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Magnetic phase diagram of $Eu_{1-x}La_xFe_2As_2$ single crystals

T. Wu, G. Wu, H. Chen, Y.L. Xie, R.H. Liu, X.F. Wang, X.H. Chen *

Hefei National Laboratory for Physical Science at Microscale, Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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ABSTRACT

We have systematically measured resistivity, susceptibility and specific heat under different magnetic fields (H) in $Eu_{1-x}La_xFe_2As_2$ single crystals. It is found that a metamagnetic transition from A-type antiferromagnetism to ferromagnetism occurs at a critical field for magnetic sublattice of Eu^{2+} ions. The jump of specific heat is suppressed and shifts to low temperature with increasing H up to the critical value, then shifts to high temperature with further increasing H. Such behavior supports the metamagnetic transition. Further, a twofold in-plane magnetization is found in antiferromagnetic state which is similar to spin density wave (SDW) order. In contrast, isotropic in-plane magnetization is presented in both ferromagnetic and paramagnetic states. Moreover, ferromagnetic state becomes more easily established under external field with suppressing SDW order. An anisotropic exchange model is proposed to understand our findings. Our results suggest that metamagnetism of Eu^{2+} ions is somewhat related to SDW order. Finally, detailed H–T phase diagrams for $x = 0$ and 0.15 crystals are given, and possible magnetic structure is proposed.

The discovery of superconductivity [1–4] in iron-pnicitides $LnFeAsO_{1-x}F_x$ ($Ln = La$, Sm, Ce and Pr) has generated much interest for extensive study on such iron-based superconductors, which is the second family of high-T_c superconductors except for the high-T_c cuprates. Similar to high-T_c cuprates, the spin density wave (SDW) in parent compound is suppressed with doping, while the superconductivity emerges [8–12]. The magnetic ordering of the rare earth ions Ln^{3+} at low temperature has been observed by neutron scattering [5–7] except for the spin density wave arose from Fe^{2+}. The coupling between Ln^{3+} and Fe^{2+} has been found above ordering temperature for local moment of rare earth ions Ln^{3+} [5]. These results indicate that the coupling between spins of rare earth ions and Fe^{2+} ions seems to be one important ingredient to understand magnetic properties at low temperatures.

$EuFe_2As_2$ is one of the FeAs parent compounds with $ThCr_2Si_2$-type structure. It shows not only SDW transition around 190 K, but also an antiferromagnetic transition of Eu^{2+} ions at $T_N \sim 20$ K [13]. Superconductivity at $\sim$30 K can also be achieved by K or Na doping [14,15]. This compound is believed to be more complicated than other parent compounds due to the large local moment of Eu^{2+} ions. Similar to electron-type $Nd_{2-x}Ce_xCu_2O_{4-\delta}$ [16–21], the interaction between magnetic moments of Fe^{2+} and Eu^{2+} may lead to rich physical phenomena. In this paper, we have studied magnetic transition by resistivity, susceptibility and specific heat in $Eu_{1-x}La_xFe_2As_2$ single crystals. The magnetic structure of Eu^{2+} ions is found to be strongly dependent on external magnetic field. A metamagnetic transition from A-type antiferromagnetism to ferromagnetism is observed with increasing magnetic field along ab-plane and c-axis. With La doping, the SDW is strongly suppressed whereas ferromagnetic state of Eu^{2+} ions becomes more easily established under external field. Meanwhile, the antiferromagnetic state of Eu^{2+} ions has a twofold symmetry within ab-plane which is consistent with SDW order [22]. But ferromagnetic and paramagnetic states are found to be isotropic within ab-plane. Our results indicate that the metamagnetism of Eu^{2+} ions is somewhat related to SDW order. Finally, a detailed H–T phase diagram is given, and possible magnetic structure of Eu^{2+} ions is proposed to understand our findings.

High quality single crystals with nominal composition $Eu_{1-x}La_xFe_2As_2$ ($x = 0$, 0.4 and 0.5) were grown by self-flux method as described in the growth of $BaFe_2As_2$ single crystals with FeAs as flux [22]. Many shinning plate-like $Eu_{1-x}La_xFe_2As_2$ crystals were obtained. The typical dimension is about $4 \times 4 \times 0.05\,mm^3$. Elemental analysis of the samples was performed using energy dispersive X-ray spectroscopy (EDX). The obtained actual La content is 0.15 and 0.18 for the samples with $x = 0.4$ and 0.5, respectively. The c-axis parameter is determined by single crystal X-ray diffraction pattern (XRD). The XRD results show that c-axis parameter shrinks from 12.13 to 12.03 Å with La doping from $x = 0$ to 0.18.

Temperature dependence of in-plane and out-of-plane resistivity for $x = 0$, 0.15 and 0.18 crystals is shown in Fig. 1. Both in-plane and out-of-plane resistivities show similar temperature

* Corresponding author.
E-mail address: chenxh@ustc.edu.cn (X.H. Chen).

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dependent behavior. In-plane and out-of-plane resistivities for parent compound show almost a linear temperature dependence above ~188 K, and a steep increase at 188 K, then changes to metallic behavior. This transition is ascribed to SDW/structural transition [22]. With La doping, the SDW/structural transition is suppressed with decreasing T_s from 188 to 110 K for the crystal with $x = 0.18$. It suggests that electrons are introduced into the system with La doping, and lead to a decrease of T_s. For all samples, there exists a kink in resistivity around 20 K. Such kink can be ascribed to antiferromagnetic transition of Eu^{2+} ions.

Temperature dependence of susceptibility (χ) for the crystals with $x = 0$ and 0.15 measured in field cooled process under different H up to 7 T applied within ab-plane and along c-axis is shown in Fig. 2, respectively. For the crystal with $x = 0$, a standard Curie–Weiss behavior was observed in high temperature region ($T > 50$ K) for both $H \parallel ab$ and $H \perp ab$. Below 20 K, a steep decrease in χ happens with $H \parallel ab$ plane, while the χ with $H \perp ab$ plane emerges a small peak, then almost remains constant. It suggests that an antiferromagnetic transition occurs below 20 K. For $x = 0.15$ crystal, temperature dependent susceptibility at high temperature is also Curie-Weiss behavior. The antiferromagnetic transition shows up at T_N of 16 K. All these phenomena occur only at low magnetic fields. With increasing H larger than a critical magnetic field, the antiferromagnetic character in $\chi(T)$ disappears as shown in Fig. 2. As shown in Fig. 3, the magnetization (M) increases linearly with H applied along c-axis, then the M saturates above a critical magnetic field (H_c) of about 1.5 and 0.8 T for the crystals with $x = 0$ and 0.15, respectively. Similar

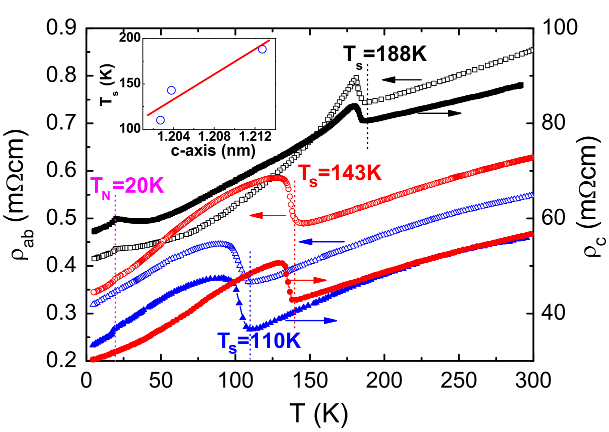

Fig. 1. (Color online) Temperature dependence of in-plane and out-of-plane resistivities for $Eu_{1-x}La_xFe_2As_2$ single crystals with $x = 0$ (squares), 0.15 (circles) and 0.18 (up-triangles). The inset shows c-axis parameter dependent SDW/structural transition temperature.

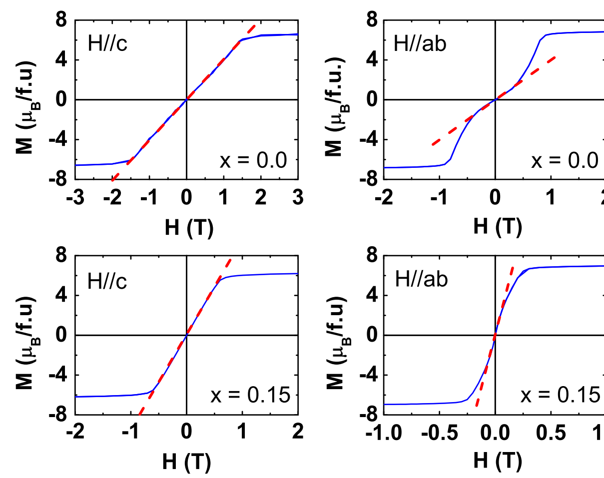

Fig. 3. (Color online) M–H curves for $x = 0$ and 0.15 at 2 K. (a) $H \parallel c$ and (b) $H \perp c$ for $x = 0$ crystal; (c) $H \parallel c$ and (d) $H \perp c$ for $x = 0.15$ crystal.

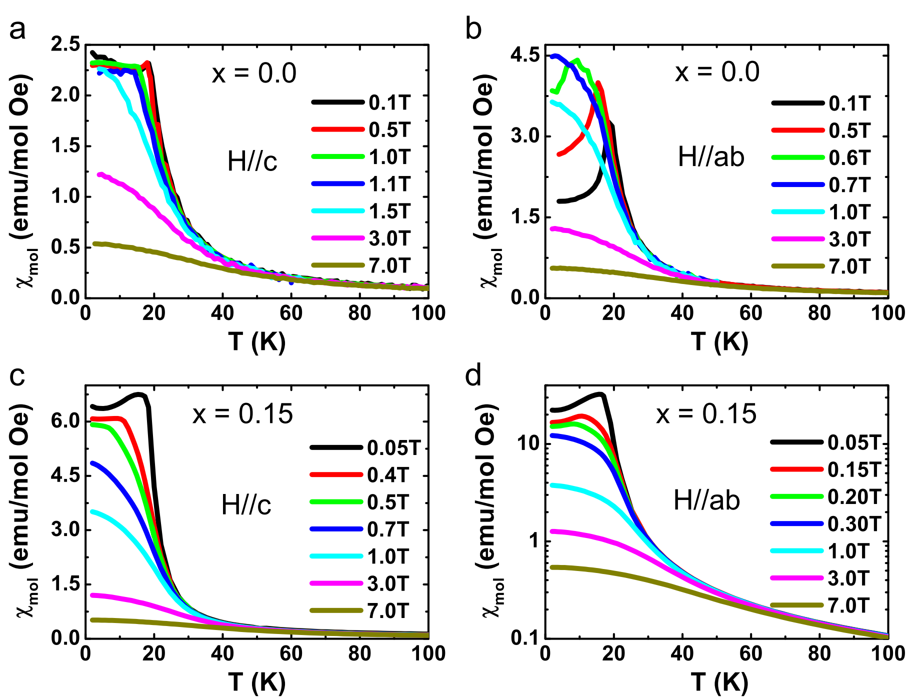

Fig. 2. (Color online) Temperature dependence of susceptibility measured in field-cooled process under different H's. (a) $H \parallel c$ and (b) $H \perp c$ for $x = 0$ crystal; (c) $H \parallel c$ and (d): $H \perp c$ for $x = 0.15$ crystal.

Table 1
Magnetic parameters obtained by fitting the high temperature (100–300 K) susceptibility data for $Eu_{1-x}La_xFe_2As_2$ crystals with $x=0$ and 0.15 with Curie–Weiss law: $\chi(T)=\chi_0+C/(T+\theta)$.

	$H\|$ab	$H\|c$
$EuFe_2As_2$		
θ (K)	−24.67	−21.60
C (emu/K Oe mol)	7.78	7.52
μ_{eff} (μ_B)	7.89	7.76
$Eu_{0.85}La_{0.15}Fe_2As_2$		
θ (K)	−22.82	−22.20
C (emu/K Oe mol)	7.86	7.45
μ_{eff} (μ_B)	7.93	7.72

behavior was observed with H applied within ab-plane, the H_c is about 1 and 0.3 T for the crystals with $x=0$ and 0.15, respectively. These results indicate that a metamagnetic transition from antiferromagnetism (AFM) to ferromagnetism (FM) occurs with increasing magnetic field. It should be pointed out that the M–H curve is linear before saturation without loop for $H\|c$, while a step increase in M is observed between linear behavior and saturation with a small loop for $H\perp c$. The saturated magnetization for $H\perp c$ is larger than that for $H\|c$, e.g. 7.01μ_B with $H\|$ab and 6.71μ_B with $H\|$c for $x=0$ crystal. It indicates that the easy axis is within ab-plane. It should be claimed that we have not considered the demagnetization factor in the present study, which is difficult to calculate for our samples with arbitrary shape. Similar result is reported by Jiang et al. [23]. The high temperature susceptibility data ($100\,K<T<300\,K$) were fitted by the Curie–Weiss formula: $\chi(T)=\chi_0+C/(T+\theta)$. χ_0 is the temperature-independent susceptibility, C is the Curie–Weiss constant and θ is the Weiss temperature. The effective magnetic moment and Weiss temperature are listed in Table 1. Effective magnetic moment is close to the theoretical value of Eu^{2+} ion: 7.94μ_B. The Weiss temperature is negative, indicating a ferromagnetic interaction between Eu^{2+} ions. However, an antiferromagnetic ordering occurs at low magnetic fields. A possible magnetic structure is that the coupling of Eu^{2+} ions is ferromagnetic within ab-plane, while antiferromagnetic for inter-plane; that is, A-type antiferromagnetism. It needs neutron experiment to confirm this speculation.

In order to further study effect of H on magnetic ordering, specific heat was measured with H applied along c-axis for $x=0$ crystal as shown in Fig. 4. A sharp jump around 185 K was observed. Such anomaly should arise from SDW/structural transition as observed in resistivity. Fig. 4(b) shows no change for the anomaly at 185 K under $H=14$ T relative to the case of $H=0$ T. It suggests that the effect of $H=14$ T on the SDW/structural transition is negligible. Another jump around 20 K, associated with the magnetic ordering of Eu^{2+} ions observed in $\chi(T)$, shows up as shown in Fig. 4(a). In contrast to the anomaly related with SDW/structural transition at 185 K, the jump associated with the magnetic ordering of Eu^{2+} ions is suppressed and shifts to low temperature with increasing H up to about 1 T. When $H>1$ T, the sharp jump becomes a broad peak and shifts to high temperature with further increasing H. These results are consistent with susceptibility behavior shown in Fig. 2, and further confirm that a metamagnetism from antiferromagnetism to ferromagnetism occurs with increasing H. Similar behavior in specific heat is observed in $Na_{0.85}CoO_2$ due to a metamagnetic transition [25].

In order to further understand metamagnetism of Eu^{2+} ions, the angular dependent magnetization with rotating H within ab-plane is measured for $x=0$ crystal. As shown in Fig. 5, an

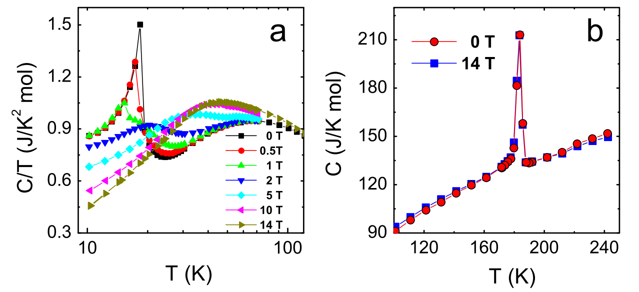

Fig. 4. (Color online) Specific heat as a function of temperature under H applied along c-axis for $x=0$ crystal. (a) Below 100 K; (b) above 100 K.

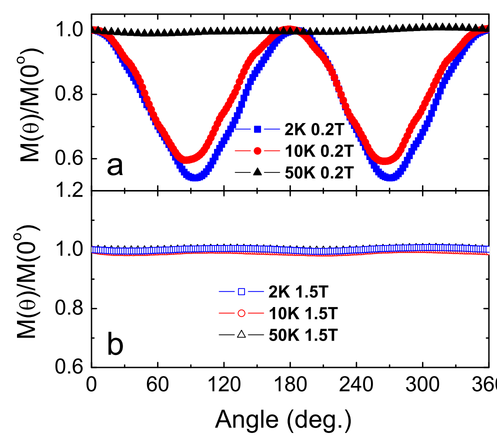

Fig. 5. (Color online) Angle dependent in-plane magnetization for $x=0$ sample at 2, 10 and 50 K under (a): $H=0.2$ T and (b): 1.5 T, respectively.

apparent twofold symmetry is observed at 10 and 2 K under $H=0.2$ T. The anisotropy is about 2.0 at 2 K. With T increasing to 50 K, the magnetization under $H=0.2$ T is changed to be isotropic. It is intriguing that the magnetization is also isotropic at 2 and 10 K under $H=1.5$ T. It suggests that the magnetization in antiferromagnetic state is anisotropic in ab-plane, while in ferromagnetic state is isotropic. An interesting question is naturally proposed: what makes them different? In structural aspect, Eu^{2+} layer is separated by FeAs layer and it can be considered as a quasi-2D Eu^{2+} structure. We consider that the quasi-2D structure can lead to an anisotropic exchange model: $H_{eff}=J_\perp\sum_{i,j}S_i\cdot S_j+J_\|\sum_{i,j}S_i\cdot S_j$. The $J_\perp$ is inter-layer coupling between Eu^{2+} ions and $J_\|$ is intra-layer coupling between Eu^{2+} ions. In our situation, $|J_\||\gg|J_\perp|$ due to quasi-2D structure and $J_\perp$ coupling is mediated by FeAs layer. As discussed above, the ground state of Eu^{2+} ions without external field is A-type antiferromagnetic state. It suggests that $J_\|$ is ferromagnetic and $J_\perp$ is antiferromagnetic. Within ab-plane, the exchange interaction of Eu^{2+} ions is naturally considered to be isotropic and no strong L–S coupling is expected due to $L=0$ for Eu^{2+} ions. Therefore, the anisotropic magnetization is imputed to anisotropic $J_\perp$. As we know, magnetic structure of $BaFe_2As_2$ is stripe-like AFM in FeAs layer from neutron scattering [24], and a twofold magnetic symmetry at 4 K with anisotropy of 1.14 has been reported [22]. Therefore, it is easily understood that the twofold symmetry is observed in antiferromagnetic state of Eu^{2+} ions induced by anisotropic $J_\perp$ which is mediated by FeAs layer. In ferromagnetic state, the small $J_\perp$ coupling is counteracted by external field and the magnetic structure is ruled by $J_\|$ for intra-plane and external field for inter-plane. As mentioned above, the $J_\|$ is isotropic and

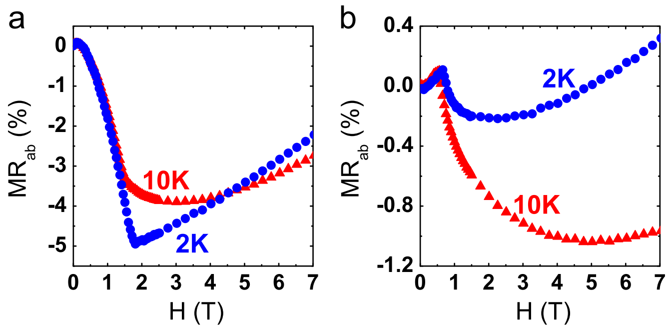

Fig. 6. (Color online) Isothermal in-plane magnetoresistance with H along c-axis for (a) $x=0$ and (b) $x=0.15$ crystals, respectively.

there is no strong L–S coupling. So the anisotropy in magnetization disappears in ferromagnetic state. In this consideration, we can estimate the energy scale of $J_{\perp}$ from 0.46 to 0.69 meV. It also suggests that a weak coupling between Eu^{2+} ions and FeAs layer.

Fig. 6 shows the isothermal in-plane magnetoresistance (MR) with H along c-axis at 2 and 10 K for $x=0$ and 0.15 crystals, respectively. Fig. 6(a) shows that negative in-plane MR increases with increasing H up to a certain magnetic field, then decreases with further increasing H. The clear kink in in-plane MR at 2 K is observed at $H\sim1.7$ T for $x=0$ crystal. As shown in Fig. 6(b), the in-plane MR is positive for $x=0.15$ crystal, and increases with increasing H up to $\sim$0.7 T, then decreases with further increasing H. The magnetic field corresponding to the kink at 2 K is almost the same as the critical magnetic field induced metamagnetic transition observed in Fig. 3. As shown in Fig. 3(a) and (b), the kink shifts to low magnetic field with increasing temperature. This is easily understood because the kink is closely associated with metamagnetic transition from AFM to FM. It also supports the metamagnetic transition.

Fig. 7(a)–(d) shows detailed H–T phase diagram for magnetism of Eu^{2+} ions for $x=0$ and 0.15 crystals for $H\parallel$ab plane and $H\perp$ ab plane, respectively. The antiferromagnetic transition temperature is determined by the kink in $\chi(T)$. The ferromagnetic temperature is determined by the extremum in $d\chi(T)/dT$. At low field, the magnetic structure is A-type antiferromagnetism, while ferromagnetic state above critical magnetic field. As shown in Fig. 7(a)–(d), the critical field with H along c-axis is two times of that with H applied within ab-plane for both of the $x=0$ and 0.15 crystals. La doping suppresses the AFM phase and leads to a decrease in the critical field. The critical field with H along c-axis is about 1.5 T for $x=0$ crystal and 0.8 T for $x=0.15$ crystal. Possible magnetic structures for the spins of Eu^{2+} are proposed as shown in Fig. 7(e) and (f) based on the results of susceptibility and specific heat. In the possible magnetic structures, the antiferromagnetic SDW in FeAs layer keep the same as that in $BaFe_2As_2$ determined by neutron scattering [24] since the different ions in Ba site have no effect on magnetic structure of Fe^{2+} for MFe_2As_2 (M = Ba, Sr, and Ca). At low fields, the inter-plane coupling among Eu^{2+} ions is antiferromagnetic, and the intra-plane coupling is ferromagnetic; that is, A-type AFM structure for Eu^{2+} spins. The spin orientation of Eu^{2+} ions has two possibilities relative to the spin direction of Fe^{2+}. One possibility is that the spin direction of Eu^{2+} ions is perpendicular to that of Fe^{2+} ions, that is, noncollinear AFM structure, similar to that of Nd_2CuO_4 [16–18]. Another possibility is that the spin direction of Eu^{2+} ions is parallel to that of Fe^{2+} ions, that is, collinear AFM structure. With increasing H, the inter-plane coupling changes to ferromagnetic as shown in Fig. 7(g). The proposed AF structures are possible magnetic structures

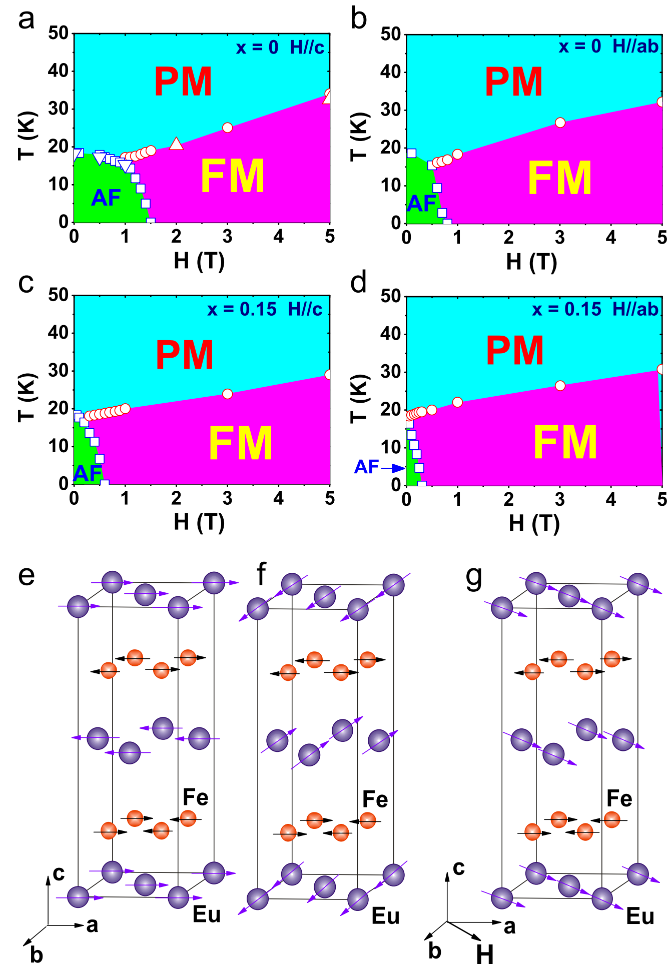

Fig. 7. (Color online) Detailed H–T phase diagram for magnetism of Eu^{2+}. (a) $H\parallel c$ and (b) $H\parallel$ab for $x=0$ crystal; (c) $H\parallel c$ and (d) $H\parallel$ab for $x=0.15$ crystal. The open squares stand for antiferromagnetic transition temperature (T_N) determined by susceptibility. The open circles present ferromagnetic transition temperature (T_c) determine by $d\chi(T)/dT$. The open up-triangles and down triangles in (a) present T_c and T_N determined by the peak position of specific heat, respectively; (e) collinear AF magnetic structures; (f) noncollinear AF magnetic structures; (g) ferromagnetic structure induced by H applied along (110) direction.

and need to be further confirmed. As mentioned above, anisotropic exchange model can be used to understand our findings. In this model, small $J_{\perp}$ can be counteracted by external magnetic field and it causes the metamagnetic transition. But the detailed physics of $J_{\perp}$ is still unclear. As shown in Fig. 7, the SDW is suppressed with La doping and the metamagnetic transition is also suppressed. One explanation is that the SDW order is related to antiferromagnetic state of Eu^{2+} ions. In another words, $J_{\perp}$ is an SDW order dependent quantity. It suggests that magnetic state of Eu^{2+} ions maybe a mirror of magnetic order symmetry in FeAs layer. It could be used to test pairing symmetry in FeAs layer. Recent result on $EuFe_2As_2$ with high pressure also support this idea [26]. But metamagnetism is ignored there. More work should be needed to test this idea.

In summary, we systematically study the magnetic ordering of Eu^{2+} through the resistivity, susceptibility and specific heat measurements in high-quality single crystal $Eu_{1-x}La_xFe_2As_2$. A metamagnetic transition from A-type antiferromagnetism to ferromagnetism is found for magnetic sublattice of Eu^{2+} ions. Moreover, a twofold symmetry is found in antiferromagnetic state and then disappears in ferromangetic and paramagnetic states. An anisotropic exchange model is proposed to understand our findings. Detailed H–T phase diagrams for $x = 0$ and 0.15 crystals are given, and possible magnetic structure for Eu^{2+} spins is proposed. Our results indicate that magnetism of Eu^{2+} ions maybe used as a good test of pairing symmetry in FeAs layer.

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Note: At completion of this work we became aware of one paper reported susceptibility of $EuFe_2As_2$ in Ref. [23].

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