Reentrant superconductivity in Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$

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Abstract

The interplay between superconductivity and Eu$^{2+}$ magnetic ordering in Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ is studied by means of electrical transport and magnetic measurements. For the near optimally doped sample Eu(Fe$_{0.75}$Ir$_{0.25}$)$_2$As$_2$, we witnessed two distinct transitions: a superconducting transition below 22.6 K which is followed by a resistivity reentrance caused by the ordering of the Eu$^{2+}$ moments. Further, the low field magnetization measurements show a prominent diamagnetic signal due to superconductivity, which is remarkable in the presence of a large-moment magnetically ordered system. The electronic structure for 12.5% Ir doped EuFe$_{25}$Ir$_{25}$As$_2$ is investigated along with the parent compound EuFe$_2$As$_2$. As compared to EuFe$_2$As$_2$, the doped compound has an effectively lower value of density of states throughout the energy scale with a more extended bandwidth and stronger hybridization involving Ir. Shifting of the Fermi energy and a change in band filling in EuFe$_{1.75}$Ir$_{0.25}$As$_2$ with respect to the pure compound indicate electron doping in the system.

(Some figures may appear in colour only in the online journal)
the proximity of Eu$^{2+}$ magnetic ordering. On the other hand, Ni doping in EuFe$_{2-x}$Ni$_x$As$_2$ [24] showed only FM ordering of the Eu$^{2+}$ moments but no SC. However, 4d and 5d transition metals are quite different from their 3d counterparts in several aspects. Since 4d and 5d orbitals are more extended than the 3d orbitals, there will be more hybridization with As as well as with Fe. So, the effective Hund’s coupling on the atoms will be weaker, which works against magnetism and thereby suppresses the SDW in favor of SC [25]. There are reports on Ir doped ‘122’ systems which give the highest superconducting transition temperatures ($T_c$) among the transition metal doped ‘122’ systems [26, 27]. This has motivated us to dope Fe with Ir in EuFe$_2$As$_2$ which might exhibit $T_c$ higher than the Eu$^{2+}$ magnetic ordering temperature.

In this paper, we study the interplay between SC and magnetism in Ir doped EuFe$_2$As$_2$ polycrystalline samples through electrical resistivity $\rho(T)$ and magnetization measurements. We observe a sharp resistivity drop below 22.6 K which is ascribed to a SC transition. On further reducing the temperature, $\rho(T)$ increases again and exhibits a maximum at 15 K caused by the ordering of the Eu$^{2+}$ moments. Interestingly, we notice a prominent diamagnetic signal in the low field magnetization measurements.

The polycrystalline samples of Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ ($x = 0$, 0.05, 0.11 and 0.14) were prepared using the solid state reaction method as described in our earlier reports [16, 17, 28]. Stoichiometric amounts of the starting elements of Eu chips (99.9%), Fe powder (99.999%), Ir powder (99.99%) and As chips (99.999%) were used for the reaction. The crushed polycrystalline samples were characterized by x-ray diffraction with Cu-Kα radiation to determine the single phase nature and crystal structure. A scanning electron microscope (SEM) equipped with energy dispersive x-ray (EDX) analysis...
was used to check the homogeneity and composition of the samples. The electrical transport properties were measured by a standard four-probe technique using a physical properties measurement system (PPMS, Quantum Design, USA) and a closed-cycle refrigerator (Oxford Instruments). The magnetic properties of the samples have been probed using a commercial SQUID magnetometer (MPMS, Quantum Design).

The room temperature powder x-ray diffraction patterns (figure 1(a)) for the Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ ($x = 0, 0.05, 0.11$ and $0.14$) samples reveal that all the samples crystallize in a ThCr$_2$Si$_2$-type tetragonal crystal structure (space group I4/mmm). The single phase nature of the samples is evident along with a very small amount of FeAs impurity phase [29] which can be removed by optimizing the annealing process. From the EDX analysis, the atomic ratio Ir/Fe was found to be 5.45/94.55, 11.50/88.50 and 14.85/85.15 for the samples $x = 0.05, 0.11$ and $0.14$, respectively. We find that for $x = 0.14$, the SDW transition is shifted towards lower temperature by 20 K and corresponds to the SDW/structural transition [15]. We find that for $x = 0$, the SDW transition is shifted towards lower temperature by 20 K and there is no signature of SC. On further increasing the doping concentration to $x = 0.11$, a superconducting phase appears at around 21 K with a reentrant behavior in addition to an SDW transition at 90 K. For a critical concentration of $x = 0.14$, the SDW/structural transition gets completely suppressed and a sharp drop in resistivity is observed below 22.6 K. After achieving zero value, the resistivity again starts to increase and exhibits a maximum at $\sim 15$ K ($T_M$) and then again heads towards zero. We attribute this to the interplay between SC and the magnetic ordering of Eu$^{2+}$ moments below 18 K which hinders the SC and hence the zero resistance state. This behavior is reminiscent of reentrant SC observed in the ternary Chevrel phases [5] or in the rare-earth nickel borocarbides [6–8]. For $x \sim 0.16$, we find that the $T_M$ is shifted to 19 K and the resistivity does not reach a zero value, which is similar to the result for the 11% doped sample.

To elucidate the resistivity anomalies observed in the near optimally doped Eu(Fe$_{0.88}$Ir$_{0.14}$)$_2$As$_2$ sample, we have investigated the magnetic field dependence of resistivity (figure 3). With increasing applied magnetic field, the resistivity drop shifts towards the lower temperature and becomes broadened, confirming the SC transition. On the other hand, the reentrant feature of the electrical resistivity gets smeared out with increasing magnetic field. For $H \geq 1$ T, only a broadened superconducting transition is seen.

**Table 1.** The lattice parameters $a$, $c$, $c/a$ ratio and unit cell volume $V$ of the ThCr$_2$Si$_2$-type tetragonal system Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ ($x = 0$, 0.05, 0.11 and 0.14).

| $x$ | $a$ (Å)       | $c$ (Å)       | $c/a$ | $V$ (Å$^3$) |
|-----|---------------|---------------|-------|-------------|
| 0   | 3.9113(2)     | 12.1360(2)    | 3.103 | 185.67(1)   |
| 0.05| 3.9163(1)     | 12.1220(3)    | 3.095 | 185.92(2)   |
| 0.11| 3.9257(3)     | 12.0790(1)    | 3.077 | 186.16(1)   |
| 0.14| 3.9328(5)     | 12.0560(3)    | 3.065 | 186.47(1)   |

**Figure 2.** The temperature dependence of the electrical resistivity normalized to $\rho(300$ K) for Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ at zero field.

**Figure 3.** The temperature dependence of the electrical resistivity of Eu(Fe$_{0.88}$Ir$_{0.14}$)$_2$As$_2$ at various applied magnetic fields. Inset: critical fields extracted from the resistivity data at 90% and 50% of the normal state resistivity.
competing with the ferromagnetic component of the Eu$^{2+}$ moment ordering, which prevents the resistivity attaining zero value. The upper critical fields $H_c(T)$ versus $T_c$ are shown in the inset of figure 3 where $T_c$ is defined at resistivity values corresponding to 90% and 50% of the normal state resistivity. The behavior of $H_c(T)$ is as expected for superconductors in the presence of magnetic ions, showing a magnetic phase transition below $T_c$. Here, the Eu$^{2+}$ magnetic transition around 18 K is clearly influencing the change of slope in $H_c(T)$. A similar scenario has been observed in the case of the Co doped EuFe$_2$As$_2$ system [22] whereas a deep minimum of $H_c(T)$ appears around the antiferromagnetic transition temperature of rare-earth ions in RNi$_2$B$_2$C ($R$ = rare-earth) [30]. Here we have made a rough estimation of the upper critical field $H_C(0)$ using the Werthamer–Helfand–Hohenberg formula $H_C(0) = -0.693T_c(\partial H_C/\partial T)_{T=T_c}$ where we have used the initial slope $\mu_0(\partial H_C/\partial T) = -0.95$ T K$^{-1}$, yielding an upper critical field of $\sim 15$ T. This upper critical field is lower than the Pauli paramagnetic limit $\mu_0H_P = 1.847T_c = 39.7$ T. The lower value of $H_C(0)$ in Eu-containing superconductors, for instance in Co doped EuFe$_2$As$_2$ ($H_C(0) = 26$ T) [22] and P doped EuFe$_2$As$_2$ ($H_C(0) = 30$ T) [31], suggests the presence of a significant internal magnetic field from Eu$^{2+}$ moments.

Further evidence of the reentrant superconductivity is obtained from the temperature dependence of dc magnetic susceptibility on the near optimally doped sample Eu(Fe$_{0.86}$Ir$_{0.14}$)$_2$As$_2$ under an applied field of 5 Oe (figure 4). Due to the proximity of the superconducting transition and Eu$^{2+}$ magnetic ordering, the large-moment magnetic ordering of Eu$^{2+}$ dominates the superconducting diamagnetic signal, which is very hard to observe directly as has been evidenced in the Co doped EuFe$_2$As$_2$ system [22, 23, 32] or P doped EuFe$_2$As$_2$ polycrystalline samples [31], whereas P doped EuFe$_2$As$_2$ single crystals manifest a clear diamagnetic signal when the applied magnetic field is parallel to the $ab$-plane of the crystals [18]. Interestingly, in our case of the Ir doped EuFe$_2$As$_2$ polycrystalline system, when considering the zero field cooled (ZFC) data, a prominent diamagnetic signal has been observed below 16 K above which the susceptibility becomes positive and shows a maximum at around 18 K. A drop in the ZFC susceptibility data at around 21 K is close to the onset $T_c$ as seen through a sharp drop in resistivity. In short the entire reentrant behavior as observed through resistivity measurements is re-established by the low field dc magnetic susceptibility measurements.

Figure 5 shows the field cooled (FC) dc magnetic susceptibility for Eu(Fe$_{0.86}$Ir$_{0.14}$)$_2$As$_2$ under $H = 0.1$ T. The $\chi(T)$ data could be well described by the modified Curie–Weiss law $\chi(T) = \chi_0 + C/(T - \theta)$ above 30 K, where $\chi_0$ represents the temperature independent term, $C$ is the Curie constant and $\theta$ is the Curie–Weiss temperature. The solid line through the data points in figure 5 shows the fit to this law with the fitting parameters $\chi_0 = 1.86 \times 10^{-4}$ emu mol$^{-1}$, $C = 8.23$ emu K mol$^{-1}$ and $\theta = 22.8$ K. The calculated value of effective magnetic moment $\mu_{eff} = 8.1 \mu_B$ per Eu-ion is close to the theoretical value of 7.94 $\mu_B$ for a free Eu$^{2+}$ ion with $S = 7/2$. Below 20 K, $\chi(T)$ increases steeply with decreasing temperature, however, it does not saturate at lower temperature as shown in the inset of figure 5. Furthermore, the temperature dependences of ZFC and FC dc magnetization measurements have been performed for Eu(Fe$_{0.86}$Ir$_{0.14}$)$_2$As$_2$ under various fixed magnetic fields (figure 6). The data reveal a decrease of $T_M$ (the temperature at which the magnetization shows a maximum) with increasing applied magnetic field up to 0.1 T (figure 4). For $H \geq 0.2$ T, the low temperature magnetization appears to be more of a field stabilized FM phase. Under high magnetic field, the saturation of magnetization gives a fully polarized value $\sim 6.9 \mu_B$/f.u. as expected for parallelly aligned Eu$^{2+}$ moments ($gS = 7.0 \mu_B$/f.u. with $g = 2$, $S = 7/2$). The FC and ZFC magnetization data coincide at higher temperatures, they differ significantly only at lower temperatures below $T_M$ where ZFC magnetization...
values are lower than those of FC values. All the above observations suggest that the magnetic ordering could be antiferromagnetic with the presence of a ferromagnetic component, the so-called canted antiferromagnet (C-AFM). The Co doped EuFe$_2$As$_2$ system [32] shows similar magnetic behavior where Eu$^{2+}$ moments are found to be ordered C-AFM which causes reentrance in the SC. On the other hand, in the P doped EuFe$_2$As$_2$ system [18], Eu$^{2+}$ moments order antiferromagnetically and coexist with SC but above a certain doping level Eu$^{2+}$ moments order ferromagnetically, which destroys the superconductivity. Later, the same group came up with a detailed discussion proposing that the magnetic moments of the Eu$^{2+}$ ions are not simply AFM aligned in adjacent $ab$ planes, but canted, yielding a ferromagnetic contribution along the $c$ direction and the superconducting phase coexists with the C-AFM in EuFe$_2$(As$_{1-x}$P$_x$)$_2$ crystals [33].

To get some information about the electronic states for the doped compound, we carried out the density-functional band structure calculations using the full potential linear augmented plane wave plus local orbitals (FP–LAPW + lo) method as implemented in the WIEN2K code [34]. The Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was employed for the exchange correlation potential [35]. Additionally, to account for the strong Coulomb repulsion within the Eu 4f orbitals we have included $U$ on a mean-field level using the GGA + $U$ approximation. There exist no spectroscopy data for EuFe$_2$As$_2$, therefore, we have used $U = 8$ eV, the standard value for an Eu$^{2+}$ ion [15, 28, 36]. We have employed supercell calculations to explicitly study the effect of partial Ir substitutions on the Fe site. For this purpose, a $2 \times 2 \times 1$ supercell of the EuFe$_2$As$_2$ unit cell was constructed for a 12.5% Ir doped (in between 11% and 14% doping concentration for which SC evolved) compound. We then replaced one Fe in each plane by Ir which corresponds to the nominal composition of Eu$_5$Fe$_{14}$Ir$_2$As$_{16}$. The lattice constants for the unit cell of the 12.5% Ir doped compound were obtained by interpolating linearly the experimental lattice parameters listed in table 1, the outcome of which is $a = 3.930$ Å and $c = 12.066$ Å. The atomic position of As was kept fixed at $z = 0.362$ (experimental $z_{As}$ of EuFe$_2$As$_2$) for both the compounds.

We have performed electronic structure calculations for both EuFe$_2$As$_2$ and EuFe$_{1.75}$Ir$_{0.25}$As$_2$ in the quenched paramagnetic state, that means no spin polarization is allowed on the Fe or Ir ions in the calculations. The general shape of our density of states for EuFe$_2$As$_2$ (figure 7(a)) is similar to that reported in the literature [15, 36]. Since the Eu 4f states for both the compounds are quite localized, the Eu ions are in a stable 2+ valence state. The calculated spin moment for Eu$^{2+}$ is about 6.9 $\mu_B$ for both the compounds which is consistent with the experimental values. Apart from the Eu 4f states, the remaining density of states (DOS) is modified significantly due to the Ir substitution. More importantly, near the Fermi level, the DOS for EuFe$_2$As$_2$ is almost flat as observed for other iron-pnictide parent compounds [37] whereas for the Ir doped compound, a peak appears near the Fermi level. A similar effect has been observed for an Ir doped SrFe$_2$As$_2$ superconducting system [25] or a K doped EuFe$_2$As$_2$ system [28]. The total DOS near the Fermi level is mainly contributed by Fe 3d states but a small contribution comes from the Ir 5d character as well. The total DOS at the Fermi level $N(E_F)$ is $5.48$ states/eV f.u. for EuFe$_2$As$_2$ which is reduced to $5.24$ states/eV f.u. for EuFe$_{1.75}$Ir$_{0.25}$As$_2$. Our calculation on the doped compound shows a shift in Fermi energy by 0.02 eV above the Fermi level and a change in band filling as compared to the pure compound, indicating electron doping in the system by partial substitution of Fe by Ir. As can be seen from figure 7, the overall DOS for the doped compound is reduced throughout the energy scale as compared to pure EuFe$_2$As$_2$. The reduction in DOS is associated with the extended d-band width and stronger
hybridization involving Ir. The occurrence of SC in the doped system can also be justified by the change in structural parameters and increased hybridization due to Ir substitution. Since the \( e \) lattice parameters shrink rather anisotropically i.e. \( c/a \) decreases with increasing Ir content (see table 1), the lattice becomes more three-dimensional. A similar anisotropic change in the lattice parameters leading to bulk SC was also observed for isovalent substitution of Fe by larger Ru atoms or As by smaller P atoms in AFe\(_2\)As\(_2\) (\( A = \text{Sr, Eu} \) [18, 38]). In these systems, the substitution does not provide electron or hole doping but rather suppresses the Fe SDW order in favor of SC by reducing the Stoner enhancement of Fe and increasing bandwidth due to stronger hybridization. So, apart from the electron doping, Ir substitution has a similar effect to that of pressure, i.e. broadening the bands and increasing hybridization, which also plays an important role in suppressing SDW and inducing SC in the system.

In summary, reentrant superconductivity has been evidenced in Eu\( (\text{Fe}_{1-x}\text{Ir}_x)\)\(_2\)As\(_2\) samples through our comprehensive investigation of (magneto)resistivity and low field magnetic susceptibility. With increasing Ir doping, the SDW order in EuFe\(_2\)As\(_2\) is gradually suppressed and SC is induced at \( \approx 22.6 \, \text{K} \) for a 14\% Ir doped sample. The low field magnetization measurements of Eu(Fe\(_{0.85}\text{Ir}_{0.14})_2\)As\(_2\) show a prominent diamagnetic signal due to SC with a reentrant feature. The magnetization measurements at various applied magnetic fields reveal that the magnetic ordering temperature \( T_M \) of Eu\(^{2+} \) moments shifts towards lower temperature with increasing field up to 0.1 T, above which the magnetization looks more like a field stabilized FM phase. Thus, below 18 K, Eu\(^{2+} \) moments are most likely ordered antiferromagnetically with the presence of a ferromagnetic component (canted antiferromagnet) which causes resistivity reentrance. Further experiments are planned to probe the magnetism of Eu ions as well as to investigate the possible presence of spontaneous vortices.

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