Fast recovery of the pristine magnetic and structural phases in superconducting LaFeAsO$_{0.89}$F$_{0.11}$ by Mn/Fe substitution

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Abstract

We report an experimental study on the effect of Mn impurities in the optimally doped LaFeAsO$_{0.89}$F$_{0.11}$ compound. The results show that a very tiny amount of Mn, of the order of 0.1%, is enough to destroy superconductivity and to recover at low temperatures both the magnetic ground state and the orthorhombic structure of the pristine LaFeAsO parent compound. The results are discussed within a model where electron correlations enhance the Ruderman–Kittel–Kasuya–Yosida interaction among impurities.

Keywords: Fe-based superconductors, impurity effects, electron correlation

(Some figures may appear in colour only in the online journal)

1. Introduction

The study of the effect of impurities in superconductors is relevant both in view of their technological applications [1–3] as well as for the understanding of the microscopic mechanisms driving superconductivity [4–9]. On one hand, impurities act as pinning centers and their presence is necessary for many devices. On the other hand, impurities allow to probe the local response functions of these materials and their effect on the superconducting transition temperature $T_c$ and, accordingly, to determine the symmetry of the superconducting gap and the pairing mechanism. In the iron-based superconductors (IBS) one of the most impressive effects of impurities is associated with the substitution of Fe with Mn in the LaFe$_1-y$Mn$_y$As$_1-y$O$_y$F$_y$ family [4, 10]. At optimal electron doping, namely for the $y$ values yielding the maximum $T_c$, it was observed that a Mn concentration as low as $x \gtrsim 0.001$ is enough to fully suppress superconductivity. The disappearance of the superconducting phase takes place at a quantum critical point where the spin correlation length diverges [10] and for $x \gtrsim 0.001$ a stripe magnetic order arises [11], the same type of order characterizing LaFeAsO parent compound [12, 13]. Remarkably, at the quantum phase transition a crossover in the resistivity behavior is observed, evidencing an electronic localization [4, 14]. Such a dramatic effect of a tiny amount of impurities indicates both the presence of a very large local spin susceptibility, namely the presence of strong electronic correlations, as well as a collective effect of Mn impurities. In fact, a successful explanation of the above phenomenology can be achieved by considering the Ruderman–Kittel–Kasuya–Yosida (RKKY) coupling among Mn impurities which is promoted by the enhanced spin susceptibility of the delocalized electrons [11, 15].

The unique effect of Mn substitution was ascribed to the peculiar nature of the Mn$^{2+}$ ions, a 3$d^5$ species characterized by a strong Hund’s coupling [16, 17]. Remarkably, the first
experimental evidence for the occurrence of a charge density wave state in IBS compounds was detected in the La(Fe,Mn)AsO system [16].

In the following we show that the changes in the electronic structure driven by Mn impurities also cause a change in the crystal structure and that, remarkably, Mn impurities tune the electronic, magnetic and structural properties back to those observed in the parent compound LaFeAsO.

2. Experimental and technical aspects

The LaFe$_{1-x}$Mn$_x$AsO$_{0.89}$F$_{0.11}$ polycrystalline samples investigated here, with $x = 0, 0.00025, 0.00075, 0.001, 0.002, 0.005$, and $0.0075$ are the same ones studied in [10, 11]. We reported the characterization of the superconducting phase in [10], which are in agreement with previous data [4]. We carried out high resolution x-ray diffraction measurements at the ID22 high-resolution powder diffraction beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, at selected temperatures between 5 K and 300 K. These measurements are aimed at studying the presence of structural transition, suggested by previous nuclear quadrupole resonance measurements [11]. We performed muon-spin spectroscopy ($\mu$SR) measurements on the GPS instrument of the Sp$\upmu$S facility at the Paul Scherrer Institute, Switzerland. The muons act as nanoscopic magnetic sensors which allow to probe the spin dynamics and the local field arising from the onset of a magnetic order [18, 19]. The full spin-polarization of the beams of positive muons ($\mu^+$) is the most peculiar feature exploited by $\mu$SR. Accordingly, the great advantage of $\mu$SR with respect to other magnetic resonance techniques is that there is no need to perturb the studied system with an external polarizing magnetic field. In particular, we studied the local magnetism of LaFe$_{1-x}$Mn$_x$AsO$_{0.89}$F$_{0.11}$ in conditions of external zero-magnetic field (ZF) (applied field $H_0 = 0$).

3. Results and discussion

3.1. Measurement of the structural transition

At room temperature all the samples display the standard $P4/nmm$ tetragonal structure as observed for the pure LaFeAsO compound. In particular, the compound LaFeAsO undergoes a tetragonal-to-orthorhombic structural transition on cooling at $\sim$150 K [20–22]. Nonetheless, this transition is progressively hindered by F-doping and the local field arising from the onset of a magnetic order [18, 19]. The full spin-polarization of the beams of positive muons ($\mu^+$) is the most peculiar feature exploited by $\mu$SR. Accordingly, the great advantage of $\mu$SR with respect to other magnetic resonance techniques is that there is no need to perturb the studied system with an external polarizing magnetic field. In particular, we studied the local magnetism of LaFe$_{1-x}$Mn$_x$AsO$_{0.89}$F$_{0.11}$ in conditions of external zero-magnetic field (ZF) (applied field $H_0 = 0$).

3.2. Measurement of the magnetic transition

In a typical $\mu$SR experiment two opposite detectors count the number of positrons emitted along or in the opposite direction
of the initial muon spin polarization, $N_F$ and $N_B$ respectively, arising from the asymmetric muon decay. The time evolution of the muon spin polarization is described by the muon asymmetry $A(t) = (N_F(t) - N_B(t))/(N_F(t) + N_B(t))$ normalized by the total initial decay asymmetry $A_0$. The latter is calibrated for each sample in the paramagnetic phase.

No muon precessions are expected in a non magnetic phase (non magnetic samples or above the magnetic transition temperature) and the muon asymmetry $A(t)$ is characterized by a single component with a slow gaussian decay rate ($\sim 0.1 \mu s^{-1}$), due to the interaction with the weak surrounding nuclear magnetic moments (figure 5). Below the magnetic transition, each muon spin experiences a precession around a local field at the muon site $B_{\mu} = A_i <S>$, with $A_i$ the hyperfine coupling tensor and $<S>$ the average Fe spin value, corresponding to the order parameter. The muon precession around $B_\mu$ gives rise either to an oscillating component of the muon asymmetry, when the precessions are coherent, or to a component with a fast decay rate in case of fast decoherence respect with to the period of the muon precession. The latter case is typical for a large local field distribution $\Delta B_\mu$, e.g. for short-range ordering or cluster spin ordering, characterized by overdamped oscillations of the muon signal for $\Delta B_\mu > B_\mu$.

For all the samples we fitted the muon polarization to the following phenomenological function:

$$A(t)/A_0 = a_\perp (w_1 e^{-\lambda_1 t} f(\gamma_\mu B_{\mu,1}t) + w_2 e^{-\lambda_2 t} f(\gamma_\mu B_{\mu,2}t)) + a_\parallel e^{-t/T_1} e^{-\sigma t^2} ,$$

(1)

where $\gamma_\mu$ is the muon gyromagnetic ratio, $B_{\mu,i}$ for $i = 1$ or 2 is the local field at two different muon sites, expected for 1111 compounds [19], with weights $w_i$ proportional to the site occupancy of each ith implantation position. $\lambda_{1,2}$ are the corresponding decay rates which reflect the muon field distribution $\Delta B_\mu$. The function $f(\gamma_\mu B_{\mu,i}t)$ corresponds either to the harmonic term $f = \cos(\gamma_\mu B_{\mu,i}t)$, in case of coherent muon precession, or to $f = 1$ in case of overdamped oscillations of the muon signal for $\Delta B_\mu > B_\mu$. The latter case is due to the sizable distributions of local magnetic fields indicative of short range magnetic ordering occurring close to the boundary between magnetism and superconductivity [19]. Equation (1) describes the time dependence of the muon spin polarization of the two components of the muon spin parallel and perpendicular to the local field, $B_{\mu,i}$, at the muon site, with amplitudes $a_\parallel$ and $a_\perp$ respectively. The parallel component experiences only a slow spin-lattice relaxation with a decay rate $1/T_1$ which is almost the same for different muon sites [19], beyond the instrumental resolution. The perpendicular components...
undergo precessions with site dependent Larmor frequency $\omega_i = \gamma \mu B_{\mu,i}$. In a powder sample the internal fields are randomly distributed and if the magnetic ordering occurs throughout the whole volume sample simple geometrical arguments predict $a_\parallel = 1/3$ and $a_\perp = 2/3$. The magnetic volume can be easily calculated as $V_{\text{mag}} = 3/2 a_\perp = 3/2 (1 - a_\parallel)$ [6]. When the sample is fully paramagnetic no precessions occur hence $a_\perp = 0$ and $a_\parallel = 1$ and the relaxation rate is dominated by the interaction of the muon spin with the small nuclear magnetic moments randomly distributed which yields to a gaussian relaxation rate $\sigma \sim 0.02 \mu s^{-1}$.

A representative set of measurements of the time evolution of the muon asymmetry and the best fit to equation (1) for selected temperatures are displayed in figures 5(a) and (b) for the samples with $x = 0.002$ and 0.0075, respectively. The temperature dependence of the magnetic volume fraction $V_{\text{mag}}(T) = (3/2)(1 - a_\parallel(T))$ is displayed in panel c which has been empirically fitted to $V_{\text{mag}}(T) = 0.5(1 - \text{erf}(T - T_{\text{av}}^{m}/\sqrt{2}\Delta V))$ (solid line), where $T_{av}^{m}$ represents an average magnetic transition temperature. A peak of $1/T_1$ due to critical fluctuations is observed when approaching the magnetic transition, as displayed in panel d. Below the magnetic transition the size of spontaneous magnetic local fields at the muon sites $B_{\mu,i}$ can be directly determined from the fit of the oscillating component of the muon signal for $x = 0.0075$. For the sample with $x = 0.002$ we detected no oscillations and the size of the internal fields can be roughly determined as $B_{\mu,i} \sim \lambda_i/\gamma$. The temperature dependence of $B_{\mu,i}$ for $i = 1$ and 2 is displayed in panel e for both the samples. The temperature evolution of $V_{\text{mag}}$, $B_{\mu}$ and $1/T_1$ provides three independent ways to determine the magnetic transition temperature, which are the same within about 2 K. The behavior of the magnetic transition as a function of the Mn doping is reported in figure 6.

### 3.3. The phase diagram

We summarize the results of this work in the phase diagram displayed in figure 6. The structural and microstructural characterization of the optimally electron doped $\text{LaFe}_{1-x}\text{Mn}_x\text{AsO}_{0.89}\text{F}_{0.11}$ samples reveals that the tetragonal-to-orthorhombic structural transition is recovered for $x \gtrsim 0.001$. With the further enrichment with Mn, both the transition temperature and the amplitude of the orthorhombic distortion increase. Simultaneously the superconducting phase is suppressed and a static magnetic phase is induced.
Recently a combination of nuclear magnetic resonance and Mössbauer spectroscopy [11] has shown that the magnetic structure of this phase is the \((\pi/a, 0)\) stripe ordering typical of the spin density wave phase of the undoped LaFeAsO parent compound. This means that the substitution of Fe with an extraordinarily tiny amount of Mn (\(\sim 0.1\%\)) has a dramatic effect on the electronic properties of the La1111 system. A similar qualitative behavior has been observed also in \(LnFe_{1-x}Mn_xAsO_{0.89}F_{0.11}\) with \(Ln = Sm\) [25] and La0.8Y0.2 [14, 26, 27] but here a much higher amount of Mn, few percent, is needed to suppress superconductivity and induce static magnetism. In addition electric resistivity measurements [4, 14] and nuclear quadrupole resonance spectroscopy [27] have shown that a charge localization process is induced by Mn impurities in \(Ln1111\).

The effect of the Fe/Mn substitution in \(Ln1111\) has been theoretically studied by a five band real Hamiltonian model [11, 15] which shows that the experimental results can be reproduced by considering two main ingredients: RKKY coupling among Mn impurities and electron correlation. The RKKY interaction is promoted by the enhanced spin susceptibility of the delocalized electrons and causes an enhanced spin polarization around Mn impurities. The model shows that the polarization mechanism is enhanced by increasing the electron correlation strength.

The comparison between experiments and theory [11, 15] suggests that the electron correlation is reduced upon squeezing the lattice by increasing the chemical pressure with smaller radius \(Ln\) ions, hence going from the bigger La to smaller Sm. We expect that the bandwidth of the system increases with the lattice squeezing, hence producing the enhancement of the kinetic energy and a weakening of the electron correlations. This mechanism qualitatively justifies why for \(Ln = Sm\) the effect of Mn is weaker than for

Figure 5. Representative ZF-\(\mu\)SR polarization as a function of time for \(LaFe_{1-x}Mn_xAsO_{0.89}F_{0.11}\) with \(x = 0.002\) and \(x = 0.0075\) in panels (a) and (b) respectively, with the best fit curves (solid lines) to equation (1). Temperature dependence of (c) magnetic volume fraction with their best fit curves (see text for details), (d) relaxation rate \(1/T_1\), (e) internal field at the muon sites \(B_{\mu,i}\) for \(i = 1\) (full symbols) and \(i = 2\) (open symbols). Solid lines in panel (e) are only guides for the eye.

Figure 6. Phase diagram as a function of Mn content for \(LaFe_{1-x}Mn_xAsO_{0.89}F_{0.11}\) displaying the superconducting, magnetic and structural phases. Superconducting \(T_c\) and magnetic \(T_M\) transitions are triangles and circles respectively. The dashed area indicates where the orthorhombic phase appears.
These arguments suggest that the electron correlation strength in La1111 drives the system very close to an electronic instability. A small perturbation introduced by a tiny amount of Mn is enough to dramatically change the electronic properties of the system which at low temperatures precipitates back to the magnetic (π/a, 0) stripe spin density wave ground state of the parent compound with its associated orthorhombic structure.

4. Conclusion

Based on muon spin relaxation measurements and high resolution x-ray diffraction, we draw the phase diagram of LaFe1−xMnxAsO0.88F0.11 for x = 0 − 0.0075 (figure 6). The superconducting phase is suppressed for a tiny amount of Mn doping x > 0.001 and both the magnetic (π/a, 0) stripe spin density wave phase and structural orthorhombic transition typical of the parent LaFeAsO compound are fully recovered. The structural and microstructural characterization of the optimally electron doped LaFe1−xMnxAsO0.88F0.11 samples reveals that the tetragonal-to-orthorhombic structural transition is recovered for x > 0.001. With the further addition of Mn, both the temperature transition and the amplitude of the orthorhombic distortion increases. These structural and microstructural properties underline the crossover between the magnetic and the superconducting electronic ground states characterizing the LaFe1−xMnxAsO0.88F0.11 system. For the magnetic phase we considered a model [11, 15] where RKKY interaction is promoted by the enhanced spin susceptibility of the delocalized electrons and polarizes the surrounding Fe spins. This model suggests that the fast change of the electronic and structural properties in La1111 is due to the presence of electronic correlations which drive the Ln1111 system close to an electronic instability.

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