Spin reorientation of the Fe moments in Eu0.5Ca0.5Fe2As2: Evidence for strong interplay of Eu and Fe magnetism

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Using complementary polarized and unpolarized single-crystal neutron diffraction, we have investigated the temperature-dependent magnetic structures of Eu0.5Ca0.5Fe2As2. Upon 50% dilution of the Eu sites with isovalent Ca2+, the Eu sublattice is found to be still long-range ordered below Teu = 10 K, in the A-type antiferromagnetic (AFM) structure. The moment size of Eu2+ spins is estimated to be as large as 6.74(4)μB at 2.5 K. The Fe sublattice undergoes a spin-density-wave transition at TSDW = 192(2) K and displays an in-plane AFM structure above Teu. However, at 2.5 K, the Fe2+ moments are found to be ordered in a canted AFM structure with a canting angle of 14(4)° out of the ab plane. The spin reorientation of Fe below the AFM ordering temperature of Eu provides direct evidence of a strong interplay between the two magnetic sublattices.

I. INTRODUCTION

The discovery of superconductivity (SC) with the critical temperature Tc = 26 K in fluorine-doped LaFeAsO in 2008 has opened up an “iron age of superconductivity” [1]. Shortly after that, Tc above 50 K was achieved in RFeAsO1−xFx (“1111” system, R = Ce, Sm, Pr, Nd, and Gd), with R being a rare-earth element [2–5]. SC with Tc up to 38 K was also realized by various chemical substitutions in the ternary “122” compounds AFe2As2, with A being an alkaline-earth-metal element (Ca, Ba, Sr) or the rare-earth element Eu [6–8]. It was well confirmed that the SC in the iron pnictides emerges upon the suppression of the static long-range spin-density-wave (SDW) order of Fe by means of chemical doping or applying external pressure [9,10]. Although SC is compatible with the localized moments of the rare-earth ions in either 1111 or 122 system [11–14], how the magnetism of Fe and the rare-earth element interact with each other is still not well elucidated.

In-depth experimental studies performed on a quaterary RFeAsO system have provided compelling evidence that there is a strong coupling of Fe and R magnetism for R = Ce, Sm, Pr, and Nd, respectively [15–19]. However, for ternary EuFe2As2 compounds, it is quite controversial regarding the strength of the interplay of Fe and Eu magnetism [20–27]. As a special member of the 122 system, EuFe2As2 has drawn tremendous attention, due to the strong spin-charge-lattice coupling and doping- or pressure-induced coexistence of SC and strong ferromagnetism [28–35]. In a purely ionic picture, the S-state (orbital moment L = 0) Eu2+ rare-earth ion has a 4f7 electronic configuration and a total electron spin S = 7/2, corresponding to a theoretical total effective magnetic moment of μeff = gμB√7/2 = 7.94μB (with the Landé factor g = 2) [36]. The nonsuperconducting parent compound EuFe2As2 undergoes a structural phase transition from a tetragonal to an orthorhombic phase at 190 K, coexisting with a SDW ordering of the itinerant Fe moments. In addition, the localized Eu2+ spins order below 19 K in the A-type antiferromagnetic (AFM) structure (ferromagnetic layers stacked antiferromagnetically along the c axis) [37].

According to previous neutron and nonresonant x-ray magnetic scattering experiments [20,21], the coupling between the Eu and Fe sublattices in EuFe2As2 was found to be negligible, which was further supported by density-functional electronic structure calculations [22]. Also, a direct optical pump-probe showed a slow response of the Eu2+ spins to the optical excitation of the itinerant carriers on the FeAs layers, suggesting a weak coupling between the two sublattices [23]. In contrast, magnetic Compton scattering on EuFe2((As0.73P0.27)2 indicated that the magnetism of Fe gets enhanced when the Eu magnetic order sets in [24]. In addition, nuclear magnetic resonance (NMR) and Mössbauer spectroscopy measurements revealed a strong coupling between the localized Eu2+ moments and the conduction d electrons on the FeAs layers in Co-doped EuFe2As2 [25,26]. Recently, by performing x-ray resonant magnetic scattering (XRMS)
measurements on underdoped \( \text{Eu(Fe}_{0.94}\text{Ir}_{0.06})_2\text{As}_2 \), we have observed the magnetic polarization of the \( \text{Ir} 5d \) band induced by the AFM ordering of \( \text{Eu} \), indicating a strong interplay between the two sublattices [27]. Undoubtedly, detailed knowledge about the evolution of the magnetic structures of both \( \text{Eu} \) and \( \text{Fe} \) with temperature will be crucial for understanding these observations.

Isovalent substitution of \( \text{Eu} \) with \( \text{Ca} \) offers an ideal platform for studying the delicate interplay between the two magnetic sublattices. On the one hand, under ambient pressure, \( \text{Ca} \) doping into the \( \text{Eu} \) site does not perturb the SDW order in the FeAs layers visibly and never leads to SC. On the other hand, dilution of the \( \text{Eu} \) sublattice with nonmagnetic \( \text{Ca}^{2+} \) ions suppresses its AFM ordering temperature \( (T_{\text{Eu}}) \) gradually [38–40]. A recent muon spin rotation (\( \mu \)SR) study on \( \text{Eu}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{As}_2 \) suggests a long-range magnetically ordered \( \text{Eu} \) sublattice [39]. However, it was proposed based on macroscopic measurements that substitution of 50% \( \text{Eu} \) ions might lead to a short-range-ordered nature of \( \text{Eu} \) magnetism [41]. In order to determine the ground-state magnetic structure of \( \text{Eu}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{As}_2 \) and check the interplay between two sublattices, we have performed temperature-dependent polarized and unpolarized neutron diffraction studies on the \( \text{Eu}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{As}_2 \) single crystal. The \( \text{Eu}^{2+} \) moments are found to be long-range ordered below \( T_{\text{Eu}} = 10 \) K, in the \( A \)-type AFM structure. A spin reorientation of the \( \text{Fe}^{2+} \) moments is clearly observed around \( T_{\text{Eu}} \), providing direct evidence of strong coupling between the \( \text{Fe} \) and \( \text{Eu} \) magnetism.

II. EXPERIMENTAL DETAILS

Single crystals of \( \text{Eu}_{1-x}\text{Ca}_x\text{Fe}_2\text{As}_2 \) \( (x = 0.5 \) nominally) were grown using the Sn flux method [39]. No incorporation of Sn into the crystals was evidenced according to the energy-dispersive x-ray spectroscopy (EDX) characterization. The concentration of \( \text{Ca} \) was determined to be 52(4)% by nuclear structure refinement of the neutron diffraction data, as presented below. An 88-mg plate-like single crystal with dimensions \( \sim 4 \times 3 \times 0.6 \) mm\(^3\) was selected for unpolarized and polarized neutron diffraction measurements, which were performed on the hot-neutron four-circle diffractometer HEIDi and diffuse scattering cold-neutron spectrometer DNS, respectively, at Heinz Maier-Leibnitz Zentrum (MLZ), Garching (Germany) [42,43]. For measurements at both beamlines, the single-crystal sample was mounted on a thin aluminum plate with a tiny amount of GE varnish and put inside a standard closed-cycle cryostat. At HEIDi, a Ge (311) monochromator was chosen to produce a monochromatic neutron beam with a wavelength of 1.17 Å, and an Er filter was used to minimize the \( \lambda/2 \) contamination. At DNS, the wavelength of the incident neutrons is 4.2 Å. The [0, 1, 0] direction of the crystal was aligned perpendicular to the horizontal scattering plane, so that the \( (H, 0, L) \) reciprocal plane can be mapped out by rotating the sample. Throughout this Rapid Communication, the orthorhombic notation (space group \( Fmmm \)) will be used for convenience. Single crystals from the same batches were characterized by macroscopic measurements including the resistivity, heat capacity, and dc magnetic susceptibility, using a Quantum Design physical property measurement system (PPMS) and Quantum Design magnetic property measurement system (MPMS).

III. EXPERIMENTAL RESULTS

Macroscopic properties of \( \text{Eu}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{As}_2 \) single crystal are shown in Figs. S1 and S2 in the Supplemental Material [44]. Two magnetic transitions corresponding to the SDW ordering of the \( \text{Fe} \) sublattice and AFM ordering of the \( \text{Eu}^{2+} \) moments are identified around 190 and 10 K, respectively. To clarify the ground-state magnetic structure of \( \text{Eu}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{As}_2 \), polarized neutron diffraction at 3.5 K was first performed at DNS. Figures 1(a) and 1(b) show the reciprocal-space contour maps of the \( (H, 0, L) \) plane, measured with the neutron polarization parallel to the scattering vector \( \mathbf{Q} \) (\( x \) polarization). The magnetic and nuclear scattering were separated into the spin-flip [SF, Fig. 1(a)] and non-spin-flip [NSF, Fig. 1(b)] channels, respectively [45]. The appearance of \( (0, 0, 2) \) and \( (0, 0, 4) \) reflections in the NSF channel are due to the imperfection of the polarization analysis and leakage from the XSF channel.

FIG. 1. Reciprocal-space contour maps in the \( (H, 0, L) \) plane for \( \text{Eu}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{As}_2 \) obtained at \( T = 3.5 \) K via polarized neutron diffraction at DNS, with the neutron polarization parallel to the scattering vector \( \mathbf{Q} \) (\( x \) polarization). Intensities in the (a) SF and (b) NSF channels correspond to the magnetic and nuclear reflections, respectively. The appearances of \( (0, 0, 2) \) and \( (0, 0, 4) \) reflections in the XSF channel are due to the imperfection of the polarization analysis and leakage from the X NSF channel.
The onset temperature of the SDW ordering can be estimated Figs. 3(b) and 3(c), respectively, as a function of temperature. Fe, were monitored at DNS and plotted using dark spheres in

In addition, magnetic reflections at (−1, 0, 1) and (−1, 0, 3) show up in the XSF channel, arising from the SDW ordering of the Fe moments with the propagation vector of \( k = (1, 0, 1) \) [20].

As shown in the inset of Fig. 2, the (0, 0, 3) magnetic reflection due to the AFM ordering of Eu disappears completely at 11 K in the XSF channel. The temperature dependence of its integrated intensity from the rocking scan is plotted in Fig. 2, indicating an ordering temperature of \( T_{\text{Eu}} = 10.0(5) \) K, well consistent with that from the macroscopic measurements. The temperature dependence of the integrated intensity, which is proportional to the square of the order parameter, shows a very unusual behavior. Starting with a negative curvature around \( T_{\text{Eu}} \), it continues nearly linearly down to the lowest temperature reached in this experiment. Neither typical critical behavior, nor a tendency to saturation can be seen. As discussed below, we attribute this unusual temperature dependence to the interaction between the Eu and Fe sublattices.

The peak intensities of the (1, 0, 1) and (1, 0, 3) reflections in the XSF channel, both arising from the SDW ordering of Fe, were monitored at DNS and plotted using dark spheres in Figs. 3(b) and 3(c), respectively, as a function of temperature. The onset temperature of the SDW ordering can be estimated to be \( T_{\text{SDW}} = 192(2) \) K, consistent with the high-temperature anomaly shown in the resistivity and specific heat data. Interestingly, both order parameters display a kink at the AFM ordering temperature of Eu (\( T_{\text{Eu}} = 10 \) K). Below \( T_{\text{Eu}} \), the peak intensity of (1, 0, 1) reflection increases steadily, while (1, 0, 3) weakens visibly with decreasing temperature. As shown in the insets of Figs. 3(b) and 3(c), rocking scans of the (1, 0, 1) and (1, 0, 3) reflections in the XSF channel indeed show opposite temperature-dependent tendencies. The temperature dependencies of the integrated intensity of both reflections were also measured at the four-circle neutron diffractometer HEiDi. The same behaviors were observed as shown using the open circles in Figs. 3(b) and 3(c), further confirming the different responses of (1, 0, 1) and (1, 0, 3) reflections to the AFM ordering of the Eu\(^{2+}\) moments and suggesting a possible spin reorientation of the Fe sublattice below \( T_{\text{Eu}} \). Figure 3(a) also shows the temperature dependencies of the integrated intensity and full width at half maximum (FWHM) of the (4, 0, 0) nuclear reflection measured at HEiDi. The sudden jump of the intensity and broadening of the peak width indicates the occurrence of a structural phase transition in Eu\(_2\)Ca\(_{0.5}\)Fe\(_2\)As\(_2\) from a tetragonal (space group \( I4/mmm \)) to an orthorhombic (space group \( Fmmn \)) phase at \( T_S = 191(2) \) K, coincident with the SDW ordering of Fe at \( T_{\text{SDW}} \), due to the change of extinction conditions of strong nuclear Bragg reflections caused by the emergent orthorhombic domains.

To better understand the interplay of the magnetism between Eu and Fe sublattices in Eu\(_2\)Ca\(_{0.5}\)Fe\(_2\)As\(_2\), the integrated intensities of 357 nuclear reflections and 254 magnetic reflections from Eu were collected at HEiDi at the base temperature (2.5 K). In addition, 246 nuclear reflections were collected above \( T_{\text{Eu}} \) (11 K). The obtained data sets at both
temperatures were normalized to the monitor and corrected by the Lorentz factor. After the absorption correction procedure using the DAMAP program taking into account the dimensions of the crystal [46], equivalent reflections were merged into the unique ones based on the orthorhombic symmetry. The nuclear structures at 2.5 and 11 K were refined using the FULLPROF program taking into account the dimensions of the crystal [46], equivalent reflections were merged into the unique ones based on the orthorhombic symmetry.

The magnetic structures of Eu0.5Ca0.5Fe2As2 at 2.5 K and 11 K are illustrated in Figs. 5(a) and 5(b), respectively. As concluded above, at 11 K (slightly above T Eu), the Eu sublattice is not magnetically ordered yet while the Fe sublattice displays an in-plane AFM structure. With further decreasing temperature, the Eu2+ moments start to order, while the Fe2+ moments tend to rotate towards the c axis within the ac plane, as reflected by the opposite temperature-dependent tendencies of its magnetic order parameters shown in Fig. 3. At the reachable base temperature (2.5 K) at HEIDi, the Eu2+ spins are found to align along the orthorhombic a axis within the ab plane. In other words, the spin reorientation of the Fe2+ moments occurs in coincidence with the AFM ordering of Eu, suggesting a strong interplay between the two magnetic sublattices in Eu0.5Ca0.5Fe2As2.

| Eu/Ca | B (Å²) | M_e (μ_B) | Fe | B (Å²) | 0.68(4) | 0.66(2) |
|-------|--------|-----------| As | B (Å²) | 0.3646(2) | 0.3646(2) |
|       |        |           |    |        | 0.73(5) | 0.70(3) |
| R_{F2} | 6.75 | 14.3 | 6.75 | R_{wF2} | 6.14 | 8.49 | 4.51 |
| R_F | 3.60 | 10.9 | 3.57 | \chi^2 | 4.89 | 2.31 | 9.43 |

Table I. Refined results for the nuclear structure and Eu magnetic structure of Eu0.5Ca0.5Fe2As2 at 2.5 K, as well as the nuclear structure at 11 K. The atomic positions are as follows: Eu0.5Ca0.5Fe2As2 at 2.5 K and fixed at 11 K, to be 48(4)% and 52(4)% of the Fe2+ moments. All the details about the model refinements of the magnetic structure of Fe were included in the Supplemental Material [44].

The magnetic structures of Eu0.5Ca0.5Fe2As2 at 11 and 2.5 K are illustrated in Figs. 5(a) and 5(b), respectively. As concluded above, at 11 K (slightly above T Eu), the Eu sublattice is not magnetically ordered yet while the Fe sublattice displays an in-plane AFM structure. With further decreasing temperature, the Eu2+ moments start to order, while the Fe2+ moments tend to rotate towards the c axis within the ac plane, as reflected by the opposite temperature-dependent tendencies of its magnetic order parameters shown in Fig. 3. At the reachable base temperature (2.5 K) at HEIDi, the Eu2+ spins are found to align along the a axis in the A-type AFM structure similar to the undoped parent compound, while the Fe2+ moments are ordered in a canting AFM structure with a canting angle of 14(4)° out of the ab plane. In other words, the spin reorientation of the Fe2+ moments occurs in coincidence with the AFM ordering of Eu, suggesting a strong interplay between the two magnetic sublattices in Eu0.5Ca0.5Fe2As2.
IV. DISCUSSION AND CONCLUSION

We note that the magnetic order parameter of the Eu sublattice in Fig. 2 does not saturate down to 3.5 K. However, refinements using the magnetic reflections from Eu yield the moment size of $6.74(4)\mu_B$, well consistent with a full moment of $\mu_S = g_S = 7\mu_B$ expected for the Eu$^{2+}$ spins with $S = 7/2$. This means that the Eu sublattice is fully magnetically ordered at 3.5 K. Thus, the unusual temperature dependence in Fig. 2 is very likely to arise from the change of the strength of Eu-Fe magnetic interaction concomitant with the spin reorientation of the Fe$^{2+}$ spin moments. As well documented, the coupling between two AFM sublattices may arise from quantum fluctuations via the so-called “order-by-disorder” mechanism [50–53]. The strong Eu-Fe coupling in Eu$_0$Ca$_0$Fe$_2$As$_2$, therefore, might be due to the longitudinal fluctuations of the Eu$^{2+}$ spins, which lead to a considerable change in the magnetic anisotropy energy and result in the spin reorientation of the Fe$^{2+}$ moments. For the EuFe$_2$As$_2$ system, our observation here provides experimental evidence of spin reorientation of Fe below the Eu magnetic ordering temperature. Eu$_0$Ca$_0$Fe$_2$As$_2$, therefore, undoubtedly exhibits a strong Eu-Fe interplay. However, this is not contradictory with the weak Eu-Fe coupling in the parent compound EuFe$_2$As$_2$ [20–22], since it was found that the strength of interplay between 3$d$ and 4$f$ electrons can be tunable by chemical doping [54]. Compared with undoped EuFe$_2$As$_2$, the out-of-plane lattice constant $c$ shrinks considerably by ~1% upon 50% Ca substitution. As a result, the nearest Eu-Fe distance reduces by 0.7% from 3.591 Å (in EuFe$_2$As$_2$) to 3.567 Å (in Eu$_0$Ca$_0$Fe$_2$As$_2$), favoring a stronger Eu-Fe spin interaction. Further theoretical studies on Eu$_0$Ca$_0$Fe$_2$As$_2$ will be very helpful for understanding its intriguing magnetic properties and strong Eu-Fe interplay in it.

In conclusion, using complementary polarized and unpolarized single-crystal neutron diffraction, we have investigated the temperature-dependent magnetic structures of Eu$_0$Ca$_0$Fe$_2$As$_2$. Upon 50% dilution of the Eu sites with isovalent Ca$^{2+}$, the Eu sublattice is found to be still long-range ordered below $T_{Eu} = 10$ K, in the A-type AFM structure. The moment size of Eu$^{2+}$ spins is estimated to be as large as $6.74(4)\mu_B$ at 2.5 K. The Fe sublattice undergoes a SDW transition at $T_{SDW} = 192(2)$ K and displays an in-plane AFM structure above $T_{Eu}$. However, at 2.5 K, the Fe$^{2+}$ moments are found to be ordered in a canted AFM structure with a canting angle of 14(4)$^\circ$ out of the $ab$ plane. The spin reorientation of Fe below the AFM ordering temperature of Eu provides direct evidence of a strong interplay between the two magnetic sublattices in Eu$_0$Ca$_0$Fe$_2$As$_2$.

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