Anomalous critical fields and the absence of Meissner state in Eu(Fe_{0.88}Ir_{0.12})_2As_2 crystals

Wen-He Jiao, Hui-Fei Zhai, Jin-Ke Bao, Yong-Kang Luo, Qian Tao, Chun-Mu Feng, Zhu-An Xu and Guang-Han Cao

Department of Physics, State Key Laboratory of Silicon Materials, and Center for Correlated Matter, Zhejiang University, Hangzhou 310027, People's Republic of China
E-mail: ghcao@zju.edu.cn

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Abstract. We report electrical and magnetic measurements of an optimally doped Eu(Fe_{0.88}Ir_{0.12})_2As_2 crystal which shows superconductivity at $T_{sc} = 22$ K and magnetic ordering of the Eu$^{2+}$ spins below 20 K. The results suggest that the Eu$^{2+}$ spins lie flat ferromagnetically in the $ab$ plane at $T_{m}^{ab} = 20$ K, and then tilt toward the $c$-axis at $T_{m}^{\text{tilt}} = 17.4$ K. The isothermal magnetization loop at low temperatures shows both ferromagnetic behavior and superconducting characteristics, unambiguously demonstrating the coexistence of ferromagnetism and superconductivity. The upper critical field measured is remarkably reduced, as compared to other Fe-based superconductors with the same $T_{sc}$, and it exhibits abnormal temperature dependence featured by the existence of an inflection point around $T_{m}^{ab}$, where the anisotropy ratio $\gamma$ ($\equiv H_{c2}^{ab}/H_{c2}^{c}$) shows a minimum value smaller than 1.0. These observations can be explained by a ferromagnetic exchange field of $\sim$30 T which tilts its direction toward the $c$-axis below $T_{m}^{\text{tilt}}$. The strong internal field, much higher than the intrinsic lower critical field expected, leads to the absence of Meissner state, which is confirmed by the magnetic measurements under ultra-low fields.

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1. Introduction

Superconductivity (SC) and ferromagnetism (FM) are two antagonistic cooperative phenomena in solid-state systems, thus it is very rare that SC coexists with FM (or even other magnetic states with ferromagnetic component) in a single material\(^2\) \([1, 2]\). Such material showing both SC and ferromagnetic components was earlier called ‘ferromagnetic superconductor’ (FMSC) \([1]\) or ‘magnetic superconductor’ \([3]\). Lorenz and Chu \([4]\) classified this special material into two categories according to its superconducting transition temperature \(T_{sc}\) and ferromagnetic transition temperature \(T_m\). When \(T_m > T_{sc}\), it is termed ‘superconducting ferromagnet’; and for \(T_m < T_{sc}\), it is called an FMSC.

Recently, possible FMSCs were found in the EuFe\(_2\)As\(_2\)-related system, where the Eu spins and the FeAs layers are respectively responsible for spontaneous magnetization and SC, by applying pressure \([5, 6]\) or by chemical doping with phosphorus \([7]\), cobalt \([8, 9]\) and ruthenium \([10]\). The parent compound EuFe\(_2\)As\(_2\) undergoes two antiferromagnetic transitions at \(\sim 20\) and \(\sim 195\) K, respectively, corresponding to the Eu and the Fe sublattices \([11, 12]\). The magnetic structure was revealed by a neutron diffraction study \([13]\) which shows an A-type antiferromagnetism (AFM) for the Eu\(^{2+}\) spins, and a stripe-like AFM (also called spin-density wave (SDW)) for the Fe magnetic moment. Both Eu and Fe moments are parallel to the crystallographic \(a\)-axis in the undoped EuFe\(_2\)As\(_2\). SC at 5–30 K emerges when the Fe-site SDW is sufficiently suppressed, either by applying high pressures or by an extrinsic doping. Simultaneously, the Eu\(^{2+}\) spins turn to the \(c\)-axis at low temperatures \([14, 15]\), which leads to FM \([7, 16, 17]\), helimagnetism \([8]\) or spin canting \([18, 19]\), all with significant ferromagnetic component. The coexistence of SC and FM was later confirmed and further studied by various experimental techniques \([20–27]\); nevertheless, there were different explanations for the Eu-spin ordering \([6, 28–30]\), questioning the existence of FMSCs in the EuFe\(_2\)As\(_2\)-related system.

Owing to the delicate interplay between SC and Eu-spin ordering, the superconducting and magnetic transitions of the above possible FMSCs are rather subtle, and the chemical doping in EuFe\(_2\)As\(_2\) with different elements may be non-trivial. In the case of pressure-induced SC in EuFe\(_2\)As\(_2\), different superconducting transitions with \([5, 28]\) (or without \([6]\)) re-entrant resistance were reported. Similar situation exists for the phosphorus-substituting \([7, 21–23, 29]\)

\(^2\) For a recent short review, see \([2]\).
and cobalt-doping [8, 9, 24–27] studies in EuFe$_2$As$_2$. In some cases, zero resistance could not be achieved down to 2 K [5, 8, 24]. It was even observed that the in-plane resistance goes to zero, but the inter-plane one does not, below $T_{sc}$ in Eu(Fe$_{0.75}$Ru$_{0.25}$)$_2$As$_2$ crystals [10]. Diverse results were also reported for the magnetic transition. The nature of Eu-spin ordering, especially in the region of SC of the phosphorus-substituted system, remains controversial [7, 18, 22, 29, 30].

So, it is preferable to find a system that shows robust SC and FM. Considering SC up to 24.2 K in SrFe$_{2-x}$Ir$_x$As$_2$ system [31], we carried out Ir doping in EuFe$_2$As$_2$, and sharp superconducting transition with zero resistance was observed in the Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ crystals [32]. Also, re-entrant SC was very recently reported independently in the Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ polycrystalline samples [33].

Here we report peculiar superconducting and magnetic properties revealed in an optimally doped Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ ($x = 0.12$) crystal. The isothermal magnetization loop at low temperatures was featured by a superposition of both Eu-spin FM and FeAs-layer SC, demonstrating that Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ is an FMSC. While the sample shows a sharp drop to zero in resistivity and steep diamagnetic transition in zero-field-cooling (ZFC) magnetic susceptibility at $T_{sc} = 22$ K, no obvious Meissner effect could be detected for $T < T_m$ by the field-cooling (FC) magnetization measurement under an ultra-low field down to 0.1 Oe. The lower critical field cannot be defined because the initial magnetization curve deviates from linearity at zero field. Therefore, the Meissner state is absent in the FMSC. The upper critical field is found to be remarkably reduced as compared to its analogous iron-based superconductors, and it shows abnormal temperature dependence and anomalous anisotropy around $T_m$. These results strongly suggest the existence of internal exchange field which virtually alters the magnetic properties of the superconductor.

2. Experimental details

Single crystals of Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ were grown out of the self-flux (Fe,Ir)As in a way different from that in our previous reports [10, 34]. First, a mixture of small Eu chunks and Fe, Ir, As powders (Alfa Aesar, >99.9%) in a molar ratio of Eu:Fe:Ir:As = 1:4:1:0:9:5, sealed in an evacuated quartz ampoule, was heated to 973 K for 24 h. The resultant was thoroughly ground before being loaded into an alumina crucible. The crucible was then sealed in a stainless steel tube by arc welding under an atmosphere of argon; it was subsequently heated up to 1573 K for 10 h in a muffle furnace filled with argon. After holding at 1573 K for 5 h, it was allowed to cool down to 1223 K at the rate of 5 K h$^{-1}$, followed by the switching off of the furnace. Large crystals with size up to $4 \times 4 \times 0.8 \text{ mm}^3$ could be harvested.

The as-grown crystal flakes were characterized by x-ray diffraction (XRD) using a RIGAKU D/Max-rA diffractometer with Cu-K$\alpha$ radiation. The exact composition of the crystals was determined by energy dispersive x-ray spectroscopy (EDXS) affiliated to a field-emission scanning electron microscope (FEI Model SIRION). The measurement precision was better than ±5% for the elements measured.

We mainly focused on the measurements of in-plane electrical resistivity ($\rho_{ab}$) and magnetization with the external field parallel to the crystallographic $c$-axis ($M_c$). We selected one cleaved crystal for all the measurements below. Small portion of the crystal (sample A) was cut into a thin bar with dimensions $1.4 \times 0.65 \times 0.12 \text{ mm}^3$ to test its superconducting transition. The overall uncertainty in absolute resistivity, determined from the geometric dimensions, was estimated to be $\sim 25\%$. The magnetoresistance was measured on a Cryogenic
Mini-CFM measurement system by a standard four-terminal method using Keithley 2400 Digital Sourcemeter and 2182 Nanovoltmeter. The specimen with the dimensions $1.3 \times 0.46 \times 0.12 \text{ mm}^3$ was measured successively with the applied fields parallel and perpendicular to the $ab$ plane. Gold wires were attached with silver paint onto the specimen to make four linear electrodes. The applied dc current was 5 mA. The absolute value of the zero-field resistivity was normalized to that of sample A. The uncertainty in $T_{sc}$ value under the two configurations was within 0.1 K based on the zero-field data. The dc magnetization was measured on a Quantum Design Magnetic Property Measurement System (MPMS-5). The identical crystal with the dimensions $1.3 \times 1.3 \times 0.12 \text{ mm}^3$ (15.9 mg) was carefully mounted on a sample holder, with the external field perpendicular to the sample-flake plane (thus the demagnetization factor is $N_d \sim 0.84$). Low-field susceptibility measurements were performed (using an ultra-low-field option) after degaussing the magnet and after an accurate measurement of the residual field with a fluxgate magnetometer. The residual field was compensated by an additional coil, and the lowest magnetic field around the sample achieved $\pm 0.02 \text{ Oe}$.

3. Results and discussion

3.1. Sample’s characterizations

The as-grown crystals were easily cleaved along the basal planes, displaying shiny metallic luster on the surface. Indeed, the XRD pattern of the crystal flake lying on the sample holder shows only (00l) reflections, as shown in figure 1. The full-width at half-maximum (FWHM) is less than $0.15^\circ$, indicating good crystallinity. The $c$-axis parameter, calculated by a least-squares fit, is $c = 12.037(2) \text{ Å}$, obviously smaller than that of the undoped EuFe$_2$As$_2$ (12.136 Å [12]).
Figure 2. Temperature dependence of in-plane resistivity ($\rho_{ab}$) for Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ crystals. The dashed straight line is a guide to the eye. The inset magnifies the superconducting transition.

Similar result was observed in Ru-doped EuFe$_2$As$_2$ [10]. The exact Ir content was determined by EDXS, which gives the chemical formula of Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$, consistent with the 1:2:2 stoichiometry expected.

Figure 2 presents the temperature dependence of in-plane resistivity for the Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ crystal (sample A). No resistivity anomaly associated with the Fe-site SDW ordering can be seen. Furthermore, $\rho_{ab}(T)$ shows a linear temperature dependence in a broad temperature range above $T_{sc}$. These data strongly suggest that the Ir-doping level is in the optimal regime, since the linear temperature dependence of normal-state resistivity is only found for samples with optimal doping in the related systems such as Sr(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ [31] and Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [35]. A sharp superconducting transition appears below $T_{c^{\text{onset}}}$ = 22.2 K, and zero resistance is achieved at 21 K. No re-entrant resistance was observed below $T_{sc}$. For the crystals with $x = 0.10$ and 0.13, re-entrant resistance was detected, such as the case of the Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ polycrystalline samples [33]. This result further indicates that the $x = 0.12$ crystal is optimally doped with regard to SC. The superconducting transition width, conventionally defined by $\Delta T_{sc} = T(90\%\rho_n) - T(10\%\rho_n)$, where $\rho_n$ is the normal-state resistivity just above $T_{sc}$, is as small as 0.7 K, suggesting good quality of the sample with neat homogeneity.

3.2. Upper critical fields

Figure 3 shows the result of in-plane magneto-resistance measurement. As expected, the superconducting transition shifts downwards upon increasing magnetic fields. For $H \parallel c$, the decrease in $T_{sc}$ is more pronounced under a magnetic field higher than 2 T, qualitatively consistent with the superconducting anisotropy in a layered system described by the
Figure 3. Resistive transitions under different magnetic fields parallel (a) and perpendicular (b) to the basal plane of Eu(Fe_{0.88}Ir_{0.12})_2As_2 crystals. Panel (c) highlights the crossover of the superconducting transition temperatures under two directions of magnetic field. The derived upper critical fields $H_{c2}^{ab}$ and $H_{c2}^c$ are shown in (d), where $H_{c2}$ of SrFe_{1.5}Ir_{0.5}As_2 polycrystals [31] is plotted for comparison. Panel (e) depicts the anomalous anisotropy ratio $\gamma \equiv H_{c2}^{ab}/H_{c2}^c$ (left axis) and the derivative of $H_{c2}^{ab}$ (right axis). Panel (f) magnifies the $H_{c2}(T)$ curve where $\gamma < 1.0$.

Ginzburg–Landau theory [36]. However, the $T_{sc}$ value of $H||c$ is anomalously higher than that of $H||ab$ for $\mu_0 H < 1.5$ T, as shown in figure 3(c). By using the criteria of 90% of $\rho_n$ which determines the transition temperature under a magnetic field [$T_{c}(H)$], we obtained the temperature dependence of upper critical fields $H_{c2}(T)$ shown in figure 3(d). The values of the initial slope, $\mu_0 dH_{c2}^c/dT|_{T=T_{sc}} = -0.79(7)$ T K$^{-1}$ and $\mu_0 dH_{c2}^{ab}/dT|_{T=T_{sc}} = -0.68(7)$ T K$^{-1}$, are much smaller than that of the analogous superconductor SrFe_{1.3}Ir_{0.5}As_2 ($-3.3$ T K$^{-1}$) [31], Ba(Fe_{0.9}Co_{0.1})_2As_2 ($-4.9$ T K$^{-1}$) [37] and other iron-based superconductors [38]. The suppression of $H_{c2}$ in Eu(Fe_{0.88}Ir_{0.12})_2As_2 can be ascribed to the indirect exchange interactions between Eu$^{2+}$ spins (via Fe 3d electrons) which produces a strong internal field, although the Eu-spin ordering temperature is 2 K lower (it is also noted that the external field tends to enhance the FM of the Eu$^{2+}$ spins [8, 19]). By a rough linear extrapolation, the upper limits of $\mu_0 H_{c2}^c(0)$ and $\mu_0 H_{c2}^{ab}(0)$ are estimated to be 15.7(3) and 18.9(5) T, respectively. Compared to $\mu_0 H_{c2}(0) \sim 50$ T for Ba(Fe_{0.9}Co_{0.1})_2As_2 with the same $T_{sc} = 22$ K [37], the upper critical field of Eu(Fe_{0.88}Ir_{0.12})_2As_2 was about 30 T smaller at zero temperature. Similar suppression of $H_{c2}(T)$ was also reported in the pressure-induced superconductor EuFe$_2$As$_2$ ($T_{sc} = 30$ K under 2.5 GPa) [39], which shows $\mu_0 H_{c2}^c(0) = 22$ T and $\mu_0 H_{c2}^{ab}(0) = 25$ T. In a zeroth-order approximation, which assumes that SC in the FeAs layers and FM in the Eu sublattice are decoupled, the decrease in $H_{c2}$ is simply ascribed to the internal exchange field. This point is supported by the $^{151}$Eu Mössbauer spectroscopy which indicates
a hyperfine field of 25–30 T on the Eu nuclei in the EuFe$_2$As$_2$-related systems [14, 23]. The decoupling nature between SC and FM has been ascribed to the multiorbital feature of Fe 3d electrons, which simultaneously allows SC mainly from the d$_{yz}$ and d$_{zx}$ orbitals and FM due to an effective Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions among the Eu$^{2+}$ spins mediated mainly through the d$_{2-x^2}$ and d$_{2}$ electrons [22]. The extremely high intrinsic upper critical field in iron pnictides guarantees the survival of SC in the presence of the internal exchange field.

It is noted that the upper critical fields show abnormal temperature dependence featured by a convex curvature just below $T_{sc} = 22$ K, followed by a concave curvature. Thus $H_{c2}(T)$ curves have an inflection point at $\sim$20 K, which is clearly seen in the derivative of $H_{c2}(T)$ (figure 3(e)). This anomalous $H_{c2}(T)$ behavior is related to the magnetic ordering of Eu$^{2+}$ spins (to be discussed in the next section).

The anisotropy ratio of upper critical fields, defined by $\gamma = H_{c2}^{ab}/H_{c2}^{c}$, is about 1.3 at low temperatures, resembling other 122-type Fe-based superconductors [37, 40]. However, the temperature dependence $\gamma(T)$ is qualitatively different. Normally, $\gamma$ increases monotonically with temperature [37, 40], but here for Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$, $\gamma$ decreases significantly for $T > 13$ K and, even an inverse anisotropy ($\gamma < 1$) appears around 20 K. This anomalous $\gamma(T)$ behavior is likely to be associated with the re-orientation of the internal field. Generally, the internal magnetic field ($H_{in}$) includes a dominant exchange field ($H_{ex}$) plus a spontaneously magnetized one, $H_{in} = H_{ex} + 4\pi M$ [41]. Assuming that the internal field has two components $H_{in}^{c}$ and $H_{in}^{ab}$, under a zeroth-order approximation, the intrinsic upper critical fields in the absence of internal field (denoted as $H_{c2}^{c}$) should be $H_{c2} = H_{c2}^{c} + H_{in}^{c}$ and $H_{c2}^{ab} = H_{c2}^{ab} + H_{in}^{ab}$. Thus the apparent anisotropy ratio is

$$
\gamma = \frac{H_{c2}^{ab}}{H_{c2}^{c}} = \frac{H_{c2}^{ab} - H_{in}^{ab}}{H_{c2}^{c} - H_{in}^{c}} = \frac{\gamma_s - H_{in}^{ab}/H_{c2}^{cs}}{1 - H_{in}^{c}/H_{c2}^{cs}},
$$

where $\gamma_s = H_{c2}^{ab}/H_{c2}^{cs}$. Since the in-plane internal field is along the $a$-axis in the parent compound [12, 13, 34], $H_{in}^{c}$ could be much less than $H_{in}^{ab}$ or $H_{c2}^{c}$ (thus $H_{in}^{c}/H_{c2}^{c} \ll 1$) near $T_m$. In this situation, $\gamma \approx \gamma_s - H_{in}^{ab}/H_{c2}^{cs}$, which explains the anomalously small $\gamma$-value around 20 K. At lower temperatures, the Eu-spin re-orientates toward the crystallographic $c$-axis [14, 18, 23], which means that $H_{in}^{c}$ is comparable to, or even higher than $H_{in}^{ab}$. Therefore, $\gamma$ recovers to a value larger than 1.0 at low temperatures.

3.3. Low-field magnetic susceptibility

Figure 4 shows the temperature dependence of magnetic susceptibility for Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ crystals under an external field of 10 Oe. For the ZFC susceptibility with the field along $c$-axis ($\chi^{c}_{ZFC}$), a diamagnetic transition occurs below $T_{sc} = 22.1$ K, consistent with the above resistivity measurement. However, $\chi^{c}_{ZFC}$ increases sharply with temperature decreasing below 20 K, suggesting a strong magnetism opposing the superconducting diamagnetism. Below 17.4 K, $\chi^{c}_{ZFC}$ decreases steadily. The superconducting magnetic shielding fraction is as large as 600% at 2 K. If the demagnetization factor ($N_d \sim 0.84$) is taken into account, the corrected shielding fraction $4\pi \chi(1 - N_d)$ is close to 100%, suggestive of bulk SC. For the FC susceptibility ($\chi^{ab}_{FC}$), however, no diamagnetic signal is present at all. Instead it increases with decreasing temperature until being ‘saturated’ at 17.4 K. The susceptibility with the field along the basal plane ($\chi^{ab}$) shown
Figure 4. Temperature dependence of magnetic susceptibility of \( \text{Eu(Fe}_{0.88}\text{Ir}_{0.12})_2\text{As}_2 \) crystals under an external field \( H_{\|c} = 10 \text{ Oe} \) (a) and \( H_{\|ab} = 10 \text{ Oe} \) (b) in FC and ZFC measurement modes. The anisotropy in susceptibility, defined as \( \chi_{fc}^{ab}/\chi_{fc} \), is displayed in (c). Panel (d) zooms in the FC data where the superconducting and magnetic transitions occur. \( T_m^{ab} \) and \( T_m^{\text{tilt}} \) denote the ferromagnetic ordering temperatures with Eu-spin lying in the basal plane and tilting towards the \( c \) axis, respectively. Panel (e) shows the Curie–Weiss fitting for \( \chi_c \) using equation \( \chi = \chi_0 + C/(T - \theta) \). \( \chi_0 \) (\( \sim -5.6 \times 10^{-4} \text{ emu mol}^{-1} \)) represents the temperature-independent part of susceptibility including the contribution from the sample holder.

In figure 4(b) indicates no signature of superconducting transition for both FC and ZFC modes, similar to that observed in \( \text{Eu(Fe}_{0.75}\text{Ru}_{0.25})_2\text{As}_2 \) crystals [10]. This phenomenon suggests that the Eu\(^{2+} \) spins tend to lie flat and ordered within the basal plane around \( T_{sc} \), which suppresses SC. In addition, no magnetic shielding (i.e. no diamagnetic signal in the ZFC mode) effect appears for \( H_{\|ab} \) down to 2 K, which reflects absence of zero resistance for the current along the \( c \)-axis, consistent with the ‘anisotropic SC’ reported in [10].

Here, let us discuss the possibility of the Eu-spin ordering. In an analogous \( \text{EuFe}_2\text{P}_2 \) ferromagnet, a ferromagnetic transition appears at 29 K, followed by another magnetic transition at 26 K featured by the canting of Eu moments toward the \( c \)-axis [42]. The FM as well as the spin canting at low temperatures was confirmed by neutron diffraction [17]. Similar magnetic ordering is anticipated in \( \text{Eu(Fe}_{0.88}\text{Ir}_{0.12})_2\text{As}_2 \). Figure 4(c) shows the temperature dependence of anisotropy in \( \chi_{fc} \). The anisotropic ratio increases steeply below 20 K, suggesting that the Eu\(^{2+} \) spins start to lie flat in the basal plane. The Curie–Weiss fitting using equation \( \chi = \chi_0 + C/(T - \theta) \) with the high-temperature susceptibility data (figure 4(d)) gives an effective moment of 8.0 \( \mu_\text{B} \) f.u.\(^{-1} \) (consistent with the Eu\(^{2+} \) spin state of \( S = 7/2 \)), and a paramagnetic Curie temperature of \( \theta = 22 \text{ K} \). The positive \( \theta \) value, which is close to the magnetic ordering temperature, suggests a ferromagnetic exchange interaction between the Eu\(^{2+} \) spins. We thus propose that the Eu moments lie ferromagnetically in the \( ab \) plane below \( T_m^{ab} = 20 \text{ K} \). At 17.4 K,
Figure 5. Temperature dependence of magnetic susceptibility of Eu(Fe_{0.88}Ir_{0.12})_2As_2 crystals under ultra-low fields  H_{lc} = 0.1 Oe (a), 0.15 Oe (b) and 0.25 Oe (c). The data of FC measurements are highlighted to detect possible Meissner effect. Panel (d) plots the difference in χ_{fc} between (a) and (c). Superconducting and magnetic transition temperatures (T_{sc}, T_{ab}^{m} and T_{tilt}^{m}) are marked by arrows in (a) and (d).

a clear kink is seen for χ_{ab} and χ_{ab}^{m}/χ_{fc}. This kink can be understood as a consequence of Eu-spin tilting or canting [14, 15, 19] as observed in many EuFe_{2}As_{2}-related system. However, the canted AFM [18, 19, 33], which is expected to show pure AFM behavior for H∥ab, is unlikely because χ_{ab} increases below T_{m}^{tilt} (note that χ_{ab} of EuFe_{2}As_{2} crystals decreases steeply below the magnetic ordering temperature [34]). Besides, the FM-like hysteresis in magnetization with the field along the basal plane (see figure S1 in the supplementary data (available from stacks.iop.org/NJP/15/113002/mmedia)) also suggests FM component in the basal plane, which is incompatible with the canted AFM. The ‘saturation’ in χ_{fc} below T_{m}^{tilt} = 17.4 K (figures 4(a) and (d)) is probably due to the formation of antiparallel ferromagnetic domains that are difficult to be ‘magnetized’. The peak at a lower temperature ~15 K seems to be related to the freezing of the magnetic (micro)domains, resembling the recently reported re-entrant spin-glass behavior in the EuFe_{2}(As_{1−x}P_{x})_2 system [43]. Note that the heat capacity data (not shown here) show an abrupt jump at T_{m}^{tilt} rather than at T_{m}^{ab}, suggesting that the full magnetic ordering occurs below T_{m}^{tilt}, and the magnetic ordering at T_{m}^{ab} is basically two dimensional in nature. Indeed, the M(T) curves for different fields parallel and perpendicular to the basal plane (see figure S2 in the supplementary data) show that T_{m}^{ab} increases with magnetic field. Meanwhile, T_{m}^{tilt} decreases with the field for both H∥c and H∥ab, which can be explained by spin tilting/canting. It is pointed out that this scenario of spin re-orientation fully supports the above explanation for the anomalous anisotropy in upper critical field for T > T_{m}^{tilt} (figure 3(f)).

Since T_{m}^{ab} and T_{m}^{tilt} are respectively 2 and 4.6 K lower than T_{sc}, superconducting Meissner effect should be detected in the temperature range of T_{m}^{tilt} < T < T_{sc} for the applied field parallel to the c direction. Indeed, a significant Meissner signal (magnetic expulsion in the paramagnetic background) is present under an ultra-low magnetic field (H < 0.25 Oe), as shown in figure 5.
For $T < T_{m}^{ab}$, however, $\chi_{lc}$ increases with decreasing temperature, indicating a spontaneous field that penetrates the superconductor. According to the discussions above, the internal field is much larger than the intrinsic lower critical field, i.e. $H_{in} \gg H_{c1}^{*}$. This means that the Meissner state is absent below $T_{m}^{ab}$ even under zero external field. Nevertheless, the Meissner effect, which describes a phenomenon where the applied magnetic field is expelled from a superconductor during its transition to superconducting state, is reflected from the evidence that the susceptibility at low temperatures is smaller for lower external field applied. This can be seen in figure 5(d), which shows relatively strong ‘diamagnetic’ signal by subtracting $\chi_{lc}^{0.25 \text{Oe}}$ from $\chi_{lc}^{0.1 \text{Oe}}$. This effect was also reported in Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ system [8].

3.4. Low-temperature isothermal magnetization

The isothermal magnetization curve [$M(H)$] below $T_m$ (or $T_c$) reflects its magnetic (or superconducting) characteristics for a ferromagnet (or a superconductor). For an FMSC, both characteristics could be present. Figure 6(a) shows the $M(H)$ data at 4 K in a broad range of magnetic fields parallel to the $c$-axis for the Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ crystal. Indeed, the $M-H$ loop is basically featured by a ferromagnetic-like magnetization superposed by a type-II superconducting loop. The equilibrium magnetization ($M_{eq}$), calculated by averaging the field-up magnetization ($M_{up}$) and field-down one ($M_{dn}$), is similar to the as-measured $M(H)$ curve of the analogous ferromagnets EuFe$_{1.8}$Ni$_{0.2}$As$_2$ [16] and EuFe$_2$P$_2$ [42] where SC was absent. The saturated magnetization $M_\text{s} = 6.9 \mu_B$ f.u.$^{-1}$ is consistent with the ferromagnetic ordering of the Eu$^{2+}$ spins (the theoretical ordered moment is $gJ = gS = 7.0 \mu_B$ f.u.$^{-1}$). Since the ferromagnets EuFe$_{1.8}$Ni$_{0.2}$As$_2$ and EuFe$_2$P$_2$ show only tiny magnetic hysteresis with a coercive field of 10–30 Oe [16, 42] that can be ignored in a rough approximation, we made a subtraction of $M_{eq}$ from $M_{up}$ (or $M_{dn}$), shown in figure 6(b). The resultant $\Delta M(H)$ indeed resembles a magnetization loop of a non-ideal type-II superconductor with strong flux pinning. Therefore, our low-$T$ magnetization data unambiguously indicate the coexistence of SC and FM in Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$. The steeper increase in $\Delta M_c$ below the saturated field $H_{sat}$ can be explained below. Since the effective field along the $c$-axis can be expressed as $H^* = H_{in}^{*} + H = H_{ex}^{*} + 4\pi M_c + H$, the slope of $\Delta M_c$ is

$$\frac{\partial (\Delta M_c)}{\partial H} = \frac{\partial (\Delta M_c)}{\partial H^*} \frac{\partial H^*}{\partial H} = \frac{\partial (\Delta M_c)}{\partial H^*} \left( 1 + 4\pi \frac{\partial M_c}{\partial H^*} \right).$$ (2)

When $H < H_{sat}$, $|\partial (\Delta M_c)/\partial H| > |\partial (\Delta M_c)/\partial H^*|$ and for $H > H_{sat}$, $|\partial (\Delta M_c)/\partial H| = |\partial (\Delta M_c)/\partial H^*|$.

To examine the detailed magnetization in the superconducting state, the $M(H)$ curve in the field range of $-1 < H < 1$ kOe is shown in figure 7. The initial magnetization curve $M_{in}(H)$ shows the magnetic shielding effect. However, unlike common type-II superconductors, $M_{in}(H)$ has no linear region, and the lower critical field $H_{c1}$ cannot be defined. Similar observation was also found in Eu(Fe$_{0.75}$Ru$_{0.25}$)$_2$As$_2$ crystals [10]. Furthermore, the equilibrium

3 Although the spontaneous magnetization seems to be perpendicular to the $c$-axis at $T_{m}^{ab} < T < T_{m}^{ab}$ under zero field, the magnetization direction tilts a little upon applying the external field along the $c$-axis, which explains the increase of $\chi_{lc}$ below $T_{m}^{ab}$.

4 The minimum of $M_{in}(H)$ in figure 7 is basically the result of the superposition of superconducting shielding effect with the normal initial magnetization of the ferromagnet. It has nothing to do with the crossover from Meissner state to mixed state.
Figure 6. (a) A broad-range ($-50 \leq H \leq 50$ kOe) isothermal magnetization for Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ crystals under $H \parallel c$ at 4 K. The equilibrium magnetization $M_{eq}$, being the average of the field-up magnetization ($M_{up}$) and the field-down one ($M_{dn}$), is also plotted in the upper panel. (b) The difference ($\Delta M_c$) between $M_{up}$ (or $M_{dn}$) and $M_{eq}$, which forms a loop dominated by superconducting contribution.

magnetization $M_{eq}$ does not show a typical peak-like anomaly associated with the transition from the Meissner state ($0 < H < H_{c1}$) to the mixed state ($H_{c1} < H < H_{c2}$). This simply points to the loss of Meissner state in the present system, consistent with the above low-field susceptibility measurement. The $M_{ini}(H)$ slope at zero-field limit also agrees with the low-field magnetic susceptibility data above.

In general, the Meissner state will be lost if the internal magnetic field $H_{in}$ surpasses the intrinsic lower critical field $H_{c1}$. Considering the strong internal field which suppresses $H_{c2}$ significantly, the absence of Meissner state in the Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ FMSC is not surprising. Here we should mention that the loss of Meissner state was previously reported in the superconducting ferromagnets UCoGe [44] and RuSr$_2$GdCu$_2$O$_8$ [45]. These superconducting ferromagnets with $T_m > T_c$ show much lower ferromagnetic internal field.
Figure 7. A narrow-range ($-1 \leq H \leq 1$ kOe) isothermal magnetization for Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ crystals under $H \parallel c$ at 4 K. $M_{\text{ini}}$ denotes the initial magnetization after ZFC, and $M_{\text{eq}}$ represents the equilibrium magnetization by averaging the field-up and field-down magnetizations. The ideal initial magnetization in the absence of internal magnetic field is displayed by the straight line $-\xi H/(4\pi)$, where the coefficient $\xi$ comes from the demagnetization effect: $\xi \sim 1/(1 - N_d)$.

4. Conclusion

We have studied high-quality Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ single crystals in terms of electrical and magnetic measurements. The crystals are optimally doped, and show SC at $T_{\text{sc}} = 22$ K as well as Eu-spin successive orderings at $T_{\text{ab}} = 20$ K with a possible two-dimensional FM and at $T_{\text{tilt}} = 17.4$ K with spin tilting. The isothermal magnetization loop at low temperatures shows ferromagnetic behavior superposed by the superconducting one, demonstrating that Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ is a ferromagnetic superconductor in which peculiar superconducting and magnetic phenomena are displayed.

The upper critical fields were found to be remarkably reduced, compared to other Fe-based superconductors with comparable $T_{\text{sc}}$, indicating the existence of a strong internal field ($\sim 30$ T at zero temperature) due to the exchange interaction with the Eu spins. The internal field also leads to an abnormal temperature dependence of upper critical field and an anisotropy ratio $\gamma$ less than 1.0 around $T_{\text{ab}}$, consistent with the re-orientation of the exchange field below $T_{\text{tilt}}$. Another consequence of the internal field is the loss of the Meissner state at low temperatures, which was experimentally proved by the low-field susceptibility and the initial magnetization measurements.

Finally, it is worth mentioning that the ‘coexistence’ of the two antagonistic phenomena, SC and FM, in this compound is not so surprising, because SC forms in the FeAs layers and FM in the Eu sublattice. Nevertheless, there are two necessary conditions to warrant the coexistence. One is that the intrinsic upper critical field of the superconducting layers should be higher than the exchange fields with the Eu spins. The other is that the RKKY interaction mediated by the...
itinerant electrons should still hold in the superconducting state. In EuFe$_2$As$_2$-related FeSCs, the two criteria are satisfied because of (i) very high (over 50 T) upper critical field and (ii) the multi-orbital character of Fe 3d electrons, in particular. We have proposed that the ($d_{yz}$, $d_{zx}$) and ($d_{x^2−y^2}$, $d_{z^2}$) orbitals are mainly responsible for SC and FM, respectively [22].

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