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Unique crystal field splitting and multiband RKKY interactions in Ni-doped $\text{EuRbFe}_4\text{As}_4$

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The relationship between magnetism and superconductivity has been one of the most discussed topics in iron-based superconductors. Using first-principles calculations, we have studied the electronic structure of 1144-type iron-based superconductor $\text{EuRbFe}_4\text{As}_4$. We find the crystal field splitting of $\text{EuRbFe}_4\text{As}_4$ is unique, such that the d_{z^2} orbitals are closer to the Fermi level ϵ_F than the d_{xy} orbitals. The Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction strength is approximately 0.12 meV in pristine $\text{EuRbFe}_4\text{As}_4$. Upon Ni-doping on the Fe site, the RKKY interaction strength is barely changed upon Ni-doping due to the highly anisotropic Fermi surfaces and multiband effect, despite the drastically reduced $d_{zx(y)}$ density of state at ϵ_F . Finally, in both pristine and doped compounds, the RKKY interaction is primarily mediated through bands due to Fe- d_{z^2} orbitals. Our calculations suggest the RKKY interaction mediated by d_{z^2} orbital is probably responsible for the magnetism in $\text{EuRbFe}_4\text{As}_4$ and doesn't change upon Ni-doping.

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Over the last decade, enormous efforts have been put on iron-based superconductors (FeSCs) since the first discovery of superconductivity in F-doped LaOFeAs in 2008¹. To date the relationship between magnetism and superconductivity has been extensively investigated both experimentally and theoretically to pursue the essence of pairing mechanism. As a matter of fact, a multitude of the FeSCs are magnetic metals with quasi-2D electron and hole pockets. Usually the parent compounds of FeSCs are non-superconducting and undergo structural transition from tetragonal lattice to orthorhombic lattice followed by a spin density wave (SDW) transition when the temperature is decreased. Once the system is doped, however, both structural and SDW transitions are suppressed and superconductivity emerges^{2,3}.

Recently a new type of FeSC structure, AeFe₄As₄ (AeA-1144; Ae = Ca, Sr; A = K, Rb, Cs), has been successfully synthesized by Iyo et al.⁴ with superconducting transition temperature $T_c > 30$ K without doping. Despite the same stoichiometric ratio, these 1144-type compounds are different from the 50% K-doped BaFe₂As₂ compounds such that the Ae atoms are separated from the A atoms in different layers, and therefore the structure can be viewed as layer-by-layer stacked AeFe₂As₂ (Ae-122) and AFe₂As₂ (A-122). Independently, Liu et al. and Kawashima et al.^{5,6} managed to make an intergrowth structure of RbFe₂As₂ and EuFe₂As₂ leading to another 1144-type compound EuRbFe₄As₄. Similar to the AeAFe₄As₄ (Ae = Ca, Sr; A = K, Rb, Cs) compounds, EuRbFe₄As₄ exhibits superconductivity at 35 K without any doping. In addition, ferromagnetic (FM) behavior due to the Eu-layers was observed below 15 K without destroying the superconductivity, suggesting a robust coexistence of superconductivity and ferromagnetism⁵. The 4*f* electrons are nearly fully localized, yielding a large moment of 6.5 μ_B /Eu. Interestingly, the Curie temperature was robust against the Ni-doping, while the superconducting T_{sc} was very sensitive⁷. It was therefore conjectured that the *d*-*f* superexchange or Eu-As-Eu superexchange is likely to be the mechanism mediating the magnetic interactions.

In this article, we present a systematic first-principles study of EuRbFe₄As₄ compound. We compare EuRbFe₄As₄ with the CaRbFe₄As₄ as well as the traditional BaFe₂As₂ compound. The band structure of EuRbFe₄As₄ resembles that of CaRbFe₄As₄, and there are ten bands crossing the Fermi level in both compounds. However, the *d*_{z²}-band in EuRbFe₄As₄ is now elevated close to ϵ_F around the Γ point; thus, the undoped EuRbFe₄As₄ system is very close to a Lifshitz transition. As a result, the *d*_{z²}-orbital is more

relevant in the process of electrical transport and magnetism in the EuRbFe₄As₄ compound. By decomposing the J_{RKKY} into contributions from different Fermi surface (FS) sheets, we find this interaction is primarily mediated by the outmost hole pocket due to *d*_{z²} orbital around the Γ point, suggesting that this orbital is important to the Eu-magnetism. Under nickel doping, the Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction is little affected, despite the drastically reduced density of state (DOS) from *d*_{xz} and *d*_{yz} orbitals. This may serve as a possible explanation why the magnetic transition T_{FM} is relatively constant while the superconductivity T_{sc} is quickly suppressed by Ni-doping in this compound.

Results

Crystal structure and electronic structure. The crystal structure of EuRbFe₄As₄ is tetragonal P4/mmm with lattice parameters $a = 3.89$ Å and $c = 13.31$ Å as illustrated in Fig. 1a. The crystal consists of FeAs-layers separated by alternating Rb-layers and Eu-layers. Therefore, each unit cell contains two FeAs-layers that are mirror-symmetric with respect to either the Rb-layer or the Eu-layer. In contrast to most traditional FeSCs, the two intercalating layers sandwiching each FeAs-layer are different in 1144-type FeSCs; thus the Fe atom is no longer located at the center of the tetrahedral formed by the four closest As atoms (Fig. 1b). Therefore, the S_4 local symmetry around each Fe is reduced to C_2 in 1144-type FeSCs.

The band structures of EuRbFe₄As₄ (red line), CaRbFe₄As₄ (black line), and folded BaFe₂As₂ (blue line, Γ –X) in paramagnetic (PM) phase are shown in Fig. 2a, b. Both EuRbFe₄As₄ and CaRbFe₄As₄ exhibit the same number of hole pockets around Γ points and electronic pockets around M points, and the dispersions resemble each other. Nevertheless, the highest occupied state at Γ is extremely close to the Fermi level ϵ_F in EuRbFe₄As₄ (while in CaRbFe₄As₄ it is more than 200 meV below ϵ_F), suggesting the undoped EuRbFe₄As₄ system is on the edge to a Lifshitz transition. Projected band structure shows that the orbital character of this state is *d*_{z²}. With slight hole-doping (0.5 hole per f.u.), this band will cross Fermi level and create a new Fermi surface sheet. In Ba_{1-x}Rb_xFe₂As₂, it was reported that a crossover from nodeless to nodal superconducting occurs at $x = 0.65$ as a result of a hole-doping-induced Lifshitz transition⁸. Considering the similarities between these systems, such transition may also be present in hole-doped EuRbFe₄As₄. Additionally, in contrast to BaFe₂As₂, the bands structures in 1144-system splits along X–M, owing to the S_4 symmetry breaking. Similar splitting is also present in CaKFe₄As₄⁹. We have also calculated EuRbFe₄As₄ (Fig. 2c) in the non-superconducting FM phase, where Eu moments align in parallel. The exchange spin splitting is less than 20 meV shown in Table 1. The projected band structure (Fig. 2d) indicates that the *d*_{z²} orbital has sizable contribution in EuRbFe₄As₄, in addition to the *d*_{xz}, *d*_{yz} and *d*_{xy} orbitals that universally dominate the electronic states near ϵ_F in FeSCs^{10,11}. The *d*_{x²-y²} orbital strongly hybridizes with As-4*p*, and is present beyond $\epsilon_F \pm 1$ eV range. The DOS of EuRbFe₄As₄ in FM phase are illustrated in Fig. 2e. Similar to all FeSCs, the DOS of FeSCs near ϵ_F is dominated by Fe-3*d* orbitals, hybridized with As-4*p* orbitals. The total DOS at ϵ_F is 9.41 eV⁻¹/f.u., equivalent to electronic specific-heat coefficient $\gamma = 21.642$ mJ/(K²mol). We note that $g(\epsilon_F)$ of CaRbFe₄As₄ is 9.78 eV⁻¹/f.u.¹², similar to what we obtained for EuRbFe₄As₄. As a comparison, the experimental value of $g(\epsilon_F)$ is 60 eV⁻¹/f.u.⁵, indicating a large electron mass renormalization factor of ≈ 6.4 . From spin-resolved DOS (Fig. 2e) the majority-spin channel/minority-spin channel of 4*f* electrons are located around 2.7 eV (10 eV) below(above) ϵ_F . By integrating the 4*f* contribution below ϵ_F , each Eu atom has a local moment of

Fig. 1 Crystal structure and crystal field splitting. **a** Crystal structure of EuRbFe₄As₄. **b** FeAs-layer centered on Fe atom. Compared with 122-type EuFe₂As₂, the Rb-substitution breaks not only the (1/2 1/2 1/2) gliding symmetry but also the S_4 symmetry

Fig. 2 Electronic band structure and density of states. **a** Electronic band structure of EuRbFe₄As₄ (red line) compared with CaRbFe₄As₄ (black line). **b** Electronic band structure of BaFe₂As₂ (blue line) in paramagnetic state in the folded Brillouin zone. The green dotted line denotes the Fermi level, which is aligned at zero. The degenerate points at X point as indicated by red circles in BaFe₂As₂ are removed in the 1144-system. **c** Spin-resolved band structure of EuRbFe₄As₄ in ferromagnetic state. The red and blue lines correspond to the two spin channels respectively. **d** Projected band structure of EuRbFe₄As₄ (ferromagnetic phase) for majority-spin channel around Fermi level. The size of the red, turquoise, blue, and gray circles is proportional to the contributions from the $d_{x(y)z}$, d_{xy} , d_{z^2} and $d_{x^2-y^2}$ respectively. **e** Total electronic density of state and projected density of state of EuRbFe₄As₄. The black, red, blue, and turquoise lines represent the total density of state, the projected density of state for Fe- d , As- p , and Eu- f orbitals respectively. The Fermi level is aligned at zero.

Table 1 The crystal field splitting and exchange splitting (in eV) of Fe-3d orbitals with respect to Fermi level for BaFe₂As₂, CaRbFe₄As₄, EuRbFe₄As₄, and EuRbNi₄As₄ (100% Ni-doping)

	BaFe ₂ As ₂	CaRbFe ₄ As ₄	EuRbFe ₄ As ₄	EuRbNi ₄ As ₄
d_{z^2}	-0.730	-0.780	-0.730	-1.948
d_{xz}/d_{yz}	-0.659	-0.730	-0.678	-1.908
$d_{x^2-y^2}$	-0.914	-0.985	-0.962	-2.061
d_{xy}	-0.700	-0.774	-0.746	-1.906
Δ_{cf}	0.128	0.127	0.142	0.078
Δ_{ex}	0.00	0.00	0.012	0.020

$7\mu_B$, consistent with the fully localized nature of 4f electrons in EuRbFe₄As₄. Six bands cross the Fermi level around the Γ point, forming the hole pockets around the Brillouin zone (BZ) center (Fig. 3a, b). In addition, another four bands cross the Fermi level around the $M(\pi, \pi)$ point forming the electron pockets corresponding to FSs in Fig. 3c. The complete FSs are shown in Fig. 3d.

Single particle Hamiltonian and crystal field. To analyze the crystal field effect in EuRbFe₄As₄, we have employed the maximally projected Wannier function method¹³ to fit the density functional theory (DFT) band structure. In order to capture the main features of the electronic structures of EuRbFe₄As₄, we take into account not only Fe-3d orbitals and As-4p orbitals, but Eu-4d and Eu-4f orbitals as well. Using these 44 orbitals not only allows us to describe the low-energy physics of this system, but also elucidates the electronic hopping process between d - p as well as

d - f orbitals, which are relevant in the superconducting and magnetic properties of this compound.

In Fig. 3e–h we compare the crystal field splitting between BaFe₂As₂, CaRbFe₄As₄, and undoped EuRbFe₄As₄ and the corresponding values are listed in Table 1. In general, the electronic bands of 3d-systems strongly depend on the crystal symmetry. Under perfect tetrahedral crystal field, the five d -orbitals split into two groups: triply degenerate t_{2g} levels and doubly degenerate e_g levels. In the family of iron-based superconductors, all the members share the similar FeAs layer with tetrahedral symmetry. Due to the combined effect of anion crystal fields and surrounding cations, the hybridization between the Fe- d orbitals and the pnictogen-/chalcogen- p orbitals appears. Therefore, both t_{2g} and e_g orbitals further split, leaving only degenerate d_{xz} and d_{yz} as exemplified in BaFe₂As₂ (Fig. 3e). In addition, we find that in EuRbFe₄As₄ the energy levels of d_{xy} and d_{z^2} are reversed, consistent with the observation in the band structure results. Furthermore, the exchange spin splitting in EuRbFe₄As₄ is one order of magnitude smaller compared to the crystal field splitting, and the formation of long-range magnetic order does not affect magnitude and order of crystal splitting.

In Table 2 we show the hopping terms related to low-energy excitation for BaFe₂As₂, CaRbFe₄As₄, and EuRbFe₄As₄ (both PM state and FM state), respectively. In the BaFe₂As₂ compound, the As atoms above (As^I) and below (As^{II}) the Fe-plane are equivalent (S_4 local symmetry); thus, the hoppings between Fe-3d and As-4p orbitals are the same. However, this symmetry is broken in 1144-type compounds; thus, the hoppings between Fe-3d and As^I-4p and those between Fe-3d and As^{II}-4p are no longer identical. For all these compounds the strongest hopping comes from Fe-3d _{$x(y)z$} and As-4p _{$y(x)$} , followed by the hopping between

Fig. 3 Fermi surfaces, crystal field splitting, and the relative contributions to Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions of Fermi surfaces. **a–d** Fermi surfaces of EuRbFe₄As₄. **a** Typical hole pocket due to d_{xy} with little dispersion along k_z ; **b** typical hole pockets due to d_{z^2} with strong dispersion along k_z ; **c** typical electron pockets due to d_{xz}/d_{yz} ; and **d** all pockets combined together. The zone center is Γ in all panels. **e–h** Crystal field splitting of Fe-3d orbitals in **e** BaFe₂As₂ (paramagnetic state), **f** CaRbFe₄As₄ (paramagnetic state), **g** EuRbFe₄As₄ (ferromagnetic state) and **h** EuRbNi₄As₄ (ferromagnetic state) respectively. **i** Band-decomposed contribution to RKKY interaction in the pristine EuRbFe₄As₄. The band indices are labeled from lowest to highest at the Γ point. There are ten bands crossing the Fermi levels, among which six are hole-like and four are electron-like. The sixth band with the largest contributions corresponds to the Γ -centered outmost hole pocket due to d_{z^2} shown in (b).

Fe-3d_{xy} and As-4p_z. Compared to the d - p hopping, the d - f hopping terms are one order smaller, among which the Fe-3d_{z²} and Eu-4f_{xyz} is largest. Remarkably, the d - p hopping terms in PM phase and FM phase are roughly the same for EuRbFe₄As₄, despite the large magnetic moment of Eu atoms. Therefore, the effect of ferromagnetic Eu-layers can be equivalently regarded as magnetic exchange splitting field for the FeAs-layers. It is worth noting that the $H_{c2}(0)$ of a similar compound, CaKFe₄As₄, can reach as high as 71 T¹⁴, while the internal field due to Eu²⁺ atom was much smaller¹⁵. Therefore, the superconductivity may coexist with the FM Eu-layer.

RKKY exchange interaction. The RKKY exchange interaction was reported to be inseparably related with the magnetic order in 122-type EuFe₂(As,P)₂^{16,17} and 1144-type EuRbFe₄As₄⁵. In the weak coupling limit, the RKKY interaction can be approximately $J_{\text{RKKY}} \sim J_K^2 g(\epsilon_F)$ ^{18–20} with a bare Kondo coupling J_K in the ordered phase and DOSs at the Fermi level $g(\epsilon_F)$. Due to the large local moment of Eu atoms (6.5 μ_B per Eu, close to half-occupied Eu-4f orbitals), the large- U_f limit should be valid for EuRbFe₄As₄. Following the Schrieffer–Wolff transformation^{21,22}, we calculate the Kondo coupling strength by

$$J_{0n} = \frac{1}{g_n(\epsilon_F)} \int d\mathbf{k} \frac{V_{nk,f}^* V_{f,nk}}{|\epsilon_f - \epsilon_{nk}|} \times \delta(\epsilon_{nk} - \epsilon_F)$$

for the conduction channel n , where $V_{nk,f} = \langle w_f | \hat{H} | n\mathbf{k} \rangle = \sum_{\alpha} \langle w_f | \hat{H} | w_{\alpha} \rangle \langle w_{\alpha} | n\mathbf{k} \rangle$. In these expressions, n is the conduction band index, $|n\mathbf{k}\rangle$ is the n th Bloch state of conduction electrons at $\mathbf{k}$, $|w_{\alpha}\rangle$ is the α th local Wannier state for the conduction electrons, ϵ_{nk} and ϵ_f are the eigen-energies of the conduction channel and local f states, $g_n(\epsilon_F)$ is the DOSs at the Fermi level of the n th conduction channel, and $|w_f\rangle$ denotes the local Wannier state of the f -electrons. The averaged Kondo coupling $\bar{J}_K$ is roughly -0.73 meV, slightly smaller than EuFe₂As₂ (-1.01 meV)²⁰. Considering the multiband effect and highly anisotropic Fermi surfaces, the RKKY interaction is obtained by summing up the contributions from all conduction bands $J_{\text{RKKY}} = \sum_n J_{0n}^2 g_n(\epsilon_F)$. The resulting J_{RKKY} is around 0.12 meV, or equivalent to $T_{\text{FM}} \approx 12.5$ K, which is in good agreement with the experimental value⁵. It is worth noting that the J_{RKKY} in our calculation is averaged in all directions. To tell the difference between the inter-layer coupling $J_{\perp}$ and intra-layer coupling $J_{\parallel}$, it

Table 2 Nearest neighboring hoppings t_{ij} (in eV) from maximally projected Wannier function method (only symmetrically inequivalent terms larger than 1 meV are shown)

	BaFe ₂ As ₂	CaRbFe ₄ As ₄	EuRbFe ₄ As ₄	
			PM	FM
$3d_{z^2} - 4p_z$	0.544	0.478	0.544	0.545
$3d_{z^2} - 4p_x$	0.186	0.247	0.220	0.221
$3d_{xz} - 4p_z$	0.029	0.106	0.059	0.061
$3d_{xz} - 4p_x$	0.179	0.143	0.170	0.171
$3d_{xz} - 4p_y$	0.759	0.689	0.747	0.751
$3d_{y^2} - 4p_x$	0.556	0.490	0.541	0.543
$3d_{xy} - 4p_z$	0.678	0.587	0.623	0.624
$3d_{xy} - 4p_x$	0.292	0.168	0.216	0.217
$3d_{z^2} - 4p_{z'}$	0.544	0.541	0.515	0.521
$3d_{z^2} - 4p_{x'}$	0.186	0.260	0.244	0.247
$3d_{xz} - 4p_{z'}$	0.029	0.096	0.092	0.093
$3d_{xz} - 4p_{x'}$	0.179	0.155	0.156	0.153
$3d_{xz} - 4p_{y'}$	0.759	0.748	0.755	0.762
$3d_{y^2} - 4p_{x'}$	0.556	0.514	0.526	0.526
$3d_{xy} - 4p_{z'}$	0.678	0.640	0.658	0.667
$3d_{xy} - 4p_{x'}$	0.292	0.162	0.206	0.205
$4p_z - 4p_{z'}$	0.335	0.360	0.349	0.347
$4p_x - 4p_{x'}$	0.570	0.362	0.440	0.448
$4p_y - 4p_{y'}$	0.147	0.197	0.196	0.209
$3d_{z^2} - 3d_{z'}$	0.108	0.137	0.132	0.134
$3d_{xz} - 3d_{x'}$	0.015	0.028	0.022	0.022
$3d_{yz} - 3d_{y'}$	0.214	0.280	0.265	0.266
$3d_{x^2} - 3d_{x'^2}$	0.346	0.363	0.367	0.366
$3d_{xy} - 3d_{xy'}$	0.182	0.276	0.254	0.254
$3d_{z^2} - f_{z^3}$	—	—	—	0.033
$3d_{z^2} - f_{xz^2}$	—	—	—	0.024
$3d_{z^2} - f_{xyz}$	—	—	—	0.051
$3d_{z^2} - f_{3xy^2}$	—	—	—	0.015
$3d_{xz} - f_{z^3}$	—	—	—	0.032
$3d_{xz} - f_{xz^2}$	—	—	—	0.015
$3d_{xz} - f_{yz^2}$	—	—	—	0.037
$3d_{x^2} - f_{xz^2}$	—	—	—	0.029

In 1144-type, the hoppings between Fe-3d and As-4p will be different for As^I (denoted with p) and As^{II} (denoted with p') due to the local S_4 symmetry broken
PM paramagnetic

Fig. 4 Effect of Ni-doping. **a** Total and projected density of states of EuRb[Fe_{1-x}Ni_xAs₄]. The panels from top to bottom are undoped ($x = 0$), $x = 0.0625$, $x = 0.125$, and $x = 1$ (EuRbNi₄As₄), respectively. **b–e** Imaginary part of bare electron susceptibilities (nesting function). From **b** to **e** are undoped, 6.25%-doped, 12.5%-doped and fully doped EuRbFe₄As₄ respectively

is necessary to employ $J_{\text{RKKY}}(\mathbf{r}) = J_K^2 \sum_{\mu\nu} \chi^{\mu\nu}(\mathbf{r})$ (where $\chi^{\mu\nu}(\mathbf{r}) = \sum_{\mathbf{k}, \mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \left[\frac{f_{\mu}(\mathbf{k}) - f_{\nu}(\mathbf{k}')}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}} \right]$)²³. Using the Wannier orbital-based tight-binding (TB) Hamiltonian, we have estimated $J_{\perp}/J_{\parallel} \approx 1.0$. Such nearly isotropic behavior can be understood by calculating the band-decomposed contributions from each Fermi surface sheet (Fig. 3i), which suggests more than 60% of J_{RKKY} is mediated by the outmost hole pocket around Γ point with prominent 3D feature. This Fermi surface sheet is mainly due to the Fe- d_{z^2} orbitals, and a similar mechanism was also previously proposed in EuFe₂As₂²⁴.

It should be emphasized that the RKKY interaction in our calculation starts from the normal state. In superconducting state, the interplay between RKKY interaction and superconductivity is more complicated. It has been illustrated by Yao et al. that the antiferromagnetic contribution from indirect spin exchange will be enhanced due to the formation of Yu–Shiba–Rusinov (YSR) bound states, provided the binding energy of YSR state is close to the middle of superconducting gap Δ ²⁵. In EuRbFe₄As₄, however, this binding energy is estimated to be close to Δ , implying the weak hybridization between YSR state and superconducting condensate. Thus, the conventional RKKY interaction will still dominate in superconducting state.

Effect of nickel doping. In order to investigate the Ni-doping effects, we have also calculated EuRbFe_{1-x}Ni_xAs₄ with $x = 6.25$, 12.5 and 100% under the virtual crystal approximation (VCA). The DOS of these system are illustrated in Fig. 4a. With nickel doping, the Fermi level moves to higher energy, demonstrating the main effect induced by nickel is electron-doping. Comparing 6.25% Ni-doping with the undoped EuRbFe₄As₄, the DOS of $d_{zx(y)}$, d_{z^2} and $d_{x^2-y^2}$ orbitals are suppressed by 17.6, 13.7 and 12.1% respectively while the DOS of d_{xy} is enhanced by 4.0%. Note that the T_{sc} for the superconductivity is usually very sensitive to the DOS at Fermi level $g(\epsilon_F)$. Therefore, the large decreased $g(\epsilon_F)$ of $d_{zx(y)}$ is consistent with strongly suppressed superconducting temperature upon doping.

We have also calculated the imaginary part of bare electron susceptibility (nesting function) under different doping levels (Fig. 4b–e). For pristine EuRbFe₄As₄, the nesting function shows a sharp peak at M ($\pi, 0$), which signals large spin-fluctuation that

x	0%	6.25%	12.5%	100%
$\bar{J}_K$ (meV)	0.730	0.605(0.604)	0.662(0.510)	0.570
J_{RKKY} (meV)	0.120	0.093(0.117)	0.100(0.086)	0.070

Note that in the experiment the Ni-doping is within 10%⁷. For doped system ($0 < x < 1$), the numbers inside (outside) the bracket were calculated using rigid band model (virtual crystal approximation), respectively

considered to be related with the superconductivity^{26–28}. This peak is quickly suppressed by Ni-doping, and is already absent with 12.5% Ni-doping, suggesting that the superconductivity can be quickly suppressed by Ni-doping. The imaginary part of the 100%-doped compound (or EuRbNi₄As₄) is completely flat, meaning that the Ni-lattice is without spin-fluctuation. In fact, our DFT calculation confirms that Ni-lattice is completely nonmagnetic in EuRbNi₄As₄.

To evaluate the influence of doping on the crystal field splitting and the RKKY interaction, we naively calculate the 100% Ni-doping situation. With all the irons substituted, the energy level of d_{xy} orbital rises, substantially higher than d_{z^2} orbital and even nearly degenerate with $d_{zx(y)}$ orbitals (Fig. 3h). Considering the main effect of Ni-doping at small x is to shift the Fermi level upward, the averaged Kondo coupling $\bar{J}_K$ and the RKKY interaction J_{RKKY} are also calculated (Table 3) with the rigid band model (RBM). The averaged Kondo coupling $\bar{J}_K$ slightly decreases upon doping within RBM while the variation in VCA is nonmonotonic. Both of these two methods, however, show the RKKY interaction is around 0.1 meV, insensitive to the Ni-doping, which is in agreement with experimental observations⁷.

Discussion

In conclusion, we have performed first-principles calculation on a typical 1144-type iron pnictide EuRbFe₄As₄. We analyzed the detailed electronic band structure, DOS and Fermi surface as well as the distinction of electronic properties between EuRbFe₄As₄, BaFe₂As₂, and CaRbFe₄As₄. The energy levels of d_{z^2} and d_{xy} are

reversed in $\text{EuRbFe}_4\text{As}_4$, and d_{z^2} orbital becomes closer to the Fermi level around Γ point; thus, the system is close to a Lifshitz transition. Upon Ni-doping, the DOS of d_{zx}/d_{zy} orbitals at Fermi level as well as the spin-fluctuation at $(\pi, 0)$ will be substantially suppressed, and both effects are detrimental to superconductivity. Finally, the RKKY interaction between Eu-layers is little affected by Ni-doping, and is mostly mediated through the outmost hole FS pocket around the Γ point due to the d_{z^2} orbital.

Methods

The calculations were carried out based on DFT with Quantum ESPRESSO (QE)^{29–31}. Throughout the calculations, the Perdew, Burke, and Ernzerhof parameterization of generalized gradient approximation to the exchange correlation functional was used³². The energy cutoff of plane-wave basis was chosen to be 122 Ry (1220 Ry for the augmentation charge), which was sufficient to converge the total energy to 1 meV/atom. A Γ -centered $12 \times 12 \times 3$ Monkhorst-Pack³³ k-point mesh was chosen to sample the Brillouin zone in the calculations. For the calculations of PM phases, the Eu-4f states were considered to be fully localized core states and do not hybridize with any conduction electrons; while for the ferromagnetic state calculations, the Eu-4f states were explicitly considered as semi-core valence states, with an additional Hubbard-like effective interaction $U = 7$ eV^{34–36}. In addition, for ferromagnetic state calculations, only the initial magnetic moments on Eu atoms were set to non-zero values.

We have employed the experimental crystal structure to perform all the calculations, since a full structural relaxation will yield a 5.1% shorter c and wrong As-heights. This problem was known in other FeSCs^{37,38}, and was due to the fact that spin fluctuations cannot be accounted for in the static mean-field implementation of DFT³⁹.

The DFT results were then fitted to a TB model Hamiltonian with maximally projected Wannier function method^{13,40}. Although TB Hamiltonian constructed with five Fe-3d orbitals is sufficient to describe the low-energy excitations in FeSCs, one must include Eu-4f orbitals and other relevant ones in $\text{EuRbFe}_4\text{As}_4$ in order to analyze the crystal field splitting and magnetic exchange coupling interactions. Therefore, we have employed 44 atomic orbitals including the Fe-3d, As-4p, Eu-5d, and Eu-4f orbitals in the fitting procedure.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

C.X. performed most of the calculations; C.X. and C.C. were responsible for the data analysis and drafted the manuscript; C.X., Q.C. and C.C. participated in discussions.

Additional information

Competing interests: The authors declare no competing interests.

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