Magnetism in superconducting EuFe$_2$As$_{1.4}$P$_{0.6}$ single crystals studied by local probes

J. Munevar$^{a,b}$, H. Micklitz$^a$, M. Alzamora$^a$, C. Argüello$^b$, T. Goko$^{b,c}$, F.L. Ning$^{b,d}$, T. Munsie$^e$, T.J. Williams$^e$, A.A. Aczel$^{e,f}$, G.M. Luke$^{e,g}$, G.F. Chen$^h$, W. Yu$^h$, Y.J. Uemura$^b$, E. Baggio-Saitovitch$^a$

$^a$ Centro Brasileiro de Pesquisas Fisicas, Rua Xavier Sigaud 150, Rio de Janeiro, Brazil
$^b$ Department of Physics, Columbia University, New York, New York 10027, USA
$^c$ TRIUMF, 4004 Wesbrook Mall, Vancouver, B.C., Canada V6T 2A3
$^d$ Department of Physics, Zhejiang University, Hangzhou 310027, China
$^e$ Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1
$^f$ Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
$^g$ Canadian Institute of Advanced Research, Toronto, Ontario, Canada M5G 1Z8
$^h$ Renmin University of China, Beijing 100872, China

A R T I C L E   I N F O

Article history:
Received 22 October 2013
Received in revised form
28 January 2014
Accepted 2 February 2014
by F. Peeters
Available online 10 February 2014

Keywords:
A. Iron pnictides
C. Mössbauer spectroscopy
C. μSR
D. Superconductivity

A B S T R A C T

We have studied the magnetism in superconducting single crystals of EuFe$_2$As$_{1.4}$P$_{0.6}$ by using the local probe techniques of zero-field muon spin rotation/relaxation and $^{151}$Eu/$^{57}$Fe Mössbauer spectroscopy. All of these measurements reveal magnetic hyperfine fields below the magnetic ordering temperature $T_M = 18$ K of the Eu$^{2+}$ moments. The analysis of the data shows that there is a coexistence of antiferromagnetism, resulting from Eu$^{2+}$ moments ordered along the crystallographic $c$-axis, and superconductivity below $T_{SC} \approx 10$ K. We find indications for a change in the dynamics of the small Fe magnetic moments (~0.07 $\mu_B$) at $T^*$ ~ 15 K that may be triggering the onset of superconductivity: below $T^*$ the Fe magnetic moments seem to be “frozen” within the ab-plane.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Since the initial observation of superconductivity in the iron pnictide superconductor in 2008 [1], the research in this field has been very intense, leading to the discovery of several Fe-containing compounds with superconducting transition temperatures $T_{SC}$ as high as 55 K in SmFeAsO$_x$F$_{1-x}$ [2]. These FeAs-based compounds have a FeAs layer separated by a charge reservoir composed of RO (R is a rare earth, so-called 1111), alkali atoms or Eu(122), Li and Na atoms (111), or perovskite layers (42622). This led to the classification of the Fe-containing superconductors in several families, with different properties among them mainly due to the various structures [3]. The 122 family is particularly interesting, because the structural and magnetic spin density wave (SDW) phase transition for the parent compound are at the same temperature, differing from the 1111 family where $T_{SC}$ is above $T_N$.

We have studied the magnetism in superconducting EuFe$_2$As$_{1.4}$P$_{0.6}$ single crystals by using local probe techniques of zero-field muon spin rotation/relaxation and $^{151}$Eu/$^{57}$Fe Mössbauer spectroscopy. All of these measurements reveal magnetic hyperfine fields below the magnetic ordering temperature $T_M = 18$ K of the Eu$^{2+}$ moments. The analysis of the data shows that there is a coexistence of antiferromagnetism, resulting from Eu$^{2+}$ moments ordered along the crystallographic $c$-axis, and superconductivity below $T_{SC} \approx 10$ K. We find indications for a change in the dynamics of the small Fe magnetic moments (~0.07 $\mu_B$) at $T^*$ ~ 15 K that may be triggering the onset of superconductivity: below $T^*$ the Fe magnetic moments seem to be “frozen” within the ab-plane.

Their temperatures are nearly equal [4–7]. Furthermore, the advantage of 122 systems is that clean single crystals are available.

For the EuFe$_2$As$_2$ parent compound, the Fe lattice develops an antiferromagnetic SDW transition around 190 K, while Eu moments order antiferromagnetically around 20 K [8]. Superconductivity is induced by doping and external pressure, and the interplay between magnetic order and superconductivity has been extensively studied. For example, superconductivity appears under external pressure at 30 K [9], and a reentrant behavior is found close to 20 K, where Eu moments align antiferromagnetically [10]. The effect of an external magnetic field is also remarkable, since a spin reorientation for Eu moments to ferromagnetic ordering is seen for an applied field as high as 3 T [11]. Although doping on either the Eu or Fe sites also induces superconductivity [12,13], the most interesting case may be doping the As site by P, where recent studies have implied a change of valence state for Eu [14], an increase of $T_{SC}$ up to 48.3 K under external pressure [15], and evidence for coexistence of ferromagnetism and superconductivity [12,13,16–18].

Just recently, $^{151}$Eu and $^{57}$Fe Mössbauer studies on polycrystalline EuFe$_2$(As$_{1-x}$P$_x$)$_2$ samples were reported [19]. The results of
those studies will be compared in detail with our data. We will show that due to the use of (i) single crystals and (ii) an additional local probe, namely muon spin rotation/relaxation (μSR), we are able to gain new insight on the interplay between magnetism and superconductivity in this compound.

In this work, we performed resistivity, magnetization and spectroscopic measurements \(^{57}\text{Fe}/^{151}\text{Eu Mössbauer and μSR}\) on EuFe\(_2\)As\(_1.4\)P\(_{0.6}\) single crystals, where silvery plate-like single crystals with typical size of 4 mm 3 mm 0.5 mm were obtained. X-ray diffraction (XRD) data collected with Cu Kα radiation at room temperature confirm the single phase nature of the sample. The preparation details are published elsewhere [14]. Resistivity measurements were performed with a PPMS system using the transport mode at CBPF in Brazil, and magnetization was measured with a SQUID magnetometer by the McMaster group in Canada. Zero field μ SR spectra were taken at the M20 beamline in TRIUMF, Canada. \(^{57}\text{Fe}\) and \(^{151}\text{Eu Mössbauer studies were performed at CBPF in a 4He variable temperature cryostat, moving the 57Co:Rh and 151Sm\(_2\)O\(_3\) sources in sinusoidal mode and kept at the same temperature as the sample. As an absorber, a single crystal mosaic was prepared from thin platelets (t ≈ 15 μm), with the single crystal mosaic c-axis perpendicular to the absorber plane.

Resistivity measurements were carried out on several crystals without external magnetic field with a PPMS system using transport mode as shown in Fig. 1, yielding for all of them the same drop in resistivity starting at around 15 K and having dropped to 50% at about \(T_{\text{c}} = 10\) K. The metallic behavior of the single crystal above the resistivity drop, as expected for the iron pnictide superconductors, can be seen in the right inset of Fig. 1. Application of an external magnetic field up to 7 T parallel to the c-axis results in a downshift of the resistivity curves, giving \(H_{\text{c2}} \approx 10\) T, whose extrapolation was made taking the external magnetic field, and applied temperature as the sample. As an absorber, a single crystal mosaic was prepared from thin platelets (t ≈ 15 μm), with the single crystal mosaic c-axis perpendicular to the absorber plane.

The magnetic susceptibility of a EuFe\(_2\)As\(_1.4\)P\(_{0.6}\) single crystal was measured with a SQUID magnetometer with the c-axis both parallel and perpendicular to the applied magnetic field. The data show an anomaly around 18 K that is related to the Eu moments ordering. A small change of the magnetic response is observed at \(T^* = 15\) K for \(H \perp c\) only, indicating an additional magnetic transition (see inset of Fig. 2). The magnetic susceptibility rapidly decreases at about 10 K for both \(H \perp c\) and \(H || c\) which is interpreted as the diamagnetic response due to Meissner effect. The superconducting volume fraction calculated from the susceptibility measurements in the diamagnetic state yields a value of nearly 100% of the volume sample in the SC state. This inferred superconducting transition temperature \(T_{\text{SC}} = 10\) K agrees well with our resistivity results, and we, thus, have both magnetism and superconductivity in the same sample. For each field value in Fig. 2, two measurements are shown: field cooling and zero field cooling. The field cooling measurement does not show the superconducting transition due to flux pinning of vortices. The magnetic order of the Eu\(^{2+}\) sublattice is suspected to be ferromagnetic, as fitting our high temperature data in the paramagnetic regime to a Curie–Weiss law yielded \(\theta = 25\) K. Nevertheless, an antiferromagnetic behavior is observed from the susceptibility measurements with \(H \perp c\) (Fig. 2(a)), that resembles the A-type antiferromagnetic order observed in the parent compound EuFe\(_2\)As\(_2\) [11]. No further ordering coming from impurities or Fe lattice is observed, so we assume that the doping has fully suppressed the SDW ordering for Fe atoms.

Zero field μ SR measurements were performed with the initial muon spin polarization perpendicular and parallel to the c-axis of the crystal. A clear oscillation was observed in the μSR time spectra below \(T_M\) for \(\mu \perp c\), as shown in Fig. 3(a). On the other hand, oscillation for \(\mu || c\) was found to be smaller than our detection limit. These results indicate that the internal field \(B\) at the muon site is nearly parallel to the c-axis. The muon precession frequency (Fig. 3(c)) corresponds to internal fields greater than 1 T and therefore suggests that the Eu\(^{2+}\) ordered moments are quite large, as generally expected for this magnetic atom. The magnetic volume fraction estimated from the ZF-μSR spectra for \(\mu \perp c\) and \(\mu || c\) indicates that Eu\(^{2+}\) moments are ordered in almost the entire volume. Fig. 3(d) shows temperature dependence of the muon relaxation rate \(1/T_\text{MR}\) which was derived from the spectra as shown in Fig. 3(b). The relaxation rate exhibits divergent behavior at \(T_{\text{MR}}\), suggesting the critical slowing down of Eu\(^{2+}\) moments. There is a small peak of \(1/T_\text{MR}\) at \(T \approx 16\) K, which might be related to some magnetic anomaly close to the onset of superconducting state. Efforts were also made to detect the superconducting response of the single crystal with μSR, but it was not possible due to the intrinsic magnetism of the sample that masks any response.

Fig. 4(a) show \(^{151}\text{Eu Mössbauer spectra taken at room temperature and at 4.2 K. With this technique we cannot only determine the direction of the Eu moments with respect to the crystallographic axes, but we also can see whether or not there is a Eu valence change due to P doping as proposed by Sun et al. [14], since Eu\(^{2+}\) and Eu\(^{3+}\) are easily distinguished by their different isomer shift values. All spectra were fitted with the full Hamiltonian model. The room temperature spectrum in Fig. 4(a) does not show any evidence for the Eu\(^{3+}\) valence, as only an absorption line related to the Eu\(^{2+}\) valence was observed, in agreement with recent polycrystalline work [19]. The isomer shift value is \(\delta = -11.8(2)\) mm/s, and the quadrupole splitting \(\Delta\) is equal to \(-3.5(6)\) mm/s. At 4.2 K the spectrum is magnetically split due to the magnetic ordering of the Eu moments. The hyperfine parameters are \(\delta = -11.8(1)\) mm/s, \(\Delta\) is equal to \(-4.1(8)\) mm/s, \(B_{\text{iso}} = 28.4(2)\) T, \(\theta = 12(8)\) degrees, values indicating that the Eu\(^{2+}\) moments are aligned almost parallel to the crystallographic c-axis. This is in agreement with P doping or application of an external magnetic field that breaks the weak coupling between AF coupled Eu layers, and reorients the moments along the c-axis [12,17,19]. All the hyperfine parameters given above essentially are in agreement with those found in polycrystalline samples of EuFe\(_2\)As\(_1.4\)P\(_{0.6}\) by Nowik and Felner [19].
Fig. 2. (Color online) Magnetic susceptibility measurements performed for EuFe$_2$As$_{1.4}$P$_{0.6}$ single crystal, with the c-axis both (a) perpendicular and (b) parallel to the applied field. A clear magnetic transition is observed at 18 K, followed by the superconducting transition around 10 K as evidenced by the Meissner effect. Inset figure shows the susceptibility for an applied field of 2 Oe with $H \perp c$, between 6 and 20 K.

Fig. 3. (Color online) ZF-$\mu$SR time spectra with a time range of (a) 0–80 ns and (b) 0–3 $\mu$s which were measured with the initial muon spin perpendicular to the c-axis. The spectra in (a) are vertically offset for clarify. The inset of (b) displays a schematic overview of experimental setup for the $\mu$ spin $\perp c$ orientation. (c) Muon precession frequency and magnetic volume fraction as a function of temperature. (d) Temperature dependence of relaxation rate $1/T_1$ extracted from the ZF-$\mu$SR spectra in (b).
The asymmetric shape of the spectrum is due to the orientation of the electric field gradient principal axis $V_{ZZ}$ with respect to $\gamma$ rays, and not to secondary phases. The intensity ratio of the two quadrupole lines is given by

$$I_{3/2} = \frac{1 + \cos^2 \theta}{\frac{3}{2} + \sin^2 \theta}$$

with $\theta$ being the angle between $V_{ZZ}$ and the $\gamma$-ray direction. Fitting of the spectrum results in $\theta = 15(2)$ degrees. Since $V_{ZZ}$ is parallel to $c$-axis [20], as have been found for similar single crystalline compounds, we have to conclude that some of the small single crystal platelets are slightly misoriented and may induce some error in the determination of the $V_{ZZ}$ direction. Having defined the orientation of $V_{ZZ}$, we will be able to determine the orientation of the magnetic hyperfine field seen by Fe probe below $T_M$ with respect to $V_{ZZ}$ (taken as parallel to $c$-axis). As the temperature approaches 20 K the linewidth increases continuously. The fits of these data were performed taking constant $\Delta E_Q = 0.40(1)$ mm/s below 20 K; this is expected for metallic systems at low temperatures in the absence of a structural phase transition. For example, the increase in $\Delta E_Q$ observed by Alzamora et al. for CaFe$_2$As$_2$ single crystals [20] between 20 K and 4.2 K is only 0.005(5) mm/s. Below 18 K the shape of the spectrum exhibits a dramatic change, indicating the presence of a transferred magnetic hyperfine field coming from ordered Eu atoms. The spectra have been fitted with one component only, corresponding to one Fe site in the lattice. The asymmetry due to the use of single crystal mosaics is also taken into account in our 1-site analysis. This is in sharp contrast to the finding of Nowik and Felner [19] who measured $^{57}$Fe spectra of polycrystalline EuFe$_2$As$_{1+x}$P$_x$, where two Fe components clearly have been found. The behavior of the hyperfine field, linewidth, and the angle between the hyperfine field and the $c$-axis are shown in Fig. 5. The isomer shift value is $\delta = 0.36(1)$ mm/s, with negligible variation in temperature. Linewidth $\Gamma$ is increasing, reaching its maximum around $T^* = 15$ K. This probably is due to the slowing down of the fluctuating Fe magnetic moments. Slow relaxation of the Eu magnetic moments just above 18 K may be an additional reason for the increased $\Gamma$. We can see in Fig. 5 that above $T_M$ the magnetic hf field is zero, and therefore the angle $\theta$ between $c$-axis and $B_{hf}$ is undefined. For $T^* \leq T \leq T_M$, both the transferred magnetic hyperfine fields at the
muon and the $^{57}$Fe nuclei are the same, using the muon gyromagnetic ratio $\gamma = 135.54$ MHz/T. This indicates that the muons are likely sitting within the FeAs(P) layers on sites which are magnetically equivalent to the Fe lattice sites. Both the muon and Fe nuclei are only sensing the ordering of the Eu magnetic moments occurring below $T_a$ and there seems to be no contribution coming from a Fe magnetic moment. However, at $T^*$ it is noticed a change in the dynamics of small Fe moments ($\sim 0.07 \mu_B$) that are matching with the anomaly observed in $\mu$SR data and the resistivity drop. For $T \leq T^*$ we find $B_{hf}(^{57}$Fe$) > B_{hf}(\mu)$ (refer to Fig. 5(a)) and at the same time an abrupt change in $\theta$ (angle between direction of $B_{hf}$ and c-axis) from $\theta \approx 0^\circ$ to $\theta \approx 40^\circ$ (Fig. 5(c)). Also the linewidth $\Gamma$ has a maximum close to $T^*$ (see Fig. 5(b)) and not at $T_a$ as expected. Magnetic volume fractions from both $\mu$SR and Mössbauer spectroscopies are nearly 100% below $T_a$. It means that the whole sample volume is sensing both magnetic ordering and the anomaly observed at $T^*$. Finally, below $T_{SC} \approx 10$ K we observe the SC transition coexisting with Eu $^{1+2}$ antiferromagnetically ordered moments aligned along c-axis.

All these facts could be explained as follows: the fluctuation rate of the small Fe moments, having a magnitude of the order of $\mu_B \approx 0.07 \mu_B$ [18], is slowing down in the temperature region from 50 K to $T^*$ resulting in an increase in the $^{57}$Fe linewidth. For $T \leq T^*$ the magnetic moments “freeze” within the ab-plane resulting in an increase in the magnetic field at the $^{57}$Fe nucleus (a magnetic moment of $\mu_{57}$Fe $= 0.07 \mu_B$ corresponds to a magnetic hyperfine field $B_{hf} = 1$ T [21]) and a canting of $\vec{B}_{hf} = \vec{B}_{hf}^{\parallel} + \vec{B}_{hf}^{\perp}$, with $\vec{B}_{hf}^{\parallel}$ being parallel and perpendicular to the c-axis, respectively. This is in agreement with susceptibility and $\mu$SR data where anomalies are found in the ab-plane. We are not aware that such a change in the dynamics of the Fe magnetic moment just before the onset of superconductivity has been seen in pnictides before. This slowing down of fluctuating small Fe moments and finally freezing in the ab-plane at $T^*$ may be the mechanism for triggering the superconducting order observed at 10 K, since it involves Fe electrons and SC may have to come from some of those electrons. On the other hand, this anomaly observed for Fe moments can be the SDW transition that has not been fully suppressed with P doping. This, however, would not change our interpretation of the data presented since we have Fe magnetism and superconductivity most likely coming from the FeAs layers. Independent of this, we have strong evidence that the coexistence between antiferromagnetism and superconductivity is indeed present in this pnictide and not an artifact caused by phase separation, as claimed by Jeevan et al. [17]. This just follows from the two facts: (i) hyperfine parameters from $\mu$SR, $^{57}$Fe and $^{151}$Eu probes clearly show the presence of only one, namely, a magnetic phase and (ii) the onset of superconductivity appears to be triggered by magnetic anomalies reflected in the hyperfine parameters of this magnetic phase. There clearly is an interplay between the two phenomena which could be explained by a coupling between localized and itinerant Fe 3d electrons [22].

In summary, we have used three different local probe techniques to characterize the magnetic properties of the superconducting single crystal EuFe$_2$As$_{1.5}$P$_{0.5}$. We were able to observe magnetic order and superconductivity in the full volume of the sample. We also observed an A-type antiferromagnetic order at 18 K for Eu moments, a Fe magnetic freezing of moments around 15 K and superconducting response below 10 K. All of these observations indicate that we have coexisting superconductivity and magnetism in these samples, and the superconducting behavior may be triggered by a change in the Fe magnetic moment dynamics. It would be interesting to make the above local probe studies in the presence of an applied external magnetic field. The change of the Eu magnetic moments order from antiferromagnetic to ferromagnetic [11] certainly should be reflected in the local probe data and should give important information on the interplay between ferromagnetic order and superconductivity.

Acknowledgments

This work has been supported by the US NSF under the Materials World Network (MWN: DMR-0502706 and 0806846) and the Partnership for International Research and education (PIRE: OISE-0968226) programs at Columbia, by Canadian NSERC and CIFAR at McMaster, and by CIAM (CNPq-NSF), CNPq and FAPERJ at CBPF in Rio de Janeiro, Brazil and NSFC and MOST of China: 973 project 2011CB605900 at IOP in Beijing. H. Micklitz acknowledge visitor fellowships of CAPES and CNPq to work at CBPF.

References