Magnetic phase diagram of Ca-substituted EuFe$_2$As$_2$

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The simultaneous presence of a Fe-related spin-density wave and antiferromagnetic order of Eu$^{2+}$ moments ranks EuFe$_2$As$_2$ among the most interesting parent compounds of iron-based pnictide superconductors. Here we explore the consequences of the dilution of Eu$^{2+}$ magnetic lattice through on-site Ca substitution. By employing macro- and microscopic techniques, including electrical transport and magnetometry, as well as muon-spin spectroscopy, we study the evolution of Eu magnetic order in both the weak and strong dilution regimes, achieved for Ca concentration $x$(Ca) = 0.12 and 0.43, respectively. We demonstrate the localized character of the Eu antiferromagnetism mediated via RKKY interactions, in contrast with the largely itinerant nature of Fe magnetic interactions. Our results suggest a weak coupling between the Fe and Eu magnetic sublattices and a rapid decrease of the Eu magnetic interaction strength upon Ca substitution. The latter is confirmed both by the depression of the ordering temperature of the Eu$^{2+}$ moments, $T_N$, and the decrease of magnetic volume fraction with increasing $x$(Ca). We establish that, similarly to the EuFe$_2$As$_2$ parent compound, the investigated Ca-doped compounds have a twinned structure and undergo a permanent detwinning upon applying an external magnetic field.

I. INTRODUCTION

Superconductivity and magnetic order are among the most studied topics in contemporary solid-state physics. Although commonly considered to be antagonistic phenomena, in certain cases superconductivity has been observed to coexist with magnetic order. 1

In this respect, iron-based superconductors (Fe-SC) are among the most recent examples to exhibit such an interplay between superconductivity and magnetism. 2,3 In particular, EuFe$_2$As$_2$-based compounds possess some unique properties, reflecting the simultaneous occurrence of superconductivity and of two separate magnetically-ordered subsystems (due to iron and europium layers). 4,5 In the EuFe$_2$As$_2$ parent compound, a spin-density-wave (SDW) order associated with the Fe 3$d$-electrons is observed at $T_{SDW} \approx 190$K. The SDW transition is accompanied by a structural phase transition from the tetragonal (14/mmm) to the orthorhombic (Pmmm) structure. Additionally, europium magnetic moments order antiferromagnetically at $T_N = 19$K in an A-type magnetic structure. This corresponds to magnetic moments being aligned ferromagnetically along the a-axis, and antiferromagnetically along the c-axis. 6 Superconductivity in the EuFe$_2$As$_2$-based compounds emerges when the magnetic order of the itinerant Fe 3$d$-electrons gets suppressed, achieved either via applied pressure 7,9 or chemical substitution. 8 The latter involves either isovalent substitutions in the FeAs-layers 5,10–14 or electron/hole doping in the Eu-layers. 15–17

Upon substitution in the FeAs-layers, the SDW ordering temperature decreases compared to the $T_{SDW}$ of the parent compound, with SDW order being completely suppressed in the overdoped compounds. For Co-doped compounds it was reported that chemical substitution modifies the shape of the SDW, 18 yet the doping does not change the magnetic ground state of the Fe$^{2+}$ magnetic moments, which remains antiferromagnetic as long as the order is present. 19 The magnetic ground state of the Eu-subsystem, however, changes from an A-type antiferromagnet, via a canted antiferromagnet, to a ferromagnet upon doping the FeAs-sublattice. 19–21

A rather different behavior is observed for isovalent substitution of europium. On one hand, the Ca-doping does not lead to superconductivity under ambient pressure since the Fe-related SDW remains nearly unchanged, i.e., the substitution does not modify significantly neither the shape of SDW, nor its ordering temperature. 22–25 On the other hand, the dilution of the Eu-sublattice with nonmagnetic Ca$^{2+}$ ions, decreases the temperature of the antiferromagnetic order, eventually leading to its disappearance for Eu dilutions above 50%. 23,24 Thus, we expect the interactions between Eu$^{2+}$ ions to change significantly upon Ca doping, with Eu$_{1-x}$Ca$_x$Fe$_2$As$_2$ representing an ideal system for studying the Eu-related magnetism in the EuFe$_2$As$_2$-based compounds and its possible interplay with Fe-magnetism, while keeping the SDW order unchanged.

To shed light on the magnetic phase transitions of such a system, we investigated the zero-field resistivity, ac susceptibility, dc magnetization, and muon-spin relaxation ($\mu$SR) of two Ca-doped EuFe$_2$As$_2$ compounds. It is worth noting that the $\mu$SR spectroscopy has been successfully used to investigate other EuFe$_2$As$_2$-based compounds, for which it could reveal the nature of magnetic order, the magnetic phase diagram, and the internal field values. 20,26,27 Unlike previous studies, where only the effects of Fe magnetic lattice dilution or As isoelectronic replacement were considered, here we investigate the microscopic consequences of the Eu magnetic lattice dilution via on-site substitution with nonmagnetic Ca$^{2+}$ ions. To date no microscopic studies of the Ca-doped EuFe$_2$As$_2$ system exist. By using $\mu$SR tech-
niques we aimed to explore the interplay of Fe-3d and Eu-
4f magnetism, as well as a possible coupling between the
two, with a particular focus on the low-temperature antifer-
romagnetic region, dominated by the rare-earth magnetic
interactions.

II. EXPERIMENTAL DETAILS

Single crystals of $\text{Eu}_{1-x}\text{Ca}_x\text{Fe}_2\text{As}_2$ were grown using the
Sn-flux method. The Eu, Fe, As, Ca, and Sn elements in
molar ratios of $(1 - x):2:2:x:30$ were loaded into alumina
crucibles and sealed in quartz ampules under vacuum. To
dissolve all the ingredients, the ampules were heated slowly
to 1050°C, kept at this temperature for several hours, and
then cooled down slowly to 650°C with a rate of 2°C/h.
Next, the liquid tin was decanted from the crucibles. The Sn
residues on the crystals were removed via etching in diluted
hydrochloric acid.

The chemical composition of the obtained crystals was
determined using the energy-dispersive x-ray spectroscopy
(EDX), whereas the crystal structure and phase purity were
characterized by powder x-ray diffraction (XRD) using an
X’Pert Pro powder diffractometer (PANalytical, The Nether-
lands) equipped with a linear PIXcel detector.

The ac magnetic susceptibility measurements were per-
formed using an Oxford Instruments susceptometer in the
temperature range of 2–300 K and external fields up to 2 T,
probing with a driving field $\mu_0 H_{ac} \approx 1$ mT at a frequency
$f = 1.111$ kHz. The dc magnetization measurements were
conducted using a Physical Properties Measurement System
(PPMS, Quantum Design) in magnetic fields up to 9 T and
covering a temperature range of 2–320 K. The magnetiza-
tion data were collected in both zero-field-cooling (ZFC)
and field-cooling (FC) modes, whereas the ac magnetic
susceptibility measurements were performed in ZFC mode
only. Both dc and ac measurements were conducted with
the external fields applied parallel as well as perpendicular
to the c-axis.

Resistivity data were collected using the PPMS platform
in the temperature range from 2 to 300 K. Silver-wire con-
acts were mounted on the surface parallel to the crystallo-
graphic $ab$-plane using DuPont conductive silver paint; the
contact resistances were less than 0.5 Ω.

The μSR measurements were carried out at the General
Purpose Spectrometer (GPS) at the πM3 beam line of the
Swiss Muon Source at the Paul Scherrer Institut (PSI) in
Villigen, Switzerland. The temperature dependence of the
üron-spin relaxation was investigated both in zero-(ZF)
and in longitudinally (LF) applied magnetic fields. Several
single crystals, 0.5 to 1 mm thick were arranged in a mosaic
configuration with their c-axes collinear on top of an alumi-
nated mylar sheet. The latter was then folded to form an
envelope on top of which suitable 50-μm thick kapton foils
were added to optimize the muon stopping rate. The sam-
ple was finally mounted on a copper fork (fly-past setup)
with a negligible background count. Active-field compen-
sation during ZF-μSR measurements ensured a stray field
value below 1 μT. Data in both ZF and LF experiments were
collected in a temperature range of 1.6 to 60 K and, occa-
sionally, up to 240 K (to confirm the known Fe spin-density
wave at ca. 190 K). For the LF experiments magnetic fields
up to 0.6 T were applied.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Composition and crystal structure

For the current study we prepared single crystals of
$\text{EuFe}_2\text{As}_2$ and $\text{CaFe}_2\text{As}_2$, as well as of $\text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2$
and $\text{Eu}_{0.57}\text{Ca}_{0.43}\text{Fe}_2\text{As}_2$. All the observed x-ray diffraction
reflections for the investigated samples could be indexed
to the tetragonal ThCr$_2$Si$_2$-type structure ($I4/mmm$ space
group), expected for the AFe$_2$As$_2$-based systems. The re-
ined $a$ and $c$ lattice parameters and the calculated unit cell
volumes $V$ are shown in Fig. 1(a,b). Both lattice para-
eters (and the unit cell volume) decrease with increasing
Ca-concentration and are in good agreement with those re-
ported by Mitsuda et al.}

![FIG. 1. Dependence of (a) $a$ and $c$ lattice parameters, (b) unit

cell volume $V$, and (c) $T_N$ and $T_{SDW}$ temperatures on the Ca-

concentration $x$ in $\text{Eu}_{1-x}\text{Ca}_x\text{Fe}_2\text{As}_2$. Dashed lines are guides to
the eye.](image-url)
FIG. 2. Normalized resistivity \( \rho / \rho_{300K} \) vs. temperature \( T \) for the \( \text{Eu}_{1-x}\text{Ca}_x\text{Fe}_2\text{As}_2 \) series with \( x = 0, 0.12, 0.43 \), and 1. The \( T_N \) and \( T_{SDW} \) temperatures are marked with arrows. For clarity, the resistivity curves for \( x > 0 \) are shifted vertically by 0.2 units, with the horizontal lines marking the respective \( \rho / \rho_{300K} = 1 \) levels.

B. Electrical resistivity

The temperature dependencies of resistivity normalized to the 300-K resistivity values for the whole \( \text{Eu}_{1-x}\text{Ca}_x\text{Fe}_2\text{As}_2 \) series (\( x = 0, 0.12, 0.43 \), and 1) are shown in Fig. 2. For all the compositions a pronounced anomaly is observed at the spin-density-wave (SDW) ordering temperature of the Fe conduction electrons (\( T_{SDW} \)), coinciding with a tetragonal-to-orthorhombic structural phase transition. The \( T_{SDW} \sim 190K \) is nearly the same for all compounds, except for \( \text{CaFe}_2\text{As}_2 \) (\( T_{SDW} \sim 170K \)), in good agreement with the literature data.\(^{23,24,28}\)

A much weaker anomaly, corresponding to the antiferromagnetic ordering of Eu\(^{2+} \) magnetic moments, is observed below 19 K. As expected, the dilution of the Eu magnetic sublattice (via nonmagnetic Ca ions) leads to a decreased Néel temperature \( T_N \). The observed \( T_N \) for \( \text{Eu}_{1-x}\text{Ca}_x\text{Fe}_2\text{As}_2 \) are in good agreement with those reported by Mitsuda et al.\(^{24}\) The evolution of both the \( T_{SDW} \) and \( T_N \) values with Ca-concentration is summarized in Fig. 1(c).

C. Magnetization

The field-dependent magnetization \( M(H) \) of both 12% and 43% Ca-doped compounds was investigated in external magnetic fields applied either parallel (not shown) or perpendicular (Fig. 3 and 4) to the \( c \)-axis. The measurements were carried out in both increasing and decreasing fields. No spontaneous magnetization was detected in any of the compounds and the initial slope is linear, as expected for antiferromagnetic systems. Magnetic hysteresis was observed for both systems, however only for fields applied perpendicular to the \( c \)-axis and at temperatures below 5 K.

FIG. 3. Magnetic field dependence of magnetization per Eu atom for (a) \( \text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2 \) and (b) \( \text{Eu}_{0.57}\text{Ca}_{0.43}\text{Fe}_2\text{As}_2 \) measured at selected temperatures and in increasing fields applied perpendicular to the \( c \)-axis.

The \( M(H) \)-curves measured in the magnetic fields applied perpendicular to the \( c \)-axis are presented in Fig. 3. At \( T = 2 \) K, the magnetization of both \( \text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2 \) and \( \text{Eu}_{0.57}\text{Ca}_{0.43}\text{Fe}_2\text{As}_2 \) is characterized by a linear initial slope, a small magnetic hysteresis at 0.2 T, and a metamagnetic transition at 0.6 and 0.7 T, respectively (Fig. 4). In the \( \text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2 \) case, an additional hysteresis is observed at \( \sim 0.6 \) T [see Fig. 4(a)].

As can be seen in Fig. 4(a), the field-dependent magnetization of \( \text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2 \) changes from linear (first field increase) to one with a positive curvature (subsequent measurements), suggesting the presence of ferromagnetic correlations. On the other hand, a linear dependence up to \( 0.1 \) T is observed in \( \text{Eu}_{0.57}\text{Ca}_{0.43}\text{Fe}_2\text{As}_2 \) for both increase- and decrease-field measurements [Fig. 4(b)].

For both investigated compounds the low-field hysteresis (at \( \sim 0.2 \) T) disappears in subsequently repeated increase- and decrease-field measurements and the \( M(H) \)-curves follow the same dependence as the first decrease-fields dependence (cf. solid lines in Fig. 4). Additionally, in the
EuFe\textsubscript{2}As\textsubscript{2}-based systems, the fields allowing for a persistent detwinning are much smaller than those required in other AFe\textsubscript{2}As\textsubscript{2}-systems (A = Ba, Ca, ...), thus reflecting the large-spin Eu ions and the coupling of the Fe and Eu sublattices.

The close resemblance of the Eu\textsubscript{0.88}Ca\textsubscript{0.12}Fe\textsubscript{2}As\textsubscript{2} magnetization curve to that of the undoped EuFe\textsubscript{2}As\textsubscript{2} suggests that the 12\% Ca-doped compound undergoes a similar “detwinning” transitions as the EuFe\textsubscript{2}As\textsubscript{2} parent compound. By contrast, the magnetization of the Eu\textsubscript{0.57}Ca\textsubscript{0.43}Fe\textsubscript{2}As\textsubscript{2} compound exhibits only the low-temperature magnetic hysteresis. Additionally, its $M(H)$-dependence exhibits a negative curvature in the rebound field, contrary to the Eu\textsubscript{0.88}Ca\textsubscript{0.12}Fe\textsubscript{2}As\textsubscript{2} positive curvature. Remarkably, such intermediate metamagnetic states were not observed in the magnetization curves of systems with substituted FeAs-sublattice that possess the canted-AF structure of Eu\textsuperscript{2+} magnetic moments.\textsuperscript{5,10,18}

For each magnetization isotherm measured at $T < T_N$, the saturation magnetization can be determined. For instance, at 2 K the saturation magnetization $\mu_{\text{sat}}$ corresponds to $7 \mu_B$, which is the expected theoretical value for magnetic Eu\textsuperscript{2+} ions ($\mu_{\text{th}} = g\mu_B$, with $g = 2$ and $J = 7/2$). It was shown that in EuFe\textsubscript{2}As\textsubscript{2}-based systems the saturation state is equivalent to a field-induced ferromagnetic state.\textsuperscript{5,11,29,32} The field at which the system “switches” from an antiferromagnetic (AF) to a field-induced ferromagnetic state (FI-FM) is represented by the “crossover” field $H_{crt}$. Such $H_{crt}$ values can, therefore, be calculated by determining the minimum in the second derivative of magnetization $d^2M/dH^2$.

Eu\textsubscript{0.57}Ca\textsubscript{0.43}Fe\textsubscript{2}As\textsubscript{2} case, the width of the high-field hysteresis loop (at $\sim 0.6$ T) decreases in the subsequent measurements. Moreover, the initial field dependence of magnetization can only be reproduced after heating the samples above the respective $T_{SDW}$.

A similar field dependent magnetization was found in the EuFe\textsubscript{2}As\textsubscript{2} parent compound. As shown by Jiang et al.,\textsuperscript{29} when an external magnetic field is applied perpendicular to the $c$-axis, subsequent metamagnetic transitions are observed. Neutron-spectroscopy studies have revealed that EuFe\textsubscript{2}As\textsubscript{2} crystals have a twinned structure, whereby the application of an external magnetic field modifies the twinning fraction, at fields corresponding to the metamagnetic transitions.\textsuperscript{6} A study by Zapf et al.\textsuperscript{30} suggests that both the metamagnetic transitions and the hysteretic behavior are due to “detwinning”. There was shown not only that EuFe\textsubscript{2}As\textsubscript{2} undergoes two “detwinning” processes (at 0.1 and at 1 T), but also that the “detwinning” is permanent as long as the sample is not heated above $T_{SDW}$. A recent theoretical study indicates that the “detwinning” in magnetic fields is characteristic of Fe-SC systems.\textsuperscript{31} However, in

![Figure 4](image_url)  
**FIG. 4.** Field dependence of (a) Eu\textsubscript{0.88}Ca\textsubscript{0.12}Fe\textsubscript{2}As\textsubscript{2} and (b) Eu\textsubscript{0.57}Ca\textsubscript{0.43}Fe\textsubscript{2}As\textsubscript{2} magnetization (in units of magnetic moment per Eu atom) measured at 2 K in increasing (full circles) and decreasing (open squares) external magnetic fields applied perpendicular to the $c$-axis. Thick solid lines represent the magnetization measured in the second run (see text) in increasing/decreasing fields.

![Figure 5](image_url)  
**FIG. 5.** Temperature dependence of magnetization of Eu\textsubscript{0.88}Ca\textsubscript{0.12}Fe\textsubscript{2}As\textsubscript{2} measured in ZFC-mode in several magnetic fields ($\mu_0H$) applied perpendicular to the $c$-axis.
determined by using the Fisher’s method — i.e., from the maximum of the derivative of the \( T \chi(T) \) product.\(^{33} \) Note, however, that for fields above 0.5 T, \( M(T) \) does not show a maximum, but only a smooth increase with decreasing temperature (up to \( M \sim 7 \mu_B/\text{Eu} \) close to \( T = 0 \) K).

In contrast to the Eu-related AF transition, the anomaly associated with the Fe-SDW transition is barely visible in the magnetization measurements. And when so, it can be observed only at high magnetic fields (\( \mu_0 H > 2 \) T), as marked with blue vertical arrows in Fig. 6. These results are different from those of resistivity, where the SDW transition is much more prominent than the AF transition.

The 9-T dc magnetization data were used to calculate the magnetic susceptibility \( \chi = M/H \). A typical temperature dependence of susceptibility and of its inverse \( 1/\chi \) (open squares, right axis) for \( \text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2 \) measured in a 9-T magnetic field applied parallel to the \( c \)-axis. The solid line represent the fit by means of a modified Curie-Weiss law \([\text{Eq. } (1)]\) in the 100–180 K temperature range. The \( T_{\text{SDW}} \) is marked with an arrow.

\[ \chi = \frac{N_A}{3 k_B} \frac{\mu_{\text{eff}}^2}{T - \theta_p} + \chi_0. \]  

(1)

Here \( N_A \) is the Avogadro’s constant, \( k_B \) the Boltzmann constant, \( \theta_p \) the Weiss temperature, and \( \chi_0 \) a temperature-independent paramagnetic susceptibility. The fit parameters in both cases are reported in Table I. The evaluated effective magnetic moments per Eu atom \( \mu_{\text{eff}} \) have slightly larger values for measurements in magnetic fields applied parallel to the \( c \)-axis than for measurements with \( H \perp c \). This was observed also in other EuFe\(_2\)As\(_2\)-based systems.\(^{4,5,10,11,29} \) The determined \( \mu_{\text{eff}} \sim 8 \mu_B \) is marginally larger than \( \mu_{\text{eff}}^{\text{theo}} = g \sqrt{J(J+1)} = 7.9 \mu_B \) expected from theory, which is also consistent with previously reported results\(^4 \) and is usually attributed to a possible contribution of Fe\(^{2+} \) magnetic moments. The constant \( \chi_0 \) contribution is negligibly small when compared to the main magnetic susceptibility, confirming the absence of spurious phases.

| Orientation | \( H \perp c \) | \( H \parallel c \) |
|-------------|----------------|----------------|
| \( \mu_{\text{eff}} (\mu_B) \) | 8.1 | 7.9 | 8.2 |
| \( \theta_p (K) \) | 17.1 | 13.9 | 11.9 | 7.8 |
| \( \chi_0 (\text{cm}^3/\text{Eu}) \) | 0.005 | — | 0.025 | 0.008 |

Positive Weiss temperatures \( \theta_p \) suggest dominant ferromagnetic interactions in both compounds. Similar results were obtained in \( \text{EuFe}_2\text{As}_2 \)\(^{29} \) and \( \text{EuCo}_2\text{As}_2 \)\(^{24} \), too, most likely indicating also there the presence of ferromagnetic interactions between nearest-neighbor Eu\(^{2+} \) ions in the \( ab \)-planes.

D. ac susceptibility

The temperature dependence of the real part of ac susceptibility \( \chi' \) of \( \text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2 \) and \( \text{Eu}_{0.57}\text{Ca}_{0.43}\text{Fe}_2\text{As}_2 \) measured at selected \( H \perp c \) fields is shown in Fig. 7. The zero-field data, show a rather wide peak associated with the AF ordering of Eu\(^{2+} \) ions (at \( T_N \approx 15.6 \) K for \( \text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2 \) and at 10 K for \( \text{Eu}_{0.57}\text{Ca}_{0.43}\text{Fe}_2\text{As}_2 \)). As expected for an AF transition, the peak shifts towards lower temperatures as the external magnetic field increases.

At temperatures below \( T_N \) and for fields below 0.1 T both the real and imaginary part of the \( \text{Eu}_{0.88}\text{Ca}_{0.12}\text{Fe}_2\text{As}_2 \) susceptibility increase (see Fig. 8). Such behavior in a magnetically-ordered state suggests the existence of additional phase transitions, especially since in the case of the P-doped \( \text{EuFe}_2\text{As}_2 \)-based compounds a spin-glass transition was observed in an already magnetically ordered state.\(^{35} \)

The zero-field (\( \mu_0 H = 0 \) T) ac-susceptibility data collected at different frequencies reveal that although the imaginary part increases slightly at higher frequencies, the real part invariably shows the same temperature dependence (cf. Fig. 8). Additionally, constructed \( \chi''(\chi') \) plots (see Supplementary Material) for investigated compounds do not show a semicircular shape expected for a spin-glass system,\(^{36,37} \) hence ruling out a spin-glass transition at low temperatures.

Taking into account the magnetization measurement results (see Sec. III C), we propose that the observed increase of ac susceptibility at low temperatures is possibly associated with the “detwinning” processes. Such suggestion is further supported by the ac-susceptibility measurements of the \( \text{EuFe}_2\text{As}_2 \) parent compound (with an A-type magnetic structure), which reveal exactly the same behavior as in the 12% Ca-doped compound, i.e., a significant increase in the
FIG. 7. Temperature dependencies of the real-part of ac susceptibility $\chi'$ of (a) Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$ and (b) Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$ measured in several external magnetic fields ($\mu_0H$) applied perpendicular to the crystallographic c-axis.

On the other hand, such behavior was not observed in Co-doped compounds with a canted-AF structure.$^5,11$

Hence, we propose that the observed increase of susceptibility with decreasing temperature below $T_N$ in both EuFe$_2$As$_2$ and Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$ is associated with the “detwinning” processes, indicated by the magnetization measurements.

real and imaginary parts of ac susceptibility below the AF transition (see Supplementary Material for more details).

E. Magnetic phase diagrams

Based on the above bulk measurements of Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$ and Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$, the respective magnetic-phase diagrams were constructed for fields applied both parallel and perpendicular to the c-axis (see Fig. 9). The vertical dashed-dotted lines represent the transition from the paramagnetic (PM) to the Fe-SDW transition. The curves corresponding to the AF to FI-FM transition, related to the Eu$^{2+}$ magnetic moments, were constructed by taking the $H_{cr}$ (triangles) and $T_N$ (circles) values, calculated from the dc magnetization data, and the $T_N$ (squares) from ac susceptibility. The transition from the paramagnetic phase of the Eu-subsystem (Eu-PM) to the ordered FI-FM phase (diamonds) was determined based on the ac-susceptibility values. The dashed lines on the diagrams represent guides for the eye.

The presented phase diagrams reveal a rather anisotropic behavior. Thus, at 2 K, in both cases the $H_{cr}$ values for $H \parallel c$ (Fig. 9 - right column) are almost twice the $H_{cr}$ values obtained for $H \perp c$ (Fig. 9 - left column). By comparing instead the $H_{cr}$ values of the two compounds (top vs. bottom panels in Fig. 9) we deduce that the RKKY interactions become weaker upon doping, since smaller magnetic fields have to be applied to reorient the nearly 50%-doped system from the AF to the FI-FM state with respect to the 12% Ca-doping case.

F. Muon-spin relaxation

Spin-polarized muons are widely used microscopic as probes of magnetism.$^{38,39}$ Once implanted in matter and thermalized at interstitial lattice sites, they act as probes of the local magnetic field, the muon-spin precession
frequency being $\nu = \gamma \mu / (2\pi) B_{\text{loc}}$, with $\gamma \mu = 2\pi \times 135.53 \text{ MHz/T}$, the muon gyromagnetic ratio. Since the final signal is carried by energetic decay positrons (emitted preferentially along the muon-spin direction), $\mu$SR enables the investigation of materials even in the absence of applied fields.

To investigate the magnetic behavior of the Ca-doped $\text{EuFe}_2\text{As}_2$ system with temperature, muons with spins parallel to the $c$-axis were implanted into the samples with $x(\text{Ca}) = 0.12$ and 0.43, representative of a weak and strong dilution of the Eu$^{2+}$ magnetic lattice, respectively. Typical time-domain asymmetry spectra for the $x = 0.43$ case, collected upon warming the sample, are shown in Fig. 10. At first sight, no asymmetry oscillations are observed on a long time scale at any of the temperatures shown, either above or below $T_N = 11 \text{ K}$. Except for a higher $T_N$, similar results are obtained also in the less diluted $x = 0.12$ case. In both cases, such an apparent lack of oscillations on either side of $T_N$ is due to rather different reasons. For temperatures above $T_N$, a smooth decay starting with a full initial asymmetry (of 22% at 30 K) corresponds to the typical behavior of fluctuating paramagnetic moments ($\text{Eu}^{2+}$ in our case). Below $T_N$ instead, a significant drop in the initial asymmetry (reaching 16% at 1.5 K) reflects the onset of a long-range magnetic order. By limiting the observation time window to 0.2 $\mu$s, one can clearly see the oscillations in the magnetically ordered phase [see Fig. 11(a)]. The rather large Eu$^{2+}$ magnetic moments ($\sim 7 \mu_B$) imply significant internal fields (above 0.4 T) and, hence, fast precessions, which then dis-
appear above $T_{N}^{\text{Eu}}$.

![Figure 12](image)

**FIG. 12.** The magnetic structure of Ca-doped EuFe$_2$As$_2$, as inferred from μSR data, is most likely the same as that of the EuFe$_2$As$_2$ parent compound. The red circle shows a possible (high-symmetry) muon stopping site. Drawing produced using VESTA.

A comparison of the forward-backward (FB) vs. up-down (UD) detector pairs (Fig. 11) is quite informative. Given the single-crystal nature of our samples, it allows us to infer also the orientation of the Eu$^{2+}$ and Fe$^{2+}$ magnetic moments in their respective ordered phases. Actually the μSR signal can only give indications about the local magnetic field at the muon site, since it does not contain direct information on the magnetic moment directions. However, by taking into account the high symmetry of the muon stopping site [most likely close to the Fe planes at (1/2, 1/2, 0.22) — see, e.g., Ref. 41 and Fig. 12], one can still draw conclusions on the direction of magnetic moments for both Fe$^{2+}$ and Eu$^{2+}$.

Since incoming muons have spins parallel to the $c$-axis, a lack of oscillations above $T_{N}^{\text{Eu}}$ in the FB pair, while they still persist in the UD detectors, implies that in the long-range ordered SDW phase the iron moments align in the $ab$-plane. Indeed, each muon has four nearest Fe$^{2+}$ ions which, considering the $k = (1, 0, 1)$ SDW propagation vector, implies two groups of counteraligned moments $m$ (see Fig. 12). For symmetry reasons, the contributions to the local field at the muon site due to the $c$ component of $m$ cancel out, whereas the $ab$-plane component gives rise to a local dipolar field along the $c$-axis. By observing (below $T_{\text{SDW}}$) a local field along $c$, we therefore infer that the Fe$^{2+}$ moments should lie in the $ab$-plane.

As for the europium moments, since $T_{N}^{\text{Eu}}$ is lower than $T_{N}^{\text{Fe}}$, one cannot unambiguously determine their orientations, since below $T_{N}^{\text{Eu}}$ muons are simultaneously affected by both magnetic systems. However, compatibly with the data shown in Fig. 11(a), we expect Eu$^{2+}$ moments most likely to lie in the $ab$-plane. Indeed, each muon has a single nearest Eu$^{2+}$ neighbor, shifted along the $c$-direction. If the Eu$^{2+}$ moment would lie along the $c$-direction, the dipolar field at the muon site would be antiparallel to the moment and along $c$ (which is not our case). If the Eu$^{2+}$ moments would lie in the $ab$-plane, the dipolar field would still be antiparallel, but now in the $ab$-plane. Since below $T_{N}$ we observe a local field in the $ab$-plane, we conclude that the Eu$^{2+}$ magnetic moments lie also in the $ab$-plane. The above conclusions are compatible with neutron diffraction results on single crystals of EuFe$_2$As$_2$, where both Eu$^{2+}$ and Fe$^{2+}$ moments are shown to align along the $a$-axis (at 2.5 K).

From the above discussion (and a comparison of Figs. 10 and 11), it is clear that the considered time-scale determines the choice of a suitable fitting function: oscillatory for short times and slowly decaying at long times. The typical time-domain μSR spectra reported in Fig. 10 show a strongly temperature-dependent decay which was fitted using the following combined function:

$$A(t) = A_0 \left[ \alpha e^{-\lambda_1 t} \cos(\gamma_B t + \phi) + \beta e^{-\lambda_2 t} \right].$$

Here $\alpha$ and $\beta = 1 - \alpha$ are the oscillating (i.e., transverse) and non-oscillating (i.e., longitudinal) fractions of
the muon signal, respectively, whose initial total asymmetry is $A_0$. Accordingly, the two decay functions are denoted as $\lambda_T$ and $\lambda_L$. The initial precession angle is denoted by $\phi$, while $\gamma_m$ is the muon gyromagnetic ratio. For the ideal case of a fully magnetic polycrystalline sample one expects $\alpha = 2/3$ and $\beta = 1/3$ (since statistically one third of the times the muon spin does not precess, being parallel to the local magnetic field $B_i$). Similar values for the two fractions have been found also for single crystals, or for partially aligned mosaics (as in our case — see discussion below).

As already mentioned, the apparent reduction of the longitudinal asymmetry $\beta A_0$ (obtained by considering the long-time $\mu$SR spectra — see Fig. 10) is a consequence of the onset of the Eu$^{2+}$ magnetic order below $T_N$. The full recovery of asymmetry to its total value of ca. 25% occurs only in the paramagnetic phase (i.e., above $T_c \sim 190$ K). However, data show that most of the asymmetry is recovered already above $T_N$. Considering this and the rather similar oscillating fractions $\alpha$ in a powder and in a mosaic sample, one can attempt an evaluation of the magnetic fraction $V_M$ as a function of doping and temperature by means of $V_M(T) = \frac{1}{2} (1 - \alpha_L) \times 100\%$. The resulting $V_M(T)$ values for the pristine and Ca-substituted EuFe$_2$As$_2$ samples are shown in Fig. 13.

![FIG. 14. Fit parameters of the long-time $\mu$SR spectra vs. temperature for the $x = 0.43$ case: (a) longitudinal muon-spin asymmetry at 0 and 200 mT, (b) longitudinal decay coefficient. Both parameters show marked features (slope change or cusp) in concomitance with the Eu$^{2+}$ AF phase transition at $T_N = 11$ K.](image)

We note that all the considered samples are fully magnetically ordered at low temperature ($V_M = 100\%$). The average Néel temperature and the corresponding transition width $\Delta$ were obtained by fitting the $V_M(T)$ data with the phenomenological function:

$$V_M(T) = \frac{1}{2} \left[ 1 - \text{erf}\left(\frac{T - T_N}{\sqrt{2} \Delta}\right)\right].$$

(3)

As can be seen from Fig. 13, as the Ca content increases there is a clear decrease of $T_N$ and a simultaneous broadening of the transition (the curves becomes smoother). These results are in very good agreement with our magnetometry data. In addition, they show that to a high Ca substitution rate corresponds an increased degree of disorder, here measured by $\Delta$. The detailed fit values are reported in Table II.

| $x$ (Ca) | $T_N$ (K) | $\Delta$ (K) | Magn. frac. (%) |
|---------|-----------|--------------|----------------|
| 0       | 18.6(1)   | 1.7(3)       | 99(4)          |
| 0.12(1) | 15.1(3)   | 2.6(3)       | 100(5)         |
| 0.43(1) | 7.2(4)    | 3.1(4)       | 100(8)         |

By considering the fit parameter $\lambda_L$, although strictly speaking the relaxation rate is not an order parameter, it still provides information on the critical dynamics, as suggested by the sharp cusps observed at $T_N$ (diamond symbols in Figs. 14 and 15). The $T$ dependence of $\lambda_L$, both above and below $T_N$, has been described by means of a critical-exponent behavior $\lambda(T) = \lambda_0 |1 - T/T_N|^{\nu}$ with the expected exponent value for a 3D ferromagnet $\nu \approx 1.05$. The fit curves, shown with solid lines in Fig. 14(b), have rather different exponents above and below $T_N$. Thus for $T < T_N$ we find $w \approx 0.84(3)$, whereas for $T > T_N$ we obtain $w \approx 0.25(2)$. While the former value is not far from that expected at a magnetic transition, the latter is much smaller and remains so even when restricting the fit range. Such anomalously small $w$ values above $T_N$ have been observed also elsewhere (see, e.g., Ref. 20), where $w$ was found to be 0.28. It has been suggested that muon-lattice dipolar interactions, known to strongly affect the paramagnetic critical dynamics near a magnetic transition point, could be responsible for the observed low value of the $w$ exponent.

By considering now the short-time $\mu$SR data (see Fig. 11) we can follow the temperature evolution of the internal magnetic field, as sensed at the muon stopping sites. The resulting fit parameters in the $x = 0.12$ case, obtained by means of Eq. (2), are shown in Figs. 15(a) and (b) for the UD and FB detector pairs, respectively. In comparison with the longitudinal relaxation data [see Fig. 14(b)] the transverse relaxation is more than two orders(!) of magnitude larger. Similarly large relaxation rates have been observed also in the isoelectronically doped EuFe$_2$(As$_{1-x}$P$_x$)$_2$ compound.

As discussed above, the UD detector dataset allow us to follow both the Eu- and Fe-related magnetic transitions, distinctly seen at $T_N = 15$ K and $T_{SDW} = 190$ K, respectively, in the field profiles and in the muon relaxation rates [see Fig. 15(a)]. By converse, the FB detector dataset is limited to the Eu$^{2+}$ transition only. Analogously to the longitudinal relaxation, also the transverse relaxation data show a critical-exponent behavior $\lambda(T) = \lambda_0 |1 - T/T_N|^{\nu_w}$, once more with rather skewed exponent values above $T_N$.

As for the internal field dependence with $T$, the very sharp increase of $B_i$ at $T_{SDW}$ is suggestive of a first-order
phase transition. As the temperature is lowered, the internal field tends to saturate at ca. 0.35 T. At $T_N$, another field jump appears, indicative of the magnetic ordering of Eu$^{2+}$ moments. Each of these transitions can be modelled by the phenomenological model:  

$$B_i(T) = \sum_{n=1}^{2} B_i^n(0) \left[ 1 - \left( \frac{T}{T_{c}} \right)^{\gamma_n} \right]^{\delta_n},$$  \hspace{1cm} (4)$$

where $B_i^n(0)$ are the internal magnetic fields at zero temperature and $\gamma_n$ and $\delta_n$ are two empirical parameters, whose typical fit values are $\gamma_n \sim 1.5$ and $\delta_n \sim 0.25$ (with error bars of ca. 0.8).

For both samples, none of the internal magnetic fields seems to track an ideal mean-field type curve, which represents the exact solution in case of an infinite-range (anti)ferromagnetic order and corresponds to $\delta_n \sim 0.5$. The reason for such discrepancy might reflect the occurrence of a magnetic (AF) order within an already ordered (SDW) phase.

IV. SUMMARY AND CONCLUSIONS

Our study suggests that similarly to the EuFe$_2$As$_2$ parent compound, Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$ (and most likely Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$) undergo analogous “detwinning” processes. Some differences observed between the two Ca-doped compounds are possibly due to the different coupling strengths between the Fe- and Eu-subsystems, associated with the different Eu-concentration in the two cases.

The $\mu$SR results offer a local-probe perspective on the Ca-doped EuFe$_2$As$_2$ system, e.g., implanted muons indicate that in the magnetically-ordered phase both the Fe$^{2+}$ and Eu$^{2+}$ magnetic moments align in the $ab$-plane. The latter is also supported by magnetometry results, which suggest an A-type AF structure for the Eu$^{2+}$ magnetic moments in the Ca-doped compounds, the same as in the EuFe$_2$As$_2$ case. At low temperatures, both samples show 100% magnetic fractions, but a dilution of the Eu$^{2+}$ sublattice implies a decrease of $T_N$ and a broadening of the transition. In both cases, muons detect magnetic fields of ca. 450 mT in the ordered phase, with the muon field profiles and relaxation rates showing distinct features at the respective phase transitions of the two magnetic sublattices. The presence of an AF order, even in the nearly 50% diluted system, excludes direct interactions among Eu$^{2+}$ moments as responsible for the observed 3D magnetic order and suggests instead the indirect RKKY couplings to be the key interactions. Such conclusion is supported also by theoretical calculations, as shown, e.g., in Ref. 47. The significant reduction of $T_N$ and $H_{c2}$ in EuFe$_2$As$_2$ upon Eu-by-Ca substitution indicates a clear weakening of the RKKY-mediated magnetic interactions among Eu$^{2+}$ moments. This result could be rationalized by considering the direct influence of local on-site substitutions and is in clear contrast with the outcome of substitutions in the FeAs-planes (such as, e.g., Co-for-Fe), for which the temperature of the AF ordering of Eu$^{2+}$ moments remains mostly unchanged upon doping.  

Finally, we observe also a small change of $T_{SDW}$ values upon doping, which might suggest some degree of interaction between the Eu and Fe layers. This is consistent with theoretical predictions, which indicate that the Eu order might be influenced by the Fe-magnetism.  However, one cannot exclude that a $T_{SDW}$ change might arise simply because of a change in the lattice parameters or other processes. Therefore, the investigation of similar compounds but with smaller or (preferably) with no changes of lattice parameters, will be helpful to solve this issue.

Given the interesting zero-pressure results reported above, future high-pressure $\mu$SR investigations of Ca-doped EuFe$_2$Ca$_2$ are promising, since the Ca-doped EuFe$_2$As$_2$ system is expected to become a superconductor above 1.5–2 GPa.

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Supplementary material: Magnetic phase diagram of Ca-substituted EuFe$_2$As$_2$

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I. AC SUSCEPTIBILITY

We investigated the ac susceptibility of EuFe$_2$As$_2$, Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$, and Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$ using a driving field of $\mu_0 H = 10 \text{ mT}$ with frequencies up to 5 kHz, in external magnetic fields up to 1.5 T applied both parallel and perpendicular to the c-axis.

The temperature dependencies of zero-field ac susceptibilities of EuFe$_2$As$_2$, Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$, and Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$ are presented in Fig. 1. All investigated compounds exhibit an anomaly in the real part of ac susceptibility, associated with the antiferromagnetic ordering at $T_N = 19$ K, 16.5 K and 10 K for EuFe$_2$As$_2$, Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$, and Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$ respectively. For EuFe$_2$As$_2$ and Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$, below $T_N$, both the real $\chi'$ and imaginary $\chi''$ parts of ac susceptibility increase with decreasing temperature, while no such behavior was observed for Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$, cf. Fig. 1.

A. Frequency dependence

To check whether this anomaly could be associated with a spin-glass transition (suggested for the P-doped compounds$^1$), ac susceptibility was measured for different driving-frequency values.

Measurements performed using frequencies of 111 and 1111 Hz reveal that the temperature dependence of the real part of ac susceptibility for each compound are the same for different frequencies, Fig. 1(a,c,e). On the other hand, the imaginary part of ac susceptibility is slightly higher at higher frequencies, Fig. 1(b,d,f).

The frequency dependence of ac susceptibility of EuFe$_2$As$_2$, Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$, and Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$ was studied at 2 K. Based on these measurements Argand diagrams$^2$ — $\chi''(\chi')$ plots or Cole-Cole plots — were constructed for each compound and are presented on Fig. 2. While $\chi''$ increases with increasing frequency, $\chi'$ decreases slightly. The typical $\chi''(\chi')$ dependence for a spin-glass system has a semicircular shape,$^2,3$ which is not the case for the investigated compounds as can be seen on Fig. 2. Instead, the $\chi''(\chi')$ dependence is nearly linear. Interestingly, both the temperature dependence and frequency dependence for the nearly 50% doped compound are qualitatively different compared to the other two compounds.

B. Field dependence

Temperature dependences of ac susceptibility studied in 0, 0.01, 0.5 and 1.5 T external magnetic fields applied perpendicular to the c-axis of investigated compounds are presented on Fig. 3.

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FIG. 1. Temperature dependence of (a, c, e) real and (b, d, f) imaginary part of ac susceptibility of Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$ investigated using 111 and 1111 Hz frequencies of the driving field $\mu_0H_{ac} = 10$ mT

FIG. 2. $\chi''(\chi')$ plot of EuFe$_2$As$_2$, Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$ and Eu$_{0.57}$Ca$_{0.43}$Fe$_2$As$_2$ investigated at $T = 2$ K using a driving field $\mu_0H_{ac} = 10$ mT in the frequency range between 111 and 5500 Hz.
FIG. 3. Temperature dependences of the real (black) and imaginary (green) parts of ac susceptibility of (a-d) EuFe$_2$As$_2$, (e-h) Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$, and (i-l) Eu$_{0.88}$Ca$_{0.12}$Fe$_2$As$_2$ investigated using $\mu_0H_{ac} = 10$ mT driving field with 1.111 kHz frequency in 0, 0.01, 0.5 and 1.5 T external magnetic fields applied perpendicular to the $c$-axis.