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A new ferromagnetic superconductor: $CsEuFe_4As_4$

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Abstract Superconductivity (SC) and ferromagnetism (FM) are in general antagonistic, which makes their coexistence very rare. Following our recent discovery of robust coexistence of SC and FM in $RbEuFe_4As_4$ (Liu et al. in Phys Rev B 93:214503, 2016), here we report another example of such a coexistence in its sister compound $CsEuFe_4As_4$, synthesized for the first time. The new material exhibits bulk SC at 35.2 K and Eu^{2+}-spin ferromagnetic ordering at 15.5 K, demonstrating that it is a new robust ferromagnetic superconductor.

Keywords Superconductivity · Ferromagnetism · Iron-based superconductors

1 Introduction

The search for ferromagnetic superconductors (FMSCs) can trace back to before the 1960s [1]. Owing to the antagonistic nature of superconductivity (SC) and ferromagnetism (FM) [1, 2], SC rarely coexists with FM, even for that SC and FM emerge in different subsystems of a complex crystalline lattice. It was not until late 1970s that both SC and FM were observed in $ErRh_4B_4$, but SC *disappears* when the Er magnetic ordering enters [3]. Since then, a few "conventional magnetic superconductors" were discovered [4], in which SC and local-moment FM (or more frequently, other types of magnetic orderings with ferromagnetic components) casually coexist in certain temperature and magnetic-field regimes. Such materials were earlier called FMSCs [2], and this terminology was also employed for the uranium compounds UGe_2, URuGe and UCoGe that are superconducting well below their Curie temperatures [5]. Here we adopt the classification [6], which gives another terminology, "superconducting ferromagnet", for the case that the superconducting transition temperature T_{sc} is lower than the Curie temperature T_{Curie}. Whilst FMSC is reserved for the scenario of $T_{sc} > T_{Curie}$. Note that, in the U-based superconducting ferromagnets, SC and FM share the same type of electrons, and the SC is widely believed to be in a spin-triplet state. For a spin-singlet superconductor, however, SC is more easily destroyed by the strong exchange fields in a ferromagnet. At the same time, a spin-singlet *s*-wave superconducting state does not allow a local-moment FM via Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions in a single-band system [7]. Therefore, it seems impossible for a single material to host both local-moment FM and spin-singlet SC (FM + SC).

However, the FM + SC-like phenomenon was observed [8, 9], and recently confirmed by X-ray resonant magnetic scattering [10] and neutron scattering [11], in the P-doped $EuFe_2As_2$ system in which SC emerges at ~26 K followed by ferromagnetic ordering at ~17 K for the Eu^{2+} spins. Similar phenomena were later demonstrated in other doped $EuFe_2As_2$ systems [12–16]. Nevertheless, strong

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experimental evidence of bulk SC in these doped $EuFe_2As_2$ systems is still lacking. Also there have been debates on the details of Eu-spin ordering [9–11, 17–19].

Very recently, motivated by our previous material design [20] as well as the latest experimental progress [21], we succeeded in synthesizing a new Eu-containing iron arsenide $RbEuFe_4As_4$ which exhibits bulk SC at $T_{sc} = 36.5$ K and Eu-spin FM at $T_{Curie} = 15$ K [22]. The robustness of both SC and FM indicates a genuine FM + SC state realized. Here we report the second robust FMSC, $CsEuFe_4As_4$, a sister compound of $RbEuFe_4As_4$. The new material shows bulk SC at 35.2 K and Eu-spin FM at 15.5 K. An additional anomaly at 5 K is observed, possibly associated with the interplay between SC and FM. Another interesting issue is that the Eu-spin ferromagnetic ordering is of a rare third order, suggesting a strong two-dimensional character of the ferromagnetic transition.

2 Experimental

$CsEuFe_4As_4$ polycrystalline sample was synthesized by solid-state reactions in a sealed vacuum, with procedures similar to the synthesis of $RbEuFe_4As_4$ [22]. First, CsAs, EuAs and FeAs were prepared respectively via the reactions of Cs (99.75 %), Eu (99.9 %) and As (99.999 %) pieces with Fe powders (99.999 %). The intermediate products were then ball milled separately for 10 min in a glove box filled with pure Ar (the water and oxygen content is below 1 ppm). Second, the powder of CsAs, EuAs, FeAs and Fe was weighed in a stoichiometric ratio. The mixture was homogenized by grinding, pressed into pellet, and then loaded in an alumina tube which was sealed in a Ta tube by arc welding in argon atmosphere. The welded Ta tube was jacketed in a quartz ampoule filled with Ar gas ($\sim$0.6 bar (1 bar = 10^5 Pa)), followed by heating the ampoule to 1123–1173 K, holding for 6 h, in a muffle furnace. The sample was quenched after the high-temperature chemical reactions.

Powder X-ray diffraction (XRD) was carried out at room temperature on a PANalytical X-ray diffractometer (Model EMPYREAN) with a monochromatic $CuK_{\alpha 1}$ radiation. To avoid severe preferred orientations, the powder was pressed softly on the sample holder. The lattice parameters and the atomic positions were refined by a Rietveld analysis using a RIETAN-FP software [23]. The electrical and heat-capacity measurements were conducted on a physical property measurement system (PPMS-9, Quantum Design). The electrical resistivity was measured using a standard four-electrode method. The as-prepared $CsEuFe_4As_4$ pellet was cut into a thin rectangular bar, on which gold wires were attached with silver paint. The Hall coefficient was measured by permutating the voltage and current electrodes under 8 T [24], using a thin-square sample ($2.2 \times 2.0 \times 0.17$ mm^3) with four symmetric electrodes attached. The heat capacity was measured by a thermal relaxation method using a square-shaped sample plate with a total mass of 16.8 mg. The dc magnetization was measured in a magnetic property measurement system (MPMS-5, Quantum Design) using a regular shape sample so that the demagnetization factor can be estimated more precisely.

3 Results and discussion

3.1 Crystal structure

The powder XRD pattern of the $CsEuFe_4As_4$ sample can be well indexed with a $RbCaFe_4As_4$-type [21] (1144-type) primitive tetragonal lattice. No evident impurity phase can be identified. Figure 1 shows the Rietveld refinement profile based on the 1144-type structure shown in the inset. The refinement yields a weighted reliable factor R_{wp} of 4.80 % and a "goodness-of-fit" parameter S of 1.48, and the resulting crystallographic parameters are tabulated in Table 1.

Isostructural to $RbEuFe_4As_4$, $CsEuFe_4As_4$ can be viewed as an intergrowth of $CsFe_2As_2$ and $EuFe_2As_2$, thus it is meaningful to compare their crystal structures. The a axis is almost the same (within the determination uncertainty) as the average value of those of $EuFe_2As_2$ [25] and $CsFe_2As_2$ [26]. In fact, the lattice mismatch between the two 122-type compounds is only 0.4 %, which explains the formation of $CsEuFe_4As_4$ [20, 21]. However, the c axis is 0.010(1) Å larger that the sum of one half of the c axes of $CsFe_2As_2$ and $EuFe_2As_2$. This result looks abnormal because in general the

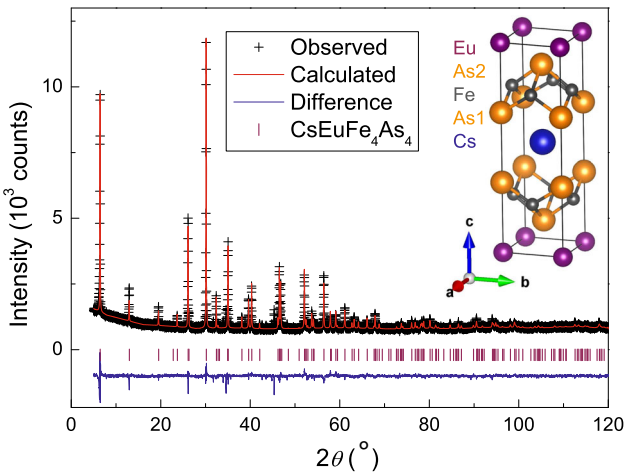

Fig. 1 (Color online) Powder X-ray diffraction and its Rietveld refinement profile for $CsEuFe_4As_4$. The inset shows the crystal structure