Superconductivity and ferromagnetism in EuFe$_2$(As$_{1-x}$P$_x$)$_2$*

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Abstract

Superconductivity and ferromagnetism are two antagonistic cooperative phenomena, which makes it difficult for them to coexist. Here we demonstrate experimentally that they do coexist in EuFe$_2$(As$_{1-x}$P$_x$)$_2$ with 0.2 ≤ x ≤ 0.4, in which superconductivity is associated with Fe 3d electrons and ferromagnetism comes from the long-range ordering of Eu 4f moments via Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions. The coexistence features large saturated ferromagnetic moments, high and comparable superconducting and magnetic transition temperatures, and broad coexistence ranges in temperature and field. We ascribe this unusual phenomenon to the robustness of superconductivity as well as the multi-orbital character of iron pnictides.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of superconductivity (SC) in mercury 100 years ago [1], thousands of superconductors have been found in various kind of materials including elements, alloys, inorganic compounds and organic compounds. Nevertheless, SC was shown to be incompatible with magnetism, simply manifested by that fact that no magnetic elements superconduct. Although SC may coexist with antiferromagnetism because superconducting coherent lengths are generally much larger than interatomic distances, it is easily destroyed by ferromagnetism (FM) owing to orbital [2] and paramagnetic [3] effects. On the other hand, SC does not support the local-moment FM via Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions [4]. Earlier experiments revealed the incompatible nature of the two collective phenomena in (La, Gd) and ($\text{Ce}$, Pr)Ru$_2$ solid solutions [5]. Until the late 1970s the possible coexistence of SC and FM was evidenced in ErRh$_4$B$_4$ [6] and Ho$_{1.2}$Mo$_6$S$_8$ [7] under narrow regimes of temperature and external field. The interplay of SC and magnetic ordering was also exhibited in a family of layered compounds $\text{RNi}_2\text{B}_2\text{C}$ (R = Tm, Er, Ho and Dy) [8] and ruthenocuprates [9, 10]. Another interesting coexistence was found in UGe$_2$ [11, 12] and URhGe [13], in which SC occurs under the ferromagnetic background ($T_c < T_M$) and, both SC and FM come from the same types of electrons.

The discovery of Fe-based superconductors [14, 15] brought about new findings on the interplay of SC and FM. EuFe$_2$As$_2$, first synthesized in late 1970s [16], is a unique ‘122’ compound which shows both SC in the FeAs-layers, upon appropriate doping, and long-range magnetic ordering in the Eu sublattice. It was found that the undoped parent compound undergoes antiferromagnetic (AFM) ordering in the Fe sublattice. It was found that the undoped parent compound undergoes antiferromagnetic (AFM) ordering in the Fe sublattice. It was found that the undoped parent compound undergoes antiferromagnetic (AFM) ordering in the Eu sublattice at 200 K, followed by another AFM ordering in the Eu sublattice at 20 K [17–20]. The two subsystems are hardly coupled, as evidenced from optical [21] and photoemission [22] studies. The magnetic structure of the latter AFM order had been proposed to be of A-type, [18, 23] in which Eu$^{2+}$ spins align ferromagnetically in the basal planes but antiferromagnetically along the c-axis, which was then confirmed by magnetic resonant x-ray scattering [24].
and neutron diffraction [25] experiments. By the partial substitution of Eu with K, SC over 30 K was reported in Eu$_{1-x}$K$_x$Fe$_2$As$_2$ [26]. However, due to the dilution effect of the Eu-site doping, no magnetic ordering for Eu$^{2+}$ spins was observed. In an attempt to obtain SC by Ni doping in EuFe$_{2-x}$Ni$_x$As$_2$ [27], we observed FM ordering for the Eu$^{2+}$ moments. In the case of Co doping, however, there was a superconducting transition at $\sim$21 K, followed by reentrance of resistivity around 17 K [28, 29]. By doping with P at the As-site, we found both SC at $T_c$ by reentrance of resistivity around 17 K [28, 29]. By doping with P at the As-site, we found both SC at $T_c$ by reentrance of resistivity around 17 K [28, 29]. By doping with P at the As-site, we found both SC at $T_c$ by reentrance of resistivity around 17 K [28, 29]. By doping with P at the As-site, we found both SC at $T_c$ by reentrance of resistivity around 17 K [28, 29]. By doping with P at the As-site, we found both SC at $T_c$ by reentrance of resistivity around 17 K [28, 29]. By doping with P at the As-site, we found both SC at $T_c$ by reentrance of resistivity around 17 K [28, 29]. By doping with P at the As-site, we found both SC at $T_c$ by reentrance of resistivity around 17 K [28, 29].

2. Experimental details

Polycrystalline samples of EuFe$_2$$_{(As_1-x)P_x}$$_2$ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.75$ and 1.0) were synthesized by solid state reaction with EuAs, Fe$_2$As and Fe$_2$P. EuAs was prepared by reacting fresh Eu grains and As powders in an evacuated quartz tube at 873 K for 10 h then at 1023 K for another 10 h, and ultimately at 1223 K for 10 h. Fe$_2$As was presynthesized by reacting Fe powders and As powders at 873 K for 10 h and at 1173 K for 15 h. Fe$_2$P was prepared by heating Fe powders and P powders very slowly to 873 K and then holding for 10 h. In an argon-filled glove-box, the EuAs, Fe$_2$As and Fe$_2$P powders were mixed in a certain stoichiometric ratio, thoroughly ground in an agate mortar and pressed into pellets. The pellets were annealed in an evacuated silica tube at 1273 K for 20 h and furnace-cooled to room temperature. The resultant EuFe$_2$$_{(As_1-x)P_x}$$_2$ samples were black in colour and rather stable in air. The chemical composition of the samples was also examined by energy-dispersive x-ray (EDX) spectroscopy on a single crystalline grain. The result indicates that the measured composition agrees with the nominal one within experimental error.

Powder x-ray diffraction (XRD) was performed at room temperature, using a D/Max-rA diffractometer with Cu Kα radiation and a graphite monochromator. The data were collected with a step-scan mode for $10^\circ \leq 2\theta \leq 80^\circ$. Lattice parameters were refined by a least-squares fit with considerations of zero shift. The electrical resistivity was measured using a standard four-probe method with an applied current density of $\sim$0.5 A cm$^{-2}$. The lowest resistance measured was 10$^{-5}$ Ω. The dc magnetization was measured on a Quantum Design magnetic property measurement system (MPMS-5).

3. Results and discussion

Figure 1(a) shows the XRD patterns of the EuFe$_2$$_{(As_1-x)P_x}$$_2$ samples. The specimens are basically of single phase with a ThCr$_2$Si$_2$-type structure. For some samples, only a minor amount (<5%) of impurities of Eu$_2$O$_3$ and Fe$_2$P were detected. The XRD patterns show systematic changes with the P doping. For example, the intensity of (002) peaks increases gradually with incorporation of phosphorus. Both (008) and (200) peaks shift towards higher angles with increasing x, indicating shrinkage of the lattice. Indeed, we see that both a and c decrease almost linearly with x in figure 1(b), suggesting that P was doped homogeneously. Notably, the magnitude of decrease of c is much bigger. This is very important for the evolution of magnetic ordering in the Eu sublattice, since the RKKY coupling is closely related to the interatomic distance of the magnetic ions [27].

Figure 2 shows the temperature dependence of resistivity for EuFe$_2$$_{(As_1-x)P_x}$$_2$. The undoped EuFe$_2$As$_2$ clearly shows two resistivity kinks at 200 and 20 K, associated with Fe-site and Eu-site AFM ordering, respectively. However, the transition temperatures for single crystal samples are 189 K and 19 K, respectively [21, 23]. We had carefully measured the chemical composition of the single crystals.
Figure 2. Temperature dependence of resistivity for EuFe$_2$(As$_{1-x}$P$_x$)$_2$ polycrystalline samples. To explicitly show the regimes that have different characteristics we separate the samples into three groups from right to left, corresponding to lower, intermediate and higher doping. The lower panels display the expanded plots using normalized resistivity for comparison. The arrows mark the positions of the related transition temperatures.

Figure 3. Temperature dependence of magnetic susceptibility for EuFe$_2$(As$_{1-x}$P$_x$)$_2$: (a) $x=0.05$; (b) $x=0.25$.

by the EDX technique, and showed that the Eu was about 4.2% deficient. Therefore, the chemical stoichiometry for Eu can be better kept using polycrystalline samples. With the P doping, the magnetic transition temperature of the Fe sublattice ($T_{FeM}^{c}$) decreases rapidly, similar to the case in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ [34]. On the other hand, the magnetic transition temperature of the Eu sublattice ($T_{EuM}^{c}$) first decreases by 4 K, then starts to increase at $x \sim 0.15$. When the P content increases up to 20%, no anomaly associated with the Fe-AFM ordering can be observed; instead, a sudden decrease in resistivity is seen below 21 K, indicative of a superconducting transition. Besides, a shoulder (resistivity reentrance) appears at 16 K, which is probably due to the magnetic ordering in the Eu sublattice. The optimal doping is at $x=0.3$ where the onset superconducting transition temperature ($T_{onset}^{c}$) achieves the maximum (29 K) with no resistivity reentrance at lower temperatures for our best sample. When $x > 0.45$, no sign of SC was detected, and the resistivity kinks reappear at $T_{EuM}^{c}$. As can be seen, $T_{EuM}^{c}$ climbs with further P substitution, and reaches 29 K for the end member EuFe$_2$P$_2$ [35, 36].

Figure 3 shows the temperature dependence of magnetic susceptibility of two representative samples. For $x=0.05$, the $\chi(T)$ curve has a peak at $T_{EuM}^{c}=18.5$ K. Meanwhile, there is bifurcation for field cooled (FC) and zero-field cooled (ZFC) branches, suggesting a ferromagnetic component. The ferromagnetic component can be understood by a recent Mössbauer study [37] which shows canting of the Eu spins towards the $c$-axis with P doping. There is another anomaly at $\sim 6$ K, suggesting a more complicated successive magnetic transition. The spin canting was very recently evidenced by measuring the anisotropic magnetization for EuFe$_2$(As$_{0.88}$P$_{0.12}$)$_2$ single crystals [38]. These authors proposed a regime around $x=0.2$ which shows ferromagnetism along the $c$-axis, but antiferromagnetism within the basal planes. The Eu spins do not align truly ferromagnetically until $x > 0.2$.

For $x=0.25$, the FC curve looks like the behaviour of a typical ferromagnet. The low-temperature susceptibility is 10 times larger than that of $x=0.05$. More obvious bifurcation is seen for the ZFC and FC curves. The $M$–$H$ loop (not shown here) has a clear magnetic hysteresis, like that previously reported for $x=0.3$ [30]. The saturated magnetization value corresponds to the fully aligned Eu moments (see below). All these facts indicate ferromagnetic ordering for the Eu$^{2+}$ spins. The ferromagnetic Curie temperature is identified at $T_{EuM}^{c}=19$ K, above which the $\chi(T)$ data obey the extended Curie law ($\chi = \chi_0 + C/(T - \theta)$, where $\chi_0$ denotes the
magnetization saturates to 7.0. Nevertheless, magnetic shielding is always expected only if the sample really has zero resistance. We deduce that the resistivity of the superconductor. For example, in many cases no Meissner effect nor magnetic shielding was observed. Here we would like to note that the superconducting properties of a system like to note that the superconducting properties of a system with coexisting SC/FM probably differ from those of usual superconductors. For example, in many cases no Meissner effect can be observed for a superconducting ferromagnet [9, 39]. This is because the internal exchange fields penetrate the superconductor. Nevertheless, magnetic shielding is always expected only if the sample really has zero resistance. We deduce that the resistivity of the x = 0.25 sample has not achieved zero yet (the measurement limit is 10\(^{-5}\) Ω) probably due to polycrystalline samples. Note that magnetic shielding was indeed observed in single crystals [40].

Figure 4 displays the field dependence of magnetization for the x = 0.3 sample. Under the field of ~1 T, the magnetization saturates to 7.1 \(\mu_B/\text{f.u.}\) at 5 K. The saturated magnetization is very close to the theoretical value of \(gJ = 7.0\ \mu_B/\text{f.u.}\), indicating full polarization of the Eu\(^{2+}\) spins. This fact further confirms the ferromagnetism. The nonlinear \(M-H\) relations above \(T_M^{\text{Eu}}\) (20 and 23 K) reflect that the external fields help to align the Eu spins ferromagnetically.

The low-field magnetization (figure 4(b)) does not show magnetic repulsion and shielding, as expected for a superconducting state. The absence of the Meissner effect could be due to the formation of a spontaneous vortex (SV) phase [39, 41]. On the other hand, the loss of magnetic shielding means that the resistivity is not really zero, which is ascribed to the weak links in polycrystalline samples and/or the motion of SV which generates flow resistance. Nevertheless, signature of SC can be seen from the concave curvature of the \(M-H\) relation at 23 K (which is higher than \(T_M^{\text{Eu}}\) but lower than \(T_c^{\text{mnee}}\)), where diamagnetism is inferred from the background of paramagnetism of Eu\(^{2+}\) spins.

\[\theta = \frac{\theta_C - \theta_{\text{Curie}}}{2}\]

\[\theta_C = \frac{\mu_B^2}{k_B}\]

\[\frac{\mu_B}{k_B}\]

\[\theta_C = -\frac{\mu_B^2}{2k_B}\]

\[\theta_{\text{Curie}} = \frac{\mu_B^2}{k_B}\]

Based on the above results, we establish the magnetic and superconducting phase diagram as shown in figure 5. For the Fe sublattice, the phase diagram is similar to those of other Fe-based superconductors [34, 42], i.e. the Fe-AFM is suppressed by P doping, and then SC emerges. The only difference is that SC is no longer present when \(T_c < T_M^{\text{Eu}}\). For the Eu sublattice, the parent EuFe\(_2\)As\(_2\) is A-type AFM ordered with Eu spins lying along the c-axis. Doping with phosphorus not only increases the interlayer RKKY coupling, but also leads to the canting of the Eu spins. According to the Mössbauer study [37], spin canting starts at \(x = 0\), and finishes at \(x \sim 0.2\), where the spin-canting angle is \(\sim 20^\circ\) from the c-axis. Therefore, for \(0.2 \leq x \leq 0.4\), SC definitely coexists with FM (at least FM components) even at zero field. Our recent magnetic Compton scattering experiment for EuFe\(_2\)(As\(_{0.7}\)P\(_{0.3}\)) also confirms this scenario [43]. For \(x > 0.4\), only the Eu-FM state is shown. Here we should mention a recent study of the phase diagram using single crystals, which positions the SC dome in a narrower window around \(x = 0.2\) [40]. This discrepancy may be due to the Eu-deficiency in the single crystal samples, as we discussed above. There remains an unresolved issue on the Eu-spin sate below the SC dome. One is a ‘pure’ FM with canted easy magnetization axis. The other is canted AFM or spiral FM with ferromagnetic components along the c-axis. To pin down this issue, a neutron diffraction study is called for.
Compared with the 'old' systems with coexisting SC and FM, then, what is special in the present Eu122 system? Here we point out three distinguishable features. (1) The FM has an unprecedentedly large saturated moment (\( \sim 7 \mu_B / \text{Eu} \)). (2) The magnetic ordering temperature \( T_M \) is very near the superconducting transition one \( T_c \), and both are relatively high: once \( T_c < T_M^5 \), SC disappears. (3) SC coexists with FM in broad ranges of temperature and field. All these features make the Eu122 system worth studying further.

Finally, we would like to discuss why SC and FM are compatible in the Eu122 system. First of all, the superconducting upper critical fields \( H_{c2} \) in 122 Fe-based superconductors are very high (e.g. \( \sim 60 \text{T} \) for BaFe\(_2\)As\(_2\) [44]). The \( H_{c2} \) values are actually higher than the hyperfine field on the Eu nucleus (\( \sim 28 \text{T} \)) from the Mössbauer measurement [37]. This makes SC survive even in the presence of a strong internal field via RKKY interactions. Secondly, it was indicated that all five Fe 3d orbitals contribute to the density of states near the Fermi level [45]. However, only \( d_{x^2} \) and \( d_{xy} \) orbitals are most probably related to SC [46]. The \( d_{x^2-y^2} \) and \( d_z^2 \) electrons are supposed to be responsible for mediating RKKY interactions [27]. Consequently, both SC and FM are well supported. In this sense, therefore, the Eu122 system seems to be a very rare platform for studying the challenging issues of the coexistence of SC and FM.

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