Evolution from helical to collinear ferromagnetic order of the Eu\(^{2+}\) spins in RbEu(Fe\(_{1-x}\)Ni\(_x\))\(_4\)As\(_4\)

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The ground-state magnetic structures of the Eu\(^{2+}\) spins in recently discovered RbEu(Fe\(_{1-x}\)Ni\(_x\))\(_4\)As\(_4\) superconductors have been investigated by neutron powder diffraction measurements. It is found that as the superconductivity gets suppressed with the increase of Ni doping, the magnetic propagation vector of the Eu sublattice diminishes, corresponding to the decrease of the rotation angle between the moments in neighboring Eu layers. The ferromagnetic Eu layers are helically modulated along the \(c\) axis with an incommensurate magnetic propagation vector in both the ferromagnetic superconductor RbEu(Fe\(_{0.95}\)Ni\(_{0.05}\))\(_4\)As\(_4\) and the superconducting ferromagnet RbEu(Fe\(_{0.93}\)Ni\(_{0.07}\))\(_4\)As\(_4\). Such a helical structure transforms into a purely collinear ferromagnetic structure for non-superconducting RbEu(Fe\(_{0.91}\)Ni\(_{0.09}\))\(_4\)As\(_4\), with all the Eu\(^{2+}\) spins lying along the tetragonal (1 1 0) direction. The evolution from helical to collinear ferromagnetic order of the Eu\(^{2+}\) spins with increasing Ni doping is supported by first-principles calculations. The variation of the rotation angle between adjacent Eu\(^{2+}\) layers can be well explained by considering the change of magnetic exchange couplings mediated by the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.

I. INTRODUCTION

The discovery of iron-based superconductors in 2008 has stimulated worldwide research interests in the investigations of the interplay between magnetism and unconventional superconductivity in these novel materials. Among various members of the iron-based superconductors, the ternary compound EuFe\(_2\)As\(_2\) (Eu122) system is a unique representative and possesses the "1144"-type structure. The intriguing coexistence of ferromagnetism and superconductivity revealed in the Eu122 system drives the experimental efforts to further explore other novel Eu-containing iron-based superconductors.

In 2016, superconductivity with the transition temperature \(T_{SC}\) of approximately 31-36 K was discovered in a new family of iron pnictides Ca\(_3\)Fe\(_4\)As\(_4\) and Sr\(_4\)Fe\(_4\)As\(_4\) (\(A = \text{K, Rb, Cs}\)) possessing the "1144"-type structure. Later on, RbEuFe\(_4\)As\(_4\) (denoted as Eu1144 below), crystallizing as an intergrowth structure of heavily hole-doped superconducting RbEuFe\(_2\)As\(_2\) \(T_{SC} = 2.6\) K and non-superconducting EuFe\(_2\)As\(_2\), was reported to be a superconductor as well with \(T_{SC} = 36\) K. The FeAs layers in Eu1144 are intrinsically hole doped due to the charge homogenization associated with the structural hybridization, which is responsible for the absence of Fe-SDW order and the occurrence of superconductivity. Ascribing to the longer interlayer distance between the Eu layers in Eu1144 compared to Eu122, the Eu\(^{2+}\) spins order magnetically at a lower temperature of \(T_m = 15\) K.

Based on the magnetization and specific heat data obtained from high-quality powder samples, RbEuFe\(_4\)As\(_4\) was speculated to be a ferromagnetic superconductor with a robust coexistence of superconductivity and ferromagnetism. Neutron diffraction measurements on a Eu1144 single crystal have been performed to clarify how the two-dimensional in-plane ferromagnetic Eu layers stack along the \(c\) axis. A magnetic propagation vector of \(k = (0, 0, 0.25)\) is revealed, suggesting the rotation angle of 90\(^o\) between the in-plane ferromagnetically aligned Eu\(^{2+}\) spins on adjacent layers. Such a helical magnetic structure of undoped Eu1144 is in stark contrast to the collinear A-type AFM structure of undoped EuFe\(_2\)As\(_2\), but resembles those of EuCo\(_2\)As\(_2\) and EuNi\(_2\)As\(_2\), showing an incommensurate magnetic propagation vector of \(k = (0, 0, 0.79)\) and \(k = (0, 0, 0.92)\), respectively.

By introducing extra itinerant electrons via the substitution of Ni\(^{2+}\) (3d\(^9\)) for Fe\(^{2+}\) (3d\(^8\)), the intrinsically doped hole carriers in RbEuFe\(_4\)As\(_4\) can be compensated. Systematic macroscopic characterizations including resistivity,
magnetization, and specific heat measurements have been performed on polycrystalline and single-crystal samples of RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ to establish the superconducting and magnetic phase diagram. It is figured out that $T_{SC}$ decreases rapidly with the Ni doping, while the magnetic ordering temperature of the Eu sublattice, $T_m$, remains essentially unchanged. Consequently, RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ transforms from the ferromagnetic superconductor (FSC) with $T_{SC} > T_m$ for $x < 0.07$, to the so-called “superconducting ferromagnet” (SFM) with $T_m > T_{SC}$ for $0.07 \leq x \leq 0.08$, and finally to the ferromagnetic non-superconductor for $x > 0.09$. Furthermore, a recovered Fe-AFM state is proposed for 0.04 $\leq x \leq 0.10$ based on the resistivity data on polycrystalline samples.

As the helical magnetic order of the Eu$^{2+}$ spins with a two-dimensional (2D) character in undoped Eu1144 is proposed to be associated with the presence of superconductivity, it is of great interest to clarify how the magnetic structure of RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ develops against the weakening of the superconductivity induced by Ni doping. Fitting to the magnetic susceptibility in the paramagnetic state yields comparable positive values of Curie-Weiss temperature for samples with different $x$. Reflecting dominant in-plane ferromagnetic interactions between the Eu$^{2+}$ moments. Detailed neutron diffraction measurements on RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ will deliver important information regarding how the stacking pattern of the ferromagnetic Eu layer along the $c$ axis changes with $x$ and how it is correlated with the suppression of superconductivity.

Here we present a systematic study of the magnetic structures of Ni-doped Eu1144 with different doping levels as determined by neutron powder diffraction. We find that as the superconductivity gets suppressed gradually with the increase of Ni doping, the magnetic propagation vector of the Eu sublattice diminishes, corresponding to the decrease of the rotation angle between the moments in neighboring Eu layers. No evidence of the proposed recovery of Fe-SDW order is observed within our experimental resolution. The variation of the rotation angle between adjacent Eu$^{2+}$ layers can be well explained by considering the change of magnetic exchange couplings mediated by the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.

II. EXPERIMENTAL DETAILS AND CALCULATION METHODS

Polycrystalline samples of RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ ($x = 0.05$, 0.07 and 0.09) of ~ 4 g were synthesized by the solid-state reaction method as described in Ref. 22. The phase purity was checked by x-ray diffraction (XRD) on a PANalytical x-ray diffractometer with a monochromatic Cu-Kα$_1$ radiation. The doping concentration of Ni in three samples was checked by energy-dispersive x-ray spectroscopy (EDS), to be 5.6(6) %, 7.1(8) %, 8.9(5) %, respectively, well consistent with the nominal values. A small amount of FeAs impurity was found to exist in the samples with $x = 0.05$ and 0.07, and small amounts of RbFe$_2$As$_2$ and EuFe$_2$As$_2$ impurities were identified in the sample with $x = 0.09$. Low-temperature neutron powder diffraction (NPD) measurements on the samples with $x = 0.05$ were performed on the high-intensity powder diffractometer Wombat$^{26}$ at the OPAL facility (Lucas Height, Australia) using incident neutrons with the wavelength of 2.41 Å and 1.54 Å, while the data of the sample with $x = 0.07$ were collected using the 1.54 Å wavelength only. NPD measurements on the sample with $x = 0.09$ were performed on the high-intensity powder diffractometer D20 at Institut Laue-Langevin (Grenoble, France) using incident neutrons with the wavelength of 2.41 Å and 1.30 Å. In order to minimize the effect of neutron absorption by the Eu atoms, we have filled the powder samples into the double-wall hollow vanadium cylinder. Refinements of both nuclear and magnetic structures were carried out using the FullProf program suite.$^{27}$

The first-principles calculations presented in this paper are performed using the projected augmented-wave method,$^{28}$ as implemented in the VASP code.$^{29}$ The exchange correlation potential is calculated using the generalized gradient approximation (GGA) as proposed by Perdew, Burke, and Ernzerhof.$^{30}$ We have included the strong Coulomb repulsion in the Eu-4$f$ orbitals on a mean-field level using the GGA+$U_{eff}$ approximation. Since there exist no spectroscopy data for RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$, we have used a $U_{eff}$ of 8 eV throughout this work, which is the standard value for an Eu$^{2+}$ ion.$^{12,13,31}$ The results have been checked for consistency with varying $U_{eff}$ values. $U_{eff}$ is not applied to the itinerant Fe-3$d$ and Ni-3$d$ orbitals. Additionally, the spin-orbit coupling is included for all atoms with the second variational method in the calculations. These calculations are performed using the experimental crystal structure, as determined by the neutron diffraction measurements.

III. RESULTS

The ground-state magnetic structures of the Eu$^{2+}$ spins in RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ with different Ni doping levels ($x = 0.05$, 0.07 and 0.09) are determined by NPD measurements and illustrated in Figure 1(b, c, d), together with the helical magnetic structure of undoped RbEuFe$_4$As$_4$ ($x = 0$) with $k = (0, 0, 0.25)$ (Fig. 1(a)) as determined in Ref. 19, which will be discussed in detail below.

Figure 2 shows the NPD patterns of RbEu(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$ at 20 K and 3.9 K. According to the superconducting and magnetic phase diagram of RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ deduced from macroscopic measurements in Ref. 22, for this composition, the temperature of 20 K is above $T_m(15$ K) but below $T_{SDW}(= 28.9$ K), which is the SDW ordering temperature of Fe. As shown in Fig. 2(a) and 2(c), the diffraction patterns at 20 K can be well fitted with the crystal structure reported in Ref. 22 (space group $P4/mnm$) with a small amount of FeAs impurity ($7\%$ wt). Within our experimental uncertainty, no magnetic reflections at (0.5, 0.5, 3) ($Q = 1.84 \text{ Å}^{-1}$) associated with possible Fe-AFM order can be identified, assuming that the Fe$^{2+}$ moments order in the hedgehog spin-vortex crystal (SVC) motif in each Fe plane and are antiferromagnetically stacked.
along the $c$ direction, similar to that observed in isostructural CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$.\cite{32,33}

Upon cooling down to 3.9 K, which is well below $T_m$, the magnetic reflections due to the magnetic ordering of Eu appear as satellite peaks close to the nuclear reflections. As shown in Fig. 2(d), the incident neutron wavelength of $\lambda = 2.41$ Å provides a better resolution at low-$Q$ region, confirming the incommensurate nature of the magnetic peaks. The magnetic reflections at (0 0 2)$^-$//(0 0 2)$^+$ and (0 0 3)$^-$//(0 0 3)$^+$ emerge in both sides of the (0 0 2) and (0 0 3) peaks, as illustrated in Fig. 1(e) and 1(f). Using the k_search program integrated in the FullProf suite, the magnetic propagation vector of $k = (0, 0, 0.136(4))$ is figured out for RbEu(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$.

According to the representation analysis performed using the Basfrep program also integrated in the FullProf suite (see the supplemental materials for details), for the space group of $P4/mmm$, only two magnetic representations are possible for the Eu (1a) site with the propagation vector of $k = (0, 0, 0.136(4))$, which we label as $\Gamma_1$ and $\Gamma_5$, respectively. $\Gamma_1$ allows the $c$-axis aligned ferromagnetic Eu layers stacking with modulated moment size values at different layers, which is not consistent with the easy-plane magnetization as revealed from the single-crystal sample with a similar Ni doping level.\cite{23}

Figure 1: The ground-state magnetic structure of RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ with $x = 0$ (a), $x = 0.05$ (b), $x = 0.07$ (c), and $x = 0.09$ (d), in which the rotation angle between the in-plane ferromagnetically aligned Eu$^{2+}$ moments on adjacent layers are 90°, ~49°, ~26°, and 0°, respectively.

Figure 2: NPD patterns of RbEu(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$ at 20 K (a, c) and 3.9 K (b, d) and the Rietveld refinments. The left (a, b) and right (c-f) panels show the data collected using the incident neutron wavelength of 1.54 Å and 2.41 Å, respectively. The patterns in (b) and (d) are the refinement results obtained by adopting a magnetic structure model with the irreducible representation $\Gamma_5$ as described in the text. The circles represent the observed intensities, and the solid lines are the calculated patterns. The differences between the observed and calculated intensities are shown at the bottom. The vertical bars in olive, magenta, navy and orange colors indicate the expected nuclear Bragg reflections from the RbEu(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$ main phase, FeAs impurity, vanadium sample container and the magnetic Bragg reflections from RbEu(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$, respectively. (e) and (f) show the enlarged high-resolution diffraction patterns at 3.9 and 20 K around the (0 0 2) and (0 0 3) nuclear peak positions, respectively, visualizing the incommensurate magnetic satellite reflections appearing at 3.9 K.
the other hand, $\Gamma_5$ allows the in-plane aligned ferromagnetic Eu layers to stack helically along the $c$ axis, with a constant moment size value at different layers. This model fits pretty well to the diffraction patterns at 3.9 K, as shown by the solid curves in Fig. 2(b) and 2(d). As a comparison between the fitting using $\Gamma_5$ and $\Gamma_1$, Fig. S2 in the supplemental materials shows a better agreement of $\Gamma_5$ with the observed intensities in the very low-Q region, where the magnetic form factor dominates. The nuclear structure parameters and the scale factor derived from the refinement of 20 K data was fixed in the refinement of 3.9 K data to derive the moment size of Eu to be 6.3(2) $\mu_B$, as listed in Table 1. As illustrated in Fig. 1(b), the Eu$^{2+}$ moments form an incommensurate helical structure, with the moment direction lying in the $ab$ plane but rotating by $\sim 49^\circ$ around the $c$ axis with respect to adjacent Eu layers. Using the Bilbao Crystallographic Server, the magnetic space group of this helical structure is determined to be $Pm\bar{1}m'$ ($No. \text{47.252}$).

Figure 3 shows the NPD patterns of RbEu(Fe$_{0.91}$Ni$_{0.09}$)$_4$As$_4$ at 20 K and 2 K. This sample is non-superconducting as evidenced from previous macroscopic characterizations. It undergoes the magnetic ordering of Eu sublattice at $T_m$ ($= 14.7$ K) and a possible recovered Fe-SDW ordering at $T_{SDW}$ ($= 31.3$ K). Similar to the case of $x = 0.5$ presented above, no visible change of intensities at $(0.5, 0.5, 1)$ ($Q = 1.25$ Å$^{-1}$) and $(0.5, 0.5, 3)$ ($Q = 1.84$ Å$^{-1}$) associated with the Fe-AFM order can be resolved at 20 K compared with 40 K (data of which is not shown). The diffraction patterns at 20 K can be well fitted using the nuclear crystal structure in the space group of $P4/mmm$, together with small amount impurities phases of RbFe$_2$As$_2$ (6.2% wt) and EuFe$_2$As$_2$ (4.4% wt), as shown in Fig. 3(a) and 3(c).

In stark contrast to the magnetic satellite peaks displayed in RbEu(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$ arising from the helical magnetic structure of Eu, here at 2 K, well below $T_m$, the magnetic scatterings due to the ordering of Eu$^{2+}$ spins appear on top of the nuclear reflections for RbEu(Fe$_{0.91}$Ni$_{0.09}$)$_4$As$_4$, which is shown in Fig. 3(e-g) for $Q = (001)$ (e), $(002)$ (f) and $(003)$ (g) measured with a high resolution using $\lambda = 2.41$ Å. This clearly indicates a magnetic propagation vector of $k = 0$.

Magnetic representation analysis for $k = 0$ for the space group of $P4/mmm$ yields only two possible irreducible representations for the Eu(1a) site (see the supplemental materials for details), labeled as $\Gamma_8$ and $\Gamma_9$, respectively. They correspond to the collinear ferromagnetic structures in which all the Eu$^{2+}$ moments are aligned along the $c$ axis and in the $ab$ plane, respectively. Although no magnetization data on single-crystal RbEu(Fe$_{0.91}$Ni$_{0.09}$)$_4$As$_4$ is available, the moment direction of Eu$^{2+}$ spins can still be identified according to the nature of magnetic neutron diffraction. As the magnetic scattering is only sensitive to the component of the moment perpendicular to $Q$, dramatic enhancements of intensities of $(00L)$ peaks and no visible changes of $(H00)$ peak intensities suggest that the Eu$^{2+}$ moments are mostly lying in the $ab$ plane so that the magnetic structure model described by $\Gamma_8$ can be excluded. Indeed the $\Gamma_9$ model with all spins aligned along in-plane $(110)$ direction fits the diffraction patterns at 2 K quite well, as shown by the solid curves in Fig. 3(b) and 3(d). The fraction of the EuFe$_2$As$_2$ impurity phase is quite

Figure 3: NPD patterns of RbEu(Fe$_{0.91}$Ni$_{0.09}$)$_4$As$_4$ at 20 K (a, c) and 2 K (b, d) and the Rietveld refinements. The left (a, b) and right (c-g) panels show the data collected using the incident neutron wavelength of 1.30 Å and 2.41 Å, respectively. The patterns in (b) and (d) are the refinement results obtained by adopting a magnetic structure model with the irreducible representation $\Gamma_9$ as described in the text. The circles represent the observed intensities, and the solid lines are the calculated patterns. The differences between the observed and calculated intensities are shown at the bottom. The vertical bars in olive, magenta, gray, orange and purple colors indicate the expected nuclear Bragg reflections from the RbEu(Fe$_{0.91}$Ni$_{0.09}$)$_4$As$_4$ main phase, EuFe$_2$As$_2$ impurity, RbFe$_2$As$_2$ impurity, vanadium sample container, as well as the magnetic Bragg reflections from the RbEu(Fe$_{0.91}$Ni$_{0.09}$)$_4$As$_4$ main phase and the EuFe$_2$As$_2$ impurity, respectively. (e), (f) and (g) show the enlarged high-resolution diffraction patterns at 2 and 20 K around the $(001)$, $(002)$ and $(003)$ nuclear peak positions, respectively, illustrating the commensurate magnetic contributions with $k = 0$ at 2 K.
Table 1: Refined results for the nuclear and magnetic structure parameters of RbEu(Fe_{1-x}Ni_x)\textsubscript{4}As\textsubscript{4} with x = 0.05, 0.07 and 0.09. The atomic positions are as follows: Eu, 1a (0, 0, 0); Rb, 1d (0.5, 0.5, 0.5); Fe/Ni, 4i (0, 0.5, 0.5); As1, 2g (0, 0, z\textsubscript{As1}); As2, 2h (0.5, 0.5, z\textsubscript{As2}). The occupancies of Fe and Ni were fixed according to the nominal compositions, respectively. The nuclear structure parameters and the scale factor derived from the refinement of 20 K data was fixed in the magnetic-structure refinements (Space group: P\textsubscript{4}m\textsubscript{mm}).

| Composition          | Temperature | RbEu(Fe\textsubscript{0.92}Ni\textsubscript{0.08})\textsubscript{4}As\textsubscript{4} | RbEu(Fe\textsubscript{0.94}Ni\textsubscript{0.06})\textsubscript{4}As\textsubscript{4} | RbEu(Fe\textsubscript{0.91}Ni\textsubscript{0.09})\textsubscript{4}As\textsubscript{4} |
|---------------------|-------------|---------------------------------|---------------------------------|---------------------------------|
|                     | 20 K        | 3.9 K                           | 3.3 K                           | 20 K                            |
| Eu                  | B_{iso} (Å\textsuperscript{2}) | 1.3(1)                          | 1.2(1)                          | 0.22(5)                         |
|                     | M (μB)     | -                               | -                               | -                               |
| Rb                  | B_{iso} (Å\textsuperscript{2}) | 1.4(1)                          | 1.3(1)                          | 1.1(1)                          |
| Fe/Ni               | z\textsubscript{Fe} | 0.2309(2)                      | 0.2310(2)                      | 0.2315(1)                      |
|                     | B_{iso} (Å\textsuperscript{2}) | 1.0(1)                          | 0.8(1)                          | 0.26(1)                         |
| As1                 | z\textsubscript{As1} | 0.3344(4)                      | 0.3339(4)                      | 0.3339(2)                      |
|                     | B_{iso} (Å\textsuperscript{2}) | 1.1(1)                          | 0.8(1)                          | 0.24(3)                         |
| As2                 | z\textsubscript{As2} | 0.1263(4)                      | 0.1263(4)                      | 0.1277(2)                      |
|                     | B_{iso} (Å\textsuperscript{2}) | 1.3(1)                          | 0.8(1)                          | 0.24(3)                         |
| a (Å)               | 3.8652(4)   | 3.8651(2)                       | 3.8649(5)                       | 3.8646(2)                       |
| c (Å)               | 13.117(2)   | 13.117(1)                       | 13.109(2)                       | 13.108(1)                       |
| R_{Kx}              | 1.29        | 1.28                            | 1.31                            | 1.34                            |
| R_{wKx}             | 1.73        | 1.72                            | 1.83                            | 1.86                            |
| R_{F}               | 0.43        | 0.44                            | 0.42                            | 0.43                            |

small (4.4% wt), including the its magnetic phase in the refinement has no visible effect on the fitting of the 2 K data and the results about the 1144 main phase. Fixing the nuclear structure parameters and the scale factor derived from the refinement of 20 K data, the refinement of 2 K data yields the moment size of Eu to be 6.5(1) μB (see Table 1). Please note that a lower saturated moment of 6.0 μB/Eu for x = 0.09 in Ref. 22 is because of some nonmagnetic Eu\textsubscript{2}O\textsubscript{3} impurities forming in older samples due to oxidation of metallic Eu. In fact, the saturated moment of Eu\textsuperscript{2+} spins should be independent of the Ni doping level. The magnetic structure of RbEu(Fe\textsubscript{0.91}Ni\textsubscript{0.09})\textsubscript{4}As\textsubscript{4} is illustrated in Fig. 1(d). Compared with the undoped Eu1144 and RbEu(Fe\textsubscript{0.95}Ni\textsubscript{0.05})\textsubscript{4}As\textsubscript{4} with x = 0.05, the rotation angle between the moments in neighboring Eu layers diminishes to zero for RbEu(Fe\textsubscript{0.91}Ni\textsubscript{0.09})\textsubscript{4}As\textsubscript{4} with x = 0.09, forming a collinear in-plane ferromagnetic structure. The magnetic space group of this helical structure is determined to be C\textsuperscript{m}mm\textsuperscript{1}m\textsuperscript{1} (No. 65.486).

After presenting the results of RbEu(Fe\textsubscript{1-x}Ni\textsubscript{x})\textsubscript{4}As\textsubscript{4} with x = 0.05 and 0.09, we come to the magnetic structure determination of the SFM RbEu(Fe\textsubscript{0.93}Ni\textsubscript{0.07})\textsubscript{4}As\textsubscript{4} (T\textsubscript{SC} = 11.2 K) with T\textsubscript{m} and T\textsubscript{SDW} being 15.1 K and 35.0 K, respectively.\textsuperscript{23} As shown in Fig. 4(a), the diffraction pattern of RbEu(Fe\textsubscript{0.93}Ni\textsubscript{0.07})\textsubscript{4}As\textsubscript{4} at 20 K can be well fitted with the nuclear crystal structure in the space group of P\textsubscript{4}/m\textsubscript{mm} together with a small amount impurities phase of FeAs (5.9% wt). Again, no magnetic peaks at (0.5, 0.5, 3) arising from the Fe-AFM order can be identified. Upon cooling down to the base temperature of 3.3 K, the magnetic scattering due to magnetic ordering of Eu\textsuperscript{2+} spins sets in. Unfortunately the high-resolution datasets with λ = 2.41 Å is lacking for this sample, due to the limited neutron beamtime. However, by setting the magnetic propagation vector k itself as a variable parameter in the refinement of 3.3 K data, the diffraction pattern can be fitted pretty well with k finally converged to (0, 0, 0.071(7)) and the moment size of Eu\textsuperscript{2+} spins being 6.3(2) μB, as shown in Table 1 and Fig. 4(b). This result corresponds to a helical magnetic structure similar to that of RbEu(Fe\textsubscript{0.95}Ni\textsubscript{0.05})\textsubscript{4}As\textsubscript{4}, but with a smaller helix rotation angle of ~26°.

Using first-principles calculations, the energetic properties of different spin configurations of the Eu\textsuperscript{2+} moments are com-
The variation of the magnetic structure of Eu in RbEu(Fe_{1-x}Ni_x)As_4 can be understood semi-quantitatively in consideration of the exchange couplings. As the magnetism of Eu in Eu1144 is believed to be of a 2D character, the helix rotation angle $\theta$ between the ferromagnetic Eu$^{2+}$ layers predominantly depend on the competition between the nearest ($J_{1,1}$) and next-nearest ($J_{1,2}$) interlayer couplings (see Fig. 6(a)), with $\cos \theta = -J_{1,2}^{\text{RKKY}}$. These exchange couplings between interlayer Eu$^{2+}$ moments is realized through the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction $J_{\text{RKKY}}$, mediated by the conduction $d$ electrons on the FeAs layers, in the form of $J_{1,2} \propto J_{\text{RKKY}} \cos(2k_FR)/r^3$, where $r$ denotes the interlayer distance between the Eu$^{2+}$ moments and $k_F$ is the Fermi vector. Using first-principles calculations, it is figured out that the RKKY interaction strength $J_{\text{RKKY}}$ is isotropic and barely changed upon Ni-doping ($\sim 0.12$ meV).\cite{41} In the undoped Eu1144, $J_{1,1}$ is expected to be zero (for $\theta = 90^\circ$ and $\cos \theta = 0$), consistent with the 2D character of the Eu magnetism. This corresponds to $2k_Fr_0 = (2n+1)\pi/2$, with $k_F$ and $r_0$ being the Fermi vector and nearest interlayer distance between the Eu$^{2+}$ moments without Ni doping. $J_{1,2} \propto J_{\text{RKKY}} \cos(4k_FR)/r^3$ is therefore negative, responsible for the antiferromagnetic next-nearest interlayer coupling. As the hole carriers are compensated by the available, will be crucial to confirm the possibly restored antiferromagnetism in the Fe sublattice.

### IV. DISCUSSION AND CONCLUSION

As shown in Fig. 1, the magnetic structure of the Eu$^{2+}$ moments in RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ undergoes a smooth evolution from the helical structure, in which the in-plane ferromagnetically aligned Eu$^{2+}$ spins on adjacent layers rotate by 90°, gradually to a collinear ferromagnetic structure, in which all in-plane ferromagnetic Eu$^{2+}$ moments on adjacent layers are vertical, antiparallel, and parallel, respectively. As shown in Fig. 5(a), the magnetic structure of the Eu$^{2+}$ spins point along the tetragonal (1 1 0) direction. The $c$-component of the magnetic propagation vector, $k_z$, and the helix rotation angle ($\theta$) are plotted in Fig. 5(a) and 5(b) as a function of the Ni content $x$, respectively. Both of them diminish with increasing Ni content, in accordance with the gradual suppression of superconductivity as reported in Ref. 22.

It was reported recently that in isostuctural CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$, the Ni doping may lead to the emergence of a hedgehog-type spin-vortex crystal (SVC) order of the Fe moments,\cite{32,33} which is different from the stripe-type Fe-SDW order observed in “122” family iron pnictides.\cite{27,28} However, within our experimental resolution, the proposed recovery of Fe-AFM order with Ni doping can not be identified at $Q = (0.5, 0.5, L)$ ($L$ = integers), probably due to the weakness of related magnetic reflections from small Fe$^{2+}$ moments and high background in the NPD measurements. Future neutron diffraction experiments on large single-crystal samples of RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$, if available, will be crucial to confirm the possibly restored antiferromagnetism in the Fe sublattice.

Table 3: Energetic properties of the different spin configurations of the Eu$^{2+}$ moments for RbEu(Fe$_{0.875}$Ni$_{0.125}$)$_4$As$_4$. The results are the total energy difference per Eu atom. The helical, antiparallel and parallel configurations correspond to the magnetic structures in which the in-plane ferromagnetic Eu$^{2+}$ moments lying in the $ab$ plane is energetically favorable for RbEu(Fe$_{0.875}$Ni$_{0.125}$)$_4$As$_4$ with $x = 0.125$. These are well consistent with our experimental findings that the rotation angle between the moments in neighboring Eu layers diminishes with increasing Ni doping and the helical structure finally transforms into a purely collinear ferromagnetic structure.

| configurations | $\Delta E$(meV) | $E_{Mx}$(µB) |
|----------------|---------------|----------------|
| helical ($k = (0, 0, 0.25)$) | 0 | 6.986 |
| antiparallel | 49.71 | 6.962 |
| parallel | 49.21 | 6.962 |

Figure 5: The evolution of magnetic propagation vector $k = (0, 0, k_z)$ (a) and the rotation angle ($\theta$) of the Eu$^{2+}$ spins between adjacent Eu layers (b) in RbEu(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ as a function of the Ni content $x$. |
Figure 6: An illustration of the spin directions in different layers of the helical magnetic structure (a) and a semi-quantitative description of the interlayer couplings as well as the rotation angle \( \theta \) in the helix as a function of \( k_F r \) (b). The nearest \( (J_{c1}, \text{black solid line}) \) and next-nearest \( (J_{c2}, \text{red solid line}) \) interlayer couplings are assumed to be in the form of \( J_{c1} = C J_{RKKY} \cos(2k_F r)/r^3 \) and \( J_{c2} = C J_{RKKY} \cos(4k_F r)/(2r)^3 \), respectively, where \( C \) is a scaling constant. The helix rotation angle \( \theta \) (in the inset) is then calculated using \( \cos \theta = -\frac{J_{c2}}{4J_{c1}} \). The vertical dashed lines in (b) mark the possible \( k_F r \) values of undoped Eu1144, where \( J_{c1} = 0 \) and \( J_{c2} < 0 \). Assuming that for undoped Eu1144 \( k_F r = 2.5 \pi \), the black, red, and olive arrows next to the corresponding solid circles represent the shifts of \( J_{c1}, J_{c2} \), and \( \theta \) values with the decrease of \( k_F r \) induced by Ni doping. The blue diamonds in the inset of (b) represent the \( \theta \) values for different Ni content \( x \) determined experimentally as shown in Fig. 5(b) for comparison.

It is argued that the emergence of helical magnetic structure with a period of four unit cells along the \( c \) axis in undoped Eu1144 \( (k = (0, 0, 0.25)) \) is favored by the exchange interaction between superconductivity and ferromagnetism, as predicted by Anderson and Suhl long time ago to be one solution for the compromise between these two antagonistic phenomena. As an alternate scenario, it is proposed theoretically that the ferromagnetic contribution to the interlayer RKKY interaction from the non-superconducting normal parts and the antiferromagnetic contribution from the superconducting layers compete with each other, giving rise to the helical ground-state magnetic configuration as a result of frustration. It is worth pointing out that our experimental results are also qualitatively consistent with these arguments. On one hand, the helix rotation angle \( \theta \) diminishes with Ni doping, thus releasing the frustration in favor of a collinear ferromagnetic structure. On the other hand, according to the prediction by Anderson and Suhl, the periodicity of the spin helix \( d \) is correlated with the superconducting coherence length \( \xi_0 \) in the form of \( d \propto (\xi_0)^{1/3} \). As the superconducting transition temperature \( T_{SC} \) and the upper critical field \( H_{c2} \) decrease with increasing Ni doping, \( \xi_0 \) increases according to the Ginzburg-Landau formalism \( H_{c2} = \Phi_0/2\pi\xi_0^2 \), which is consistent with the diminishing \( \theta \) and increasing helix periodicity \( d \). Although some recent spectroscopic measurements seem to suggest the decoupling of magnetism from Eu from superconducting FeAs layers, we note that a recent scanning Hall microscopy experiment has revealed a pronounced suppression of the superfluid density near the Eu magnetic ordering temperature in Eu1144, indicating a pronounced exchange interaction between the superconducting and magnetic subsystems.

In conclusion, the magnetic structures of RbEu(Fe_{1−x}Ni_x)_{4}As_{4} superconductors are systematically investigated by neutron powder diffraction. It is found that as the superconductivity gets suppressed gradually with the increase of Ni doping, the magnetic propagation vector of the Eu sublattice diminishes, corresponding to the decrease of the rotation angle between the moments in neighboring Eu layers with a helical structure. For non-superconducting RbEu(Fe_{0.91}Ni_{0.09})_{4}As_{4}, all the Eu^{2+} spins point along the tetragonal (1 1 0) direction, forming a purely collinear ferromagnetic structure. Such an evolution from helical to collinear ferromagnetic order of the Eu^{2+} spins with increasing Ni doping is well supported by first-principles calculations. The variation of the rotation angle between adjacent Eu^{2+} layers can be well explained by considering the change of magnetic exchange couplings mediated by the indirect RKKY interaction.
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