Magnetic polarization of Ir in underdoped nonsuperconducting Eu(Fe₀.₉₄Ir₀.₀₆)₂As₂

W. T. Jin,¹,²,* Y. Xiao,¹,³ Y. Su,² S. Nandi,¹,²,³ W. H. Jiao,⁴ G. Nisbet,⁵ S. Demirdis,² G. H. Cao,⁶ and Th. Brückel¹,²

¹Jülich Centre for Neutron Science JCSN and Peter Grünberg Institut PGI, JARA-FIT, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
²Jülich Centre for Neutron Science JCSN at Heinz-Maier-Leibnitz Zentrum (MLZ), Forschungszentrum Jülich GmbH, Lichtenbergstrasse 1, D-85747 Garching, Germany
³Department of Physics, Indian Institute of Technology, Kanpur 208016, India
⁴School of Science, Zhejiang University of Science and Technology, Hangzhou 310023, China
⁵Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus Didcot, Oxfordshire OX11 0DE, United Kingdom
⁶Department of Physics, Zhejiang University, Hangzhou 310027, China

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Using polarized neutron diffraction and x-ray resonant magnetic scattering (XRMS) techniques, multiple phase transitions were revealed in an underdoped, nonsuperconducting Eu(Fe₁₋ₓIrₓ)₂As₂ (x = 0.06) single crystal. Compared with the parent compound EuFe₂As₂, the tetragonal-to-orthorhombic structural phase transition and the antiferromagnetic order of the Fe²⁺ moments are significantly suppressed to T_S = 111(2) K and T_N,Fe = 85(2) K by 6% Ir doping, respectively. In addition, the Eu⁺ spins order within the ab plane in the A-type antiferromagnetic structure similar to the parent compound. However, the order temperature is evidently suppressed to T_{S,Eu} = 16.0(5) K by Ir doping. Most strikingly, the XRMS measurements at the Ir L₃ edge demonstrates that the Ir 5d states are also magnetically polarized, with the same propagation vector as the magnetic order of Fe. With T_{S,Eu} = 12.0(5) K, they feature a much lower onset temperature compared with T_{N,Fe}. Our observation suggests that the magnetism of the Eu sublattice has a considerable effect on the magnetic nature of the 5d Ir dopant atoms and there exists a possible interplay between the localized Eu²⁺ moments and the conduction d electrons on the FeAs layers.

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I. INTRODUCTION

Among various parent compounds of the recently discovered Fe-based superconductors [1], EuFe₂As₂ is a unique member of the ternary “122” AFe₂As₂ (A = Ba, Sr, Ca, etc.) family since it contains two magnetic sublattices. In a purely ionic picture, the A site is occupied by the S-state rare-earth Eu²⁺ ion possessing a 4f⁷ electronic configuration with an electron spin S = 7/2, corresponding to a theoretical effective magnetic moment of 7.94 μ_B [2]. With decreasing temperature, EuFe₂As₂ undergoes an antiferromagnetic spin-density-wave (SDW) transition in the Fe sublattice concomitant with a tetragonal-to-orthorhombic structural phase transition at 190 K. In addition, the localized Eu²⁺ spins order in an A-type antiferromagnetic (A-AFM) structure [ferromagnetic (FM) layers ordering antiferromagnetically along the c direction] below 19 K [3–5]. Similar to other parent compounds of the iron pnictides, chemical substitution [6–10] or application of external pressure [11,12] can lead to superconductivity in this system.

Recently, superconductivity was observed in 5d transition metal element doped Eu(Fe₁₋ₓIrₓ)₂As₂ with T_SC up to ~22 K [10,13]. The magnetic ground state of the optimally doped, superconducting Eu(Fe₀.₉₄Ir₀.₀₆)₂As₂ was determined by our single-crystal neutron diffraction measurement [14]. Below 17 K, the Eu²⁺ spins order ferromagnetically along the crystallographic c direction. Both the structural phase transition and the SDW order of the Fe sublattice were found to be fully suppressed in the optimally doped compound with bulk superconductivity. Similar conclusions were obtained on polycrystalline Eu(Fe₀.₉₄Ir₀.₀₆)₂As₂ by Anand et al. based on neutron powder diffraction measurements [15]. However, the phase diagram describing how the magnetic order of the Eu²⁺ spins is tuned by the Ir doping is still not available. In addition, although it is well established that for the iron pnictides the chemical doping suppresses the SDW order of the Fe²⁺ moments in the underdoped region of their phase diagrams, the magnetic properties of the transition metal dopants themselves were not well understood so far. To the best of our knowledge, there exists only a few experimental studies about the magnetic nature of the transition metal dopants in the iron pnictides [16–18]. For instance, 3d Co in BaCo₂As₂ does not order magnetically [16], while spin polarization of 4d Ru and 5d Ir dopant atoms was observed by x-ray resonant magnetic scattering measurements in superconducting Ba(Fe₀.₇₅Ru₀.₂₅)₂As₂ and Ba(Fe₀.₇₃Ir₀.₀₇)₂As₂, respectively, revealing strong coupling between the magnetism of Fe and the transition metal dopants [17,18]. In our case of Eu(Fe₁₋ₓIrₓ)₂As₂ containing both Fe and Eu magnetic sublattices, it will be more interesting to investigate the magnetism of the dopant atoms since both Fe and Eu might exert some influence on them.

Here we present the results of our x-ray resonant magnetic scattering (XRMS) and polarized neutron diffraction measurements on an underdoped, nonsuperconducting Eu(Fe₁₋ₓIrₓ)₂As₂ (x = 0.06) single crystal, which displays multiple phase transitions. Compared with the parent compound, the tetragonal-to-orthorhombic structural phase transition and the antiferromagnetic order of the Fe²⁺ moments are well separated, significantly suppressed to T_{S} = 111(2) K and
Single crystals of Eu(Fe\(_{1-x}\)Ir\(_x\))\(_2\)As\(_2\) (\(x = 0.06\)) were grown from self-flux (Fe, Ir)As. The chemical composition of the crystals was determined by energy dispersive x-ray (EDX) analysis. A 3 mg plate-like single crystal with dimensions \(\sim 2 \times 2 \times 0.2 \text{ mm}^2\) was selected for both the XRMS and polarized neutron diffraction measurements. The mosaicity of the crystal was less than 0.03 \(\text{Å}\), confirming the high quality of the chosen crystal. For macroscopic characterizations, the same crystal was used.

The polarized neutron diffraction measurements were carried out on the diffuse neutron spectrometer (DNS) at Heinz Maier-Leibnitz Zentrum (MLZ), Garching (Germany) [19]. The wavelength of the incident neutrons is 4.544 \(\text{Å}\). Although the neutron absorption effect of Eu at such a long wavelength is quite strong, the thin plate-like shape of the chosen crystal together with the large moment size of Fe and the dominant effect of the paramagnetic cross sections for NSF and SF processes read as

\[
\left( \frac{d\sigma}{dQ} \right)_x^{\text{NSF}} \propto N^* N + \frac{1}{3} I_{5\text{f}}
\]

and

\[
\left( \frac{d\sigma}{dQ} \right)_x^{\text{SF}} \propto M_{xY}^* M_{yX} + M_{zX}^* M_{zY} + \frac{2}{3} I_{5\text{f}},
\]

respectively, where \(N^* N\) denotes the coherent nuclear scattering and \(I_{5\text{f}}\) denotes the total spin incoherent scattering, whereas \(M_{xY}^* M_{yX}\) and \(M_{zX}^* M_{zY}\) are the components of the moment parallel and perpendicular to the scattering plane, respectively. The symbol \(\perp\) indicates that the magnetic scattering is only sensitive to the component of the moment perpendicular to \(Q\). Therefore, using \(x\) polarization, the magnetic and nuclear scattering can be completely separated into the SF and NSF channel, respectively.

The XRMS measurements were performed at the Fe \(K\) edge and Ir \(L_3\) edge at beamline I16 at the Diamond Light Source (Oxford, UK) [22]. The incident radiation was linearly polarized parallel to the horizontal scattering plane (\(\pi\) polarization) with the beam size of 0.2 mm (horizontal) \(\times 0.03 \text{ mm}\) (vertical). The magnetic reflections were probed in the \(\pi-\sigma^*\) scattering channel in which the polarization of the diffracted beam is perpendicular to the scattering plane. The crystal was mounted on a Cu sample holder with some silver paint and then mounted in a closed-cycle cryostat on a six-circle \(\kappa\) diffractometer.
FIG. 1. (a) The temperature dependence of the molar specific heat, (b) the normalized in-plane resistivity ($\rho_{ab}$), and (c) the molar magnetic susceptibility ($\chi$) of the Eu(Fe$_{0.94}$Ir$_{0.06}$)$_2$As$_2$ single crystal. The magnetic susceptibility was measured in zero-field-cooling (ZFC) process with an applied field of 0.1 T perpendicular and parallel to the c direction, respectively. The dashed and dotted curves mark the antiferromagnetic ordering temperature of the Eu$^{2+}$ moments ($T_{N,\text{Eu}}$) and the structural phase transition temperature ($T_S$), respectively. There is another kink around $T^* = 11$ K in $\chi_{ab}$, whose origin remains unclear so far.

which the in-plane component of the Eu$^{2+}$ moments undergo a glassy freezing at lower temperatures compared with $T_{N,\text{Eu}}$.

**B. Polarized neutron diffraction**

Figures 2(a)–2(c) show the reciprocal space contour maps measured at $T = 3.5$ K obtained via polarized neutron diffraction. For the neutron polarization parallel to the scattering vector $Q$ ($x$ polarization), the magnetic and nuclear scattering intensities can be completely separated into the SF and NSF channel, as shown in Figs. 2(a) and 2(b), respectively. The (0, 0, −1) and (0, 0, −3) reflections appear at the base temperature in the SF channel, indicating that magnetic order of the Eu$^{2+}$ spins in Eu(Fe$_{0.92}$Ir$_{0.08}$)$_2$As$_2$ is antiferromagnetic, similar to the case of the parent compound. In addition, no magnetic intensity is observed at the $Q = (−2,0,0)$ within the experimental resolution [Fig. 2(c)], excluding the possibility of net ferromagnetic (FM) component of the Eu$^{2+}$ spins along the c axis. Such a scenario was suggested by Zapf et al. [24] as a possible intermediate magnetic state for the doped compositions between the parent compound with the Eu$^{2+}$ moments lying completely in the ab plane and high doping levels with the Eu$^{2+}$ moments ordering ferromagnetically along the c axis. Thus the Eu$^{2+}$ magnetic structure here in the Eu(Fe$_{0.94}$Ir$_{0.06}$)$_2$As$_2$ single crystal is identical to that in the parent compound and 6% Ir substitution for Fe seems not enough to change the magnetic ground state of the Eu sublattice. Considering the FM structure determined previously in Eu(Fe$_{0.88}$Ir$_{0.12}$)$_2$As$_2$ via unpolarized neutron diffraction [14], the change of the Eu$^{2+}$ magnetic structure in the Eu(Fe$_{1−x}$Ir$_x$)$_2$As$_2$ system from the A-type AFM order to the FM order is expected to occur at intermediate Ir doping level between 6% and 12%. The temperature dependence of the (0, 0, −3) magnetic reflection is shown in Fig. 2(d). The antiferromagnetic transition temperature $T_{N,\text{Eu}}$ is determined to be $16 \pm 0.5$ K, consistent with the values expected from the macroscopic measurements. The order parameter can be fitted to the form $(T - T_{N,\text{Eu}})^{\beta}$ with $\beta = 0.32(3)$, which is not precisely determined in the critical region around the magnetic phase transition so not a real “critical exponent.” But it is quite close to the critical exponent of the three-dimensional Ising model ($\beta = 0.326$). The temperature dependence of an allowed Bragg reflection (0, 0, −2) is also shown as reference.

**C. X-ray resonant magnetic scattering**

The Eu(Fe$_{0.94}$Ir$_{0.06}$)$_2$As$_2$ single crystal was also measured using synchrotron x-ray diffraction to study its structural properties and the magnetism of the Fe sublattice. Figure 3(a)
displays the \((H, 0, 8)\) scans through the \((4, 0, 8)\) Bragg reflection at several temperatures. A single \((2, 2, 8)\) peak in the tetragonal \((T)\) phase at \(T = 113\, \text{K}\) splits into two distinct peaks \([(4, 0, 8)_0\) and \((0, 4, 8)_0\) in the orthorhombic \((O)\) phase below \(T_S = 111\, \text{K}\), due to the structural phase transition from \(I4/mmm\) to \(Fmmm\) space group. As plotted in Fig. 3(b), the orthorhombic distortion \(\delta = (a-b)/(a+b)\) increases monotonically below \(T_S\). This trend is consistent with the anomaly shown in both the specific heat and the resistivity measurements. The abrupt occurrence of the orthorhombic splitting below \(T_S\) indicates the first-order nature of the structural phase transition.

As shown in Fig. 4(a), at \(T = 7\, \text{K}\), a magnetic reflection from the \(\text{Fe}^{2+}\) moments was clearly observed in the \(\pi-\sigma'\) scattering channel when the energy of the x-ray was tuned through the Fe \(K\) edge \((E = 7.111\, \text{keV})\) at \(Q = (1, 0, 9)\). This signal arises from the spin-density-wave (SDW) type antiferromagnetic order of the Fe\(^{2+}\) spins characterized by the propagation vector \(\mathbf{k} = (1, 0, 1)\), similar to the one observed in the parent compound EuFe\(_2\)As\(_2\) by nonresonant magnetic x-ray scattering [3]. The peak is displaced from \(H = 1\) due to the orthorhombic distortion below \(T_S\). However, this peak disappears at \(100\, \text{K}\), as shown by the rocking-curve scans in Fig. 4(b). The temperature dependence of the integrated intensity of the \((1, 0, 9)\) magnetic peak normalized to the \((2, 0, 10)\) charge reflection is plotted in Fig. 4(c). The antiferromagnetic transition temperature of the \(\text{Fe}^{2+}\) moments can be determined as \(T_{\text{FSW}} = 85 \pm 2\, \text{K}\). To confirm the resonant magnetic behavior of the peak, energy scans at the Fe \(K\) edge were performed. Figure 4(d) shows the background-subtracted energy scan through the \((1, 0, 9)\) reflection at \(T = 7\, \text{K}\). The energy spectrum here is very similar to that observed in previous XRMS measurements at the Fe \(K\) edge for SmFeAsO and BaFe\(_2\)As\(_2\) [26,27]. This includes a sharp resonant feature close to the absorption threshold, whose energy is consistent with the pre-edge hump observed in the fluorescence spectrum from the sample [Fig. 4(e)], and broad resonant features extending to energies more than 20 eV above the absorption edge. Note that the antiferromagnetic transition of the \(\text{Fe}^{2+}\) moments occurs at a much lower temperature compared with the structural phase transition \((T_S = 111 \pm 2\, \text{K})\), similar to the observations in Co-doped EuFe\(_2\)As\(_2\) and BaFe\(_2\)As\(_2\) in which the two transitions become well separated with doping [20,28,29]. The existence of both, the structural phase transition and the Fe-SDW order in under-doped, nonsuperconducting Eu(Fe\(_{0.94}\)Ir\(_{0.06}\))\(_2\)As\(_2\), is in stark contrast to the case of superconducting Eu(Fe\(_{0.88}\)Ir\(_{0.12}\))\(_2\)As\(_2\),
in which both transitions are completely suppressed in favor of bulk superconductivity [14].

Furthermore, in order to probe the Ir 5d dopant states, the energy of the incident x-ray was tuned to the Ir L₃ edge (E = 11.22 keV). Interestingly, at T = 7 K, a clear peak is also present in the π−σ′ scattering channel at Q = (1, 0, 9), as shown in Fig. 5(a). The propagation vector at which the scattering is observed is identical to that of the antiferromagnetic order in Fe₂As₂. Below the absorption edge [determined by the white line of the fluorescence shown in Fig. 5(e)], there is almost no intensity. When the incident x-ray energy is tuned through the edge, the intensity increases sharply. Above the edge, the intensity shows a tendency to slowly drop. The non-Lorentzian line shape observed here is very similar to that observed at the Ir L₃ edge using XRMS for superconducting Ba(Fe₁₋ₓIrₓ)₂As₂. It was attributed to the interference between Ir resonant scattering and Fe nonresonant magnetic scattering [17]. By fitting to the peak profiles in Figs. 4(a) and 5(a) using Lorentzian-squared line shape, the full-width at half-maximum (FWHM) of the (1, 0, 9) peak at the Fe K edge and Ir L₃ edge are revealed to be quite similar, close to 0.002 r.l.u. (reciprocal lattice units). The correlation length (ζ) along the a axis for both Ir and Fe magnetic order can be roughly estimated as ζFe ≈ ζIr = 2/(απ × FWHM) = 885 Å = 160 unit cells. Therefore, the polarization of the Ir atoms is quite well correlated, with a similar correlation length as that of the Fe spins, suggesting that the Ir dopant atoms are uniformly distributed over a large length scale.

**IV. DISCUSSION AND CONCLUSION**

First of all, the origin of the resonance at the Ir L₃ edge in Eu(Fe₀.₉₄Ir₀.₀₆)₂As₂ needs to be understood. Note that the resonant x-ray scattering signal in the π−σ′ channel can originate from either the spin or orbital ordering and the spin and orbital degrees of freedom are strongly coupled for 5d Ir. Therefore, possible orbital contribution from Ir to the observed (1, 0, 9) peak cannot be excluded. In addition, it can also originate from some local structural distortion or preferred neighborhood around the Ir atoms, which makes the scattering amplitude of Ir anisotropic and leads to the resonant scattering at the Ir L₃ edge. Nevertheless, we speculate that it most likely results from the magnetic polarization of the Ir 5d states, due to two reasons. First, the resonant scattering set in below a relatively low temperature (~12 K) [30], which is coincidentally close and comparable to the A-type AFM transition temperature of EuIr₂As₂, TN,Eu = 16 ± 0.5 K. The discrepancy between TN,lr and TN,Eu is likely due to the difference of the sample-heating effect between synchrotron x-rays and neutrons. It is noteworthy to point out that TN,lr is determined from the synchrotron measurement and there is a strong sample-heating effect from the incident x-ray beam if no attenuators are applied in order to probe very weak effect [31], while TN,Eu is determined from the neutron diffraction measurement and the sample-heating effect is negligible. Note that we only observed a single anomaly around 16 K at low temperature in the heat capacity measurement shown in Fig. 1(a) and no hint for another transition around 12 K can be discernible. Second, the resonant scattering occurs at the same wave vector as is typically observed for the magnetic order in the 122 iron pnictides, with the propagation vector k = (1, 0, 1) [4,32,33].

For superconducting Ba(Fe₁₋ₓIrₓ)₂As₂, it was proposed that the Ir 5d states may be polarized by either the local field from the Fe neighbors or by other indirect interactions between the Ir and Fe states and it was found by XRMS that the Ir magnetic order persists up to the Néel transition of the majority Fe spins [17]. In Eu(Fe₀.₉₄Ir₀.₀₆)₂As₂, however, clear polarization of Ir occurs at a much lower temperature TN,lr = 12 ± 0.5 K compared with that of the majority Fe spins, TN,Fe = 85 ± 2 K. Comparison between Ba(Fe₁₋ₓIrₓ)₂As₂ and Eu(Fe₁₋ₓIrₓ)₂As₂ suggests a considerable effect of the A-site ion on the magnetic nature of the 5d Ir dopant atoms. Since the XRMS at the Ir L₃ edge corresponds to the excitation of the 2p₃/₂ core electrons into the 5d valence band of Ir, which is hybridized with the
In summary, we have performed the polarized neutron diffraction and x-ray resonant magnetic scattering (XRRS) measurements on a underdoped, nonsuperconducting Eu(Fe$_{1-x}$Ir$_x$)$_2$As$_2$ ($x = 0.06$) single crystal and found multiple phase transitions. The tetragonal-to-orthorhombic structural phase transition and the antiferromagnetic order of the Fe$^{2+}$ moments are well separated, significantly suppressed to $T_S = 111(2)$ and $T_{N,Fe} = 85(2)$ K by 6% Ir doping, respectively, compared with the parent compound. In addition, the Eu$^{2+}$ spins order within the $ab$ plane in the A-type antiferromagnetic structure similar to that in the parent compound. However, the order temperature is evidently suppressed to $T_{N,Eu} = 16.0(5)$ K by 6% Ir doping. Most strikingly, the XRRS measurements at the Ir $L_3$ edge demonstrates that the Ir 5$d$ states are magnetically polarized with the same propagation vector as the magnetic order of Fe. With $T_{N, Ir} = 12.0(5)$ K, they feature a much lower onset temperature compared with $T_{N,Fe}$. Our observation suggests that the magnetism of the Eu sublattice has a considerable effect on the magnetic nature of the 5$d$ Ir dopant atoms and there exists a possible interplay between the localized Eu$^{2+}$ moments and the conduction $d$ electrons on the FeAs layers.

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[25] Note that the magnetic reflection at (1, 0, −3) and (1, 0, −1) from Fe and Ir cannot be observed in the SF channel due to its weakness and strong absorption effect of Eu associated with cold neutrons at DNS.
[30] Even though the value of $T_{N,Eu}$ is close to that of $T^*$, we do not think the magnetic polarization of the Ir dopant atoms is responsible for such an evident kink at $T^*$ in the susceptibility data shown in Fig. 1(c). The reason is that the magnetic polarization of the Ir dopant atoms is a weak effect as evidenced in our XRMS measurement and the Ir moment is expected to be much smaller (less than 1 $\mu_B$ as revealed in other iridates) than that of Eu (close to 7 $\mu_B$). Note that even the Néel transition of the majority Fe spins cannot be resolved in Fig. 1(c). As mentioned in Sec. III A, the origin of the kink at $T^*$ remains unclear so far. It might correspond to a short-ranged glassy freezing of the Eu$^{2+}$ moments as proposed by Zapf et al. [23], which is then difficult to be identified by diffraction experiments.
[31] When measuring the (1, 0, 9) resonant peak at the Ir $L_3$ edge, we did not apply any attenuation for the synchrotron beam since the resonant signal was quite weak. It is therefore expected that the actual sample temperature might be higher than the measured value due to the noninstantaneous thermal conduction, so that $T_{N,Eu}$ might be somewhat underestimated by our XRMS measurement. In our case, the strength of such beam-heating effect can be roughly estimated to produce a temperature difference of $\delta T \approx 5.7$ K according to the heating power of the incident beam and the thermal conductivity of the sample by ignoring the influence of thermal convection and thermal radiation. Therefore, a difference of 4 K between $T_{N,Eu}$ is possible at low temperature considering the inaccuracy of our approximation.

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