. In this highly symmetric condition the sum of the dipolar contributions $B_{\text{dip}}$ from the impurities within the sphere of Lorentz construction should be negligible. Moreover, in a first instance, we neglect the hyperfine field $B_{\text{hf}}$, as well (mostly because of the significant distance between an implanted muon and an impurity). We can, hence, focus on the two non-negligible terms: the demagnetizing field $B_{\text{demag}} = -N_\mu M_\mu$ and $B_e = (1/3) \mu_0 M_\phi$ the Lorentz counter-sphere contribution. The magnetization $M_\mu$ was measured at 240 K by dc magnetometry for the same disc-shaped sample$^9$ as in figure 2, with the applied field in the same geometry as in $^8$ In TF-µSR the applied field was orthogonal to the sample surface, i.e., parallel to the disc axis of symmetry. For this reason, following the literature $^{30–32}$, we refer to the demagnetizing factor as $N_\mu$.

$^9$ With the diameter and thickness equal to 5.68 mm and 1.26 mm, respectively. This was the main piece which composed the mosaic sample used for the µSR measurements.
the TF-μSR experiment. For this configuration the demagnetization factor was estimated to be \( N_\mu = 0.9 \). Therefore, from the experimental value \( \mu_0 M_T(240 \text{ K}, 50 \text{ mT}) = 7.3 \text{ mT} \), we were able to estimate a lower bound for the expected shift
\[
B_{\text{ext}} - B_{\text{ext}} = B_{\text{diamag}} + B_T \approx -4.2 \text{ mT}
\]
in excellent agreement with the expected value
\[
-4.3 \text{ mT},
\]
for underdoped LaFeAsO\(_{1-x}\)F\(_x\) superconducting samples [33]; (ii) no variations in the local-field profile \( P(B) \), because the considerable depolarization rate measured at 15 K (5.5 μs\(^{-1}\)) could, in principle, fully mask other slowly decaying components. To our surprise, fortunately neither case was verified: we measured a sizeable increase of the transverse depolarization rate and the fit of the time-dependent asymmetry data at 5 K still required only two components (see figure 12), one of which had a relative weight of 2.4%, previously ascribed to a non-magnetic impurity phase. Therefore, since the contribution from the diluted ferromagnetic impurities is constant at a constant applied field, an increase in depolarization rate of the main component below \( T_c \) can only be associated with a superconducting phase whose vortex lattice affects the entire sample volume.

Finally, while keeping the sample at 5 K, \( B_{\text{ext}} \) was raised to 125 mT. As expected, the small peak due to the minority normal phase closely follows the field change (i.e., it remains unshifted on the relative-field scale of figure 11(b)). At the same time, the main peak, related to the SC phase, shows two important features: (i) the measured diamagnetic shift \( B_{\text{diamag}} \) increases due to an increase in bulk magnetization; (ii) the depolarization rate is further enhanced, as evidenced by the hatched region on the left side of the main peak in figure 11(b). Yet, the time-domain asymmetry data can still be fully taken into account by just two components, one of which has a marginal weight of 2% (see table 3). The presence of the hatched region cannot be exclusively ascribed to the diluted ferromagnetic impurities: if this were the case it would give rise to a symmetric peak. Evidently, since the experiments show an asymmetric shape, we conclude that the latter reflects strong pinning effects.

In conclusion, the pinning experiment strongly suggests that the superconducting state involves almost the whole sample volume, despite this phase being masked in the ZFC susceptibility data (see figure 2(a)) due to the simultaneous presence of a low-temperature SDW order and of diluted ferromagnetic impurities. Since both the SDW order (at \( T_N < 38 \text{ K} \))

\[ \text{Table 3. Summary of the main fits parameters resulting from fits of TF-\mu SR data with equation (2). The } i = 1, 2 \text{ subscripts represent the main and minority phase components, respectively. The expected internal-field shift, as calculated by means of equation (3) from the measured dc magnetization } \mu_0 M_T, \text{ is reported as well. See the text for details.} \]

| \( T \) (K) | \( B_{\text{ext}} \) (mT) | \( \lambda_s (\text{mT}^{-1}) \) (in wt%) | \( \frac{B_{\text{ext}} - B_{\text{diamag}}}{B_{\text{diamag}}} \) (mT) | \( \frac{B_{\text{ext}} - B_{\text{diamag}}}{B_{\text{diamag}}} \) (mT) | \( \mu_0 M_T \) (mT) |
|---|---|---|---|---|---|
| 240 | 50 | 2.56(5) | 2.9(8) | -4.3(2) | -4.2 | 7.34(1) |
| 15 | 100 | 5.5(3) | 2.4(5) | -7.4(4) | -6.4 | 11.29(3) |
| 5 | 100 | 6.5(2) | 2.4(4) | -7.5(3) | -6.1 | 10.77(2) |
| 5 | 125 | 7.6(3) | 1.8(4) | -7.7(5) | -6.7 | 11.90(1) |

\[ \text{Figure 12. Short-time TF asymmetry data at } 15 \text{ and } 5 \text{ K under } B_{\text{ext}} = 100 \text{ mT. The continuous lines represent two-component fits by means of equation (2).} \]

\[ \text{LaFeAsO}_{1-x} \text{F}_x \]

\[ \text{LaFeAsO}_{1-x} \text{F}_x \]
and the superconducting state (below $T_c \sim 10$ K) concern the bulk of the sample, the M-SC coexistence detected below 10 K is most probably nanoscopic, as is the case also for Sm-1111 [6], Ce-1111 [21], and Nd-1111 [7]. This result hints at a universal picture for the M-SC phase boundary of Ln-1111 compounds. Figure 13 combines existing literature data with those arising from the present study. Since the $x$ (F) values for the samples studied in [2 and 14] are nominal, while the $x$ (H) values in our case are measured ones, we can only draw a tentative La-1111 phase diagram in the range of low electron doping. Nevertheless, it is important to note that because of the $x = 0.05$ sample, the magnetic order parameter loses the discontinuity at 0.04, thus pointing to a more probable second-order-like phase transition.

4. Conclusion

Two hydrogen-doped La-1111 polycrystalline samples [12] with $x$(H) = 0.01 and 0.05 were extensively studied by means of dc resistivity, dc magnetization and ZF-, TF-, and LF-muon-spin spectroscopy. In the $x = 0.01$ case our data evidence a long-range SDW order with a Néel temperature $T_N = 119$ K. The internal fields detected in this phase are in good agreement with previous results for an $x$(F) = 0.03 sample [14]. This finding suggests a close analogy between the F–O and H–O substitutions in realizing equivalent levels of electron doping in the FeAs planes.

The $x$(F) = 0.05 sample also displays an AF magnetic order below about 38 K, but, in addition, it also shows bulk superconductivity below $T_c = 10$ K. We argue that at low temperature the M and SC phases coexist at a nanoscopic level, which contrasts with the abrupt M-SC transition previously found in the La-1111 compound [2]. Therefore, it seems that the presence of a crossover region is probably a universal feature of the electron-doped Ln-1111 pnictides, which should display qualitatively similar rare-earth-independent phase diagrams, as confirmed, e.g., by Sm-1111 [6], Ce-1111 [21], and Nd-1111 [7]. However, the details, such as the extent of the crossover region, could easily depend on the rare earth involved. Further investigations on La-1111 compounds with $x$(F) between 4% and 5% could be interesting in efforts to definitely understand the peculiar role played by lanthanum in determining the M-SC crossover in the Ln-1111 family.

Acknowledgments

This work was performed at the Swiss Muon Source SNS, Paul Scherrer Institut (PSI, Switzerland), and was in part supported by the Schweizerische Nationalfonds zur Förderung der Wissenschaftlichen Forschung (SNF) and the NCCR research pool MaNEP of SNF. The authors are grateful to A Amato for instrumental support, GL, MRC, FC, and MP gratefully acknowledge F Canepa for a careful reading of the manuscript and fruitful suggestions. This work was partially supported by the FP7-EU project SUPER-IRON (no. 283204) and by MIUR under project PRIN2012X3YFZZ. SS acknowledges financial support from Fondazione Cariplo (research grant no. 2011-0266). The study at Tokyo Tech was supported by the JSPS FIRST Programme and MEXT Element Strategy Initiative.

References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296–7
[2] Luetkens H et al 2009 Nature Mater. 8 305–9
[3] Takeshita S and Kadono R 2009 New J. Phys. 59 035006
[4] Khasanov R et al 2011 Phys. Rev. B 84 100501
[5] Shiroka T et al 2011 Phys. Rev. B 84 195123
[6] Sanna S, De Renzi R, Lamura G, Ferdeghini C, Palenzona A, Putti M, Tropeano M and Shiroka T 2009 Phys. Rev. B 80 052503
[7] Lamura G et al 2014 in preparation
[8] Sanna S, Carretta P, Bonfà P, Prando G, Allodi G, De Renzi R, Shiroka T, Lamura G, Martinelli A and Putti M 2011 Phys. Rev. Lett. 107 227003
[9] Sanna S, Carretta P, De Renzi R, Prando G, Bonfà P, Mazzani M, Lamura G, Shiroka T, Kobayashi Y and Sato M 2013 Phys. Rev. B 87 134518
[10] Prando G et al 2013 Phys. Rev. B 87 174519
[11] Miyazawa K et al 2010 Appl. Phys. Lett. 96 072514
[12] Imura S, Matsuishi S, Sato H, Hanna T, Muraba Y, Kim S W, Kim J E, Takata M and Hosono H 2012 Nature Commun. 3 943
[13] Hiraishi M et al 2014 Nature Phys. 10 300–3
[14] Carlo J P et al 2009 Phys. Rev. Lett. 102 087001
[15] Hanna T, Muraba Y, Matsuishi S, Igawa N, Kodama K, Shamoto S and Hosono H 2011 Phys. Rev. B 84 024521
[16] Hess C, Kondrat A, Narduzzo A, Hamann J E, Klingeler R, Werner J, Behr G and Büchner B 2009 Europhys. Lett. 87 17005
[17] Jesche A, Nitsche F, Probst S, Doert T, Müller P and Ruck M 2012 Phys. Rev. E 86 134511
[18] van der Marck S C 1997 Phys. Rev. E 55 1514
[19] Bernhard C, Tallon J L, Brücher E and Kremer R K 2000 Phys. Rev. B 61 R14960–3
[20] Cimberle M R, Masini R, Ferdeghini C, Artini C and Costa G 2003 Supercond. Sci. Technol. 16 726
[21] Sanna S et al 2010 Phys. Rev. B 82 060508
[22] Kohama Y, Kamihara Y, Baily A, Civale L, Riggs S C, Balakirev F F, Atake T, Jaime M, Hirano M and Hosono H 2009 Phys. Rev. B 79 144527
[23] Yaouanc A and Dalmas de Réotier P 2011 Muon Spin Rotation, Relaxation, and Resonance: Applications to Condensed Matter (Oxford: Oxford University Press)
[24] Drew A J et al 2008 Phys. Rev. Lett. 101 097010
[25] Savici A T et al 2002 Phys. Rev. B 66 014524
[26] Maeter H et al 2009 Phys. Rev. B 80 094524
[27] Bonfà P, Carretta P, Sanna S, Lamura G, Prando G, Martinelli A, Palenzona A, Tropeano M, Putti M and De Renzi R 2012 Phys. Rev. B 85 054518
[28] Sanna S, De Renzi R, Lamura G, Ferdeghini C, Martinelli A, Palenzona A, Putti M, Tropeano M and Shiroka T 2012 J. Supercond. Novel Magn. 22 585–8
[29] Bernhard C et al 2012 Phys. Rev. B 86 184509
[30] Poole C P, Farach H A and Creswick R J 1995 Superconductivity (London: Academic)
[31] Cardwell D A and Ginley D S 2003 Handbook of Superconducting Materials vol 2 (Bristol: IOP)
[32] Beleggia M, De Graef M and Millev Y T 2006 J. Phys. D: Appl. Phys. 39 891
[33] Luetkens H et al 2008 Phys. Rev. Lett. 101 097009