Magnetic phase diagram in Eu$_{1-x}$La$_x$Fe$_2$As$_2$ single crystals

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We have systematically measured resistivity, susceptibility and specific heat under different magnetic fields (H) in Eu$_{1-x}$La$_x$Fe$_2$As$_2$ 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$^{2+}$. 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. Detailed H-T phase diagrams for x=0 and 0.15 crystals are given, and possible magnetic structure is proposed. Magnetoresistance measurements indicate that there exists a strong coupling between local moment of Eu$^{2+}$ and charge in Fe-As layer. These results are very significant to understand the underlying physics of FeAs superconductors.

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The discovery of superconductivity[1, 2, 3, 4] in iron-pnictides $Ln$Fe$_2$AsO$_1-x$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. The magnetic ordering of the rare earth ions Ln$^{3+}$ at low temperature has been observed by neutron scattering[5, 6, 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$^{3+}$[8]. 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. It is well known that spin density wave (SDW) is suppressed, while superconductivity emerges with doping[9, 10, 11, 12]. However, no evidence is given for how to couple between SDW and magnetic ordering of rare earth ions Ln$^{3+}$, and effect of magnetic ordering of Ln$^{3+}$ on superconductivity. Therefore, the coupling between the SDW from Fe$^{2+}$ and magnetic ordering of rare earth ions Ln$^{3+}$ should be a very interesting issue. It maybe shed light to understand the underlying physics in Fe-As compounds.

EuFe$_2$As$_2$ is one of parent compounds with ThCr$_2$Si$_2$-type structure. It shows a SDW transition around 190 K, and an antiferromagnetic transition of Eu$^{2+}$ ions occurs at $T_N$$\sim$20 K[13]. Superconductivity at $\sim$ 30 K can be achieved by K or Na doping[14, 15]. This compound is believed to be more complicated than other parent compound due to the large local moment of Eu$^{2+}$ ions. Similar to electron-type Nd$_{2-x}$Ce$_x$CuO$_4$[16, 17, 18, 19, 20, 21], the interaction between magnetic moments of Fe$^{2+}$ and Eu$^{2+}$ may lead to rich physical phenomena, and these maybe shed light to the mechanism of superconductivity in these materials. In this paper, we have studied magnetic transition by resistivity, susceptibility and specific heat in Eu$_{1-x}$La$_x$Fe$_2$As$_2$ 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 at a certain magnetic field. The results show that the critical magnetic field is anisotropic. With La doping, the SDW is strongly suppressed and the critical magnetic field induced metamagnetic transition decreases. A detailed H-T phase diagram is given, and possible magnetic structure of Eu$^{2+}$ ions is proposed. It is found that there exists strong coupling between antiferromagnetic SDW in Fe-As layer and magnetic ordering of Eu$^{2+}$, the internal magnetic field from ferromagnetic ordering of Eu$^{2+}$ ions can polarize the antiferromagnetic SDW in Fe-As layer.

High quality single crystals with nominal composition Eu$_{1-x}$La$_x$Fe$_2$As$_2$ (x=0, 0.4 and 0.5) were grown by self-flux method as described for growth of BaFe$_2$As$_2$ single crystals with FeAs as flux[22]. Many shining plate-like Eu$_{1-x}$La$_x$Fe$_2$As$_2$ crystals were obtained. The typical dimensional is about 4 x 4 x 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 with La doping from 12.13 Å for x=0 to 12.03 Å x=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 resistivity show similar temperature dependent behavior. In-plane and out-of-plane resistivities for parent compound show almost a linear temperature dependence above $\sim$ 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 $T_c$ from 188 K. This behavior is similar to electron-type ThCr$_2$Si$_2$As. A-type antiferromagnetism to ferromagnetism occurs at a critical field for magnetic sublattice of Eu$^{2+}$. 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. Detailed H-T phase diagrams for x=0 and 0.15 crystals are given, and possible magnetic structure is proposed. Magnetoresistance measurements indicate that there exists a strong coupling between local moment of Eu$^{2+}$ and charge in Fe-As layer. These results are very significant to understand the underlying physics of FeAs superconductors.
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 $T_c$. For all samples, there exists a kink in resistivity around 20 K. Such kink is ascribed to antiferromagnetic transition of Eu$^{2+}$ ions. It suggests that there exists a coupling between the local moment of Eu$^{2+}$ ions and conducting electron in Fe-As layer.

Temperature dependence of susceptibility ($\chi$) for the crystals with x=0 and 0.15 measured in field cooled process under different H, (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. The inset shows M-H curves for x=0 and x=0.15 at 2 K.

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.3. A sharp jump around 185 K is observed, such anomaly should arise from SDW/structural transition observed in resistivity. Fig.3(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, associ-
TABLE I: Magnetic parameters obtained by fitting the high temperature (100 K~300 K) susceptibility data for \( Eu_{1-x}La_xFe_2As_2 \) crystals with \( x=0 \) and 0.15 with Curie-Weiss law: \( \chi(T) = \chi_0 + C(\theta/T - 1) \).

| \( EuFe_2As_2 \) | \( H \| ab \) | \( H \| c \) |
|-----------------|-------------|-------------|
| \( \theta(K) \)  | -24.67      | -21.60      |
| \( C(\text{emu/K Oe mol}) \) | 7.78 | 7.52 |
| \( \mu_{\text{eff}}(\mu_B) \) | 7.89 | 7.76 |

| \( Eu_{0.85}La_{0.15}Fe_2As_2 \) | \( H \| ab \) | \( H \| c \) |
|-----------------|-------------|-------------|
| \( \theta(K) \)  | -22.82      | -22.20      |
| \( C(\text{emu/K Oe mol}) \) | 7.86 | 7.45 |
| \( \mu_{\text{eff}}(\mu_B) \) | 7.93 | 7.72 |

Associated with the magnetic ordering of \( Eu^{2+} \) ions observed in \( \chi(T) \), shows up as shown in Fig.3(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 \([22]\). 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.3(c), an apparent twofold symmetry is observed at 10 K and 2 K under \( H = 0.2 \) T. The anisotropy is about 2.0 at 2 K. With increasing \( T \) 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? Magnetic structure of \( BaFe_2As_2 \) is stripe-like AFM in Fe-As layer from neutron scattering \([23]\), 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. In ferromagnetic state, the ferromagnetic arrangement of spins for \( Eu^{2+} \) leads to a large internal magnetic field. Such large internal magnetic field can polarize the spin orientation in Fe-As layer, so that the magnetization is isotropic in ferromagnetic state.

Fig.3(d) and (e) show the isothermal in-plane magnetoresistance (MR) with \( H \) along c-axis at 2 and 10 K for \( x=0 \) and \( x=0.15 \) crystals, respectively. Fig.3(d) 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 \( H \approx 1.7 \) T for \( x=0 \) crystal. As shown in Fig.3(e), 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.2. As shown in Fig.3(d) and (e), 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. These results suggest that there exist strong coupling between local moment of \( Eu^{2+} \) and charge in Fe-As layer.

Fig.4(a)-(d) show detailed H-T phase diagram for magnetism of \( Eu^{2+} \) ions for \( x=0 \) and \( x=0.15 \) crystals for \( H \| ab \) plane and \( H \bot ab \) plane, respectively. The antiferromagnetic transition temperature is determined by the kink in \( \chi(T) \). The ferromagnetic temperature is determined by...
the extremum in $\frac{d\chi(T)}{dT}$. At low field, the magnetic structure is A-type antiferromagnetism, while ferromagnetic state above critical magnetic field. As shown in Fig.4(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 and 0.8 T for x=0.15 crystal. Possible magnetic structures for the spins of Eu$^{2+}$ are proposed as shown in Fig.4(e) and 4(f) based on the results of susceptibility and specific heat. In the possible magnetic structures, the antiferromagnetic SDW in Fe-As layer keep the same as that in BaFe$_2$As$_2$ determined by neutron scattering, since the different ions in Ba site have no effect on magnetic structure of Fe$^{2+}$ for MF$_2$As$_2$ (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$_2$CuO$_4$. 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 interplane coupling changes to ferromagnetic as shown in Fig.4(g). Such interplane ferromagnetic coupling between Eu$^{2+}$ spins enhances the coupling between Eu$^{2+}$ ions and Fe-As layer, so that the internal magnetic field produced by FM of Eu$^{2+}$ has strong effect on the SDW and the anisotropy disappears. The understanding on interaction between magnetic ordering of rare earth ions and SDW state of Fe-As layer is helpful to study the underlying physics of Fe-As compound.

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$_x$Fe$_2$As$_2$. A metamagnetic transition from antiferromagnetism to ferromagnetism is found for magnetic sublattice of Eu$^{2+}$ ions. Detailed H-T phase diagrams for x=0 and 0.15 crystals are given, and possible magnetic structure for Eu$^{2+}$ spins is proposed. At low fields, the magnetic structure of Eu$^{2+}$ spins is A-type antiferromagnetic. There exists a strong coupling between local moment of Eu$^{2+}$ and charge in conducting Fe-As layer. Our results indicate a coupling between magnetism of rare earth ions and SDW ordering in Fe-As layer. These intriguing phenomena from magnetism of rare earth ions maybe shed light on the underlying physics of FeAs superconductors.

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