Phase diagram as a function of doping level and pressure in Eu$_{1-x}$La$_x$Fe$_2$As$_2$ system

M. Zhang$^1$, J. J. Ying$^1$, Y. J. Yan$^1$, A. F. Wang$^1$, X. F. Wang$^1$, Z. J. Xiang$^1$, G. J. Ye$^1$, P. Cheng$^1$, X. G. Luo$^1$, Jiangping Hu$^{2,3}$ and X. H. Chen$^1$

1. Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China
2. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
3. Department of Physics, Purdue University, West Lafayette, Indiana 47907, USA

We establish the phase diagram of Eu$_{1-x}$La$_x$Fe$_2$As$_2$ system as a function of doping level $x$ and the pressure by measuring the resistivity and magnetic susceptibility. The pressure can suppress the spin density wave (SDW) and structural transition very efficiently, while enhance the antiferromagnetic (AFM) transition temperature $T_N$ of Eu$^{2+}$. The superconductivity coexists with SDW order at the low pressure, while always coexists with the Eu$^{2+}$ AFM order. The results suggests that Eu$^{2+}$ spin dynamics is disentangeld with superconducting (SC) pairing taken place in the two-dimensional Fe-As plane, but it can strongly affect superconducting coherence along c-axis.

PACS numbers: 74.25.-q, 74.25.Ha, 75.30.-m

Iron-based superconductors have attracted great attentions these years$^{[1-3]}$. The parent compound undergoes structural and spin density wave (SDW) transitions. With chemical doping or high pressure, both structural and SDW transition can be suppressed and superconductivity emerges. AFe$_2$As$_2$ ($A=$Ca, Sr, Ba, Eu) with the ThCr$_2$Si$_2$-type structure were widely investigated because it is easy to grow large size of high quality single crystals$^{[4]}$. The maximum $T_C$ for the hole-doped samples is about 38 K and for the Co-doped samples the maximum $T_C$ is about 26 K$^{[4-6]}$. Recently, superconductivity up to 49 K was discovered in rare earth doped Ca$_2$Fe$_2$As$_2$, it is the highest $T_C$ observed in 122 system$^{[7,10]}$. EuFe$_2$As$_2$ has the same structure as that of CaFe$_2$As$_2$$^{[11]}$. EuFe$_2$As$_2$ shows superconductivity around 31 K under the pressure of 3 GPa$^{[12]}$.

The Eu122 system has an intriguingly outstanding issue regarding the interplay between the magnetism of large Eu$^{2+}$ spins and the superconductivity. The doping on the Eu122 system has been achieved in two ways: direct electron doping on Fe-As layer, such as Co-doped Eu122, and doping induced by Eu replacement with rare earth atoms such as Eu$_{1-x}$La$_x$Fe$_2$As$_2$. In the former case, a resistivity reentrance due to AFM order of Eu$^{2+}$ spins was often observed$^{[13,14]}$, an indication of the effect of Eu$^{2+}$ spins on superconductivity. However, a clear understanding of such an effect has not been established due to lack of systematic investigation. In the latter case, earlier results on Eu$_{1-x}$La$_x$Fe$_2$As$_2$ shows only gradual decrease of the spin density wave transition temperature, $T_{SDW}$, of Fe spins with increasing the La content. No superconducting transition was observed$^{[17]}$ and no information regarding of the role of Eu$^{2+}$ spins has been provided.

High pressure is confirmed to be good method to tune the phase competition of superconductivity and SDW in iron-pnictides superconductors. In this letter, we systematically investigate the superconductivity in La doped EuFe$_2$As$_2$ system under ambient and high pressure by resistivity and magnetic susceptibility measurements. We obtain a complete phase diagram obtained. It is found that one superconducting transition was observed in the highest doping level La-doped EuFe$_2$As$_2$ sample, while the zero resistivity cannot be reached under ambient pressure. Both structural and SDW transitions can be completely suppressed and zero resistivity can be achieved under high pressure. The intriguing result is that the antiferromagnetic (AFM) transition temperature $T_N$ of the local moments of the Eu$^{2+}$ ions is always higher than $T_C$, and is not affected by La doping, while slightly increases with increasing the pressure. It suggests that although the superconductivity always coexists with AFM order of Eu$^{2+}$ ions, the two orders are disengaged with each other in La doped EuFe$_2$As$_2$. Together with earlier results on Co-doped Eu122$^{[13,14]}$, these results suggest that Eu$^{2+}$ spins only strongly affect SC coherence along c-axis, but not the SC pairing in Fe-As layers.

High quality single crystals with nominal composition Eu$_{1-x}$La$_x$Fe$_2$As$_2$($x=0, 0.15, 0.3, 0.4, 0.5$) were grown by conventional solid-state reaction using FeAs as self-flux. Clean Eu bulk, Fe powder and As powder were employed as starting materials. Starting materials were weighed in the stoichiometric ratio inside an Ar-filled glove box. The mixture was loaded into an alumina crucible and then sealed into a quartz tube under vacuum. It was slowly heated to 680°C, held for 12 h, and then heated to 1170°C and heated for 10 h, and then the quartz tube was cooled to 900°C at a rate of 4 K/h. Finally, the quartz tube was cooled in the furnace after shutting.
Figure 1(a) shows the temperature dependence of resistivity for the samples of \( \text{Eu}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2 \) with different doping levels. For the parent compound, two anomalies in resistivity are observed at 188 K and 20 K, respectively. They arise from the SDW/structural transitions and the AFM order of local moments for \( \text{Eu}^{2+} \) ions\(^{[17]} \). The resistivity anomaly arose from the SDW/structural transition is gradually suppressed with increasing the doping x, while the anomaly around 20 K due to the antiferromagnetic transition of \( \text{Eu}^{2+} \) ions nearly does not change by varying the La doping.

In order to obtain a complete phase diagram in the \( \text{Eu}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2 \) system, we performed resistivity and susceptibility measurement for the sample \( x = 0.27 \). The structural/SDW transition temperature is suppressed to about 85 K, and superconductivity emerges when La doping is increased to 0.27. However, solid solution x for the \( \text{Eu}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2 \) cannot be larger than 0.27. Therefore, we cannot obtain a whole phase diagram under the ambient pressure in the \( \text{Eu}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2 \) system. The structural/SDW transition temperature is expected under the pressure in the \( \text{Eu}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2 \) system. The phase diagram shows the \( T_N \) is nearly independent of the La doping.

Off the power. The shining plate-like \( \text{Eu}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2 \) crystals were mechanically cleaved from the flux and obtained for measurements. The Energy-dispersive X-ray spectroscopy (EDX) indicates that the actually doping x was 0, 0.08, 0.15, 0.22 and 0.27 for these five La-doping samples, respectively. It has to be addressed that the maximum solid solution x cannot be achieved beyond 0.27 although the nominal doping level is much larger than 0.5. Pressure was generated in a Teflon cup filled with Daphne Oil 7373 which was inserted into a Be-Cu pressure cell. The resistivity measurements were performed using the Quantum Design PPMS-9, and magnetic susceptibility was measured using the Quantum Design SQUID-MPMS.
Based on the results of resistivity and susceptibility under pressure as shown in Fig. 2, a complete phase diagram is obtained, and plotted in Fig. 3. The phase diagram is very complicated and similar to that of $Ba_{1-x}K_xFe_2As_2$ and $BaFe_{2-x}Co_xAs_2$ [13, 14]. As shown in the phase diagram, the Eu$_{0.73}$La$_{0.27}$Fe$_2$As$_2$ system shows the coexistence of superconductivity and SDW under the pressure less than 0.8 GPa. Besides, there exists an antiferromagnetic order arose from the local moment of Eu$^{2+}$ ions. Such AFM order always occurs in the various applied pressures. It should be pointed out that $T_N$ is always higher than the $T_C$. It indicates that the three phases of superconductivity, SDW and AFM order coexist under the pressure less than 0.8 Gpa. In this sense, the phase diagram is complicated relative to those of $Ba_{1-x}K_xFe_2As_2$ and $BaFe_{2-x}Co_xAs_2$. The superconductivity is completely suppressed under the pressure of 1.5 Gpa much less than that in the parent compound EuFe$_2$As$_2$. It suggests that the La-doping and pressure have the same effect on the superconductivity and on SDW. However, the pressure can enhance the $T_N$.

We also studied the phase diagram of the sample Eu$_{0.78}$La$_{0.22}$Fe$_2$As$_2$ by measuring resistivity and susceptibility. Figure 4(a) shows the temperature dependence of resistivity under the various pressure. Eu$_{0.78}$La$_{0.22}$Fe$_2$As$_2$ shows structural and SDW transitions around 96 K and no superconducting transition is detected under the ambient pressure. When applying a small pressure of about 0.5 Gpa, resistivity shows trace of superconducting transition, being similar to the case for the sample $x=0.27$ under the ambient pressure. $T_C$ gradually increases and zero resistivity is achieved with further increasing the pressure. When the applied pressure larger than 0.7 GPa, $T_C$ starts to decrease with increasing the pressure, and superconductivity is completely suppressed when applied pressure up to 1.62 GPa. The resistivity behavior of Eu$_{0.78}$La$_{0.22}$Fe$_2$As$_2$ under small pressure is very similar to that observed in the sample Eu$_{0.73}$La$_{0.27}$Fe$_2$As$_2$ at ambient pressure. It further indicates that La doping has the same effect on SDW and superconductivity as the applied pressure. The phase diagram of the sample Eu$_{0.78}$La$_{0.22}$Fe$_2$As$_2$ as a function of pressure is plotted in Fig.4(b). The phase diagram is the same as that with the control parameter of $x$ observed in $Ba_{1-x}K_xFe_2As_2$ and $BaFe_{2-x}Co_xAs_2$ system except for the existence of AFM order of Eu$^{2+}$ ions.

Both structural and SDW transition are suppressed with La doping, and only superconducting transition can be achieved and no zero-resistance is reached in the Eu$_{1-x}$La$_x$Fe$_2$As$_2$ system. The AFM transition of Eu$^{2+}$ ions is barely affected by La-doping. With applying an external pressure, the superconductivity can be improved drastically on the highly La-doping samples. The SC dome appears in the T-P phase. However, the AFM tran-

![FIG. 2: (color online). (a): Temperature dependence of resistivity for Eu$_{0.73}$La$_{0.27}$Fe$_2$As$_2$ under different pressures. (b): The enlarged area of the temperature dependent resistivity under various pressures around $T_N$. (c): The enlarged area of the temperature dependence of susceptibility under various pressures around $T_N$.](image1)

![FIG. 3: (color online). The pressure phase diagram of Eu$_{0.73}$La$_{0.27}$Fe$_2$As$_2$ derived from resistivity and susceptibility. The AFM indicates the antiferromagnetic state of Eu$^{2+}$.](image2)
major effect of Eu$^{2+}$ spins on SC is along c-axis. In a quasi-two dimensional system, a global SC state is only formed when the SC coherence is reached along c-axis. In La-doped Eu122, the doped electrons to Fe-As layer stems from La. The SC coherence along c-axis can be achieved by virtual hopping through La atoms, which minimizes the effect of the dynamics of Eu$^{2+}$ spins. However, in the parent compounds or Co-doped Eu122, the similar processes go through Eu and Eu$^{2+}$ spins can strongly affects the SC coherence along c-axis. If the pairing in Fe-As is strong, the resistivity reentrance can take place due to the block of c-axis coherence by the critical fluctuations of Eu$^{2+}$ spins near the AFM transition, which explains the observed phenomena in the parent compounds of Eu122. If the pairing in Fe-As is weak, the phase coherence along c-axis may be never developed under the influence of Eu$^{2+}$ spin, which accounts for what observed in the Co-doped Eu122.

In conclusion, we established the complete phase diagram by measuring the resistivity and susceptibility under various pressure for the crystals of Eu$_{1-x}$La$_x$Fe$_2$As$_2$ with different x. Only trace of superconductivity was observed in the highly La-doped samples under ambient pressure. High pressure efficiently suppresses the SDW and structure transition, and improves the superconductivity, while leads to an increase in T$_N$. The superconductivity coexists with SDW order at the low pressure, while always coexists with the antiferromagnetic order of Eu$^{2+}$ spins.

ACKNOWLEDGEMENT This work is supported by the National Natural Science Foundation of China (Grant No. 51021091), National Basic Research Program of China (973 Program, Grant No. 2011CB900101 and No. 2012CB922002) and Chinese Academy of Sciences.

1. Y. Kamihara et al., J. Am. Chem. Soc. 130, 3296 (2008).
2. X. H. Chen et al., Nature 453, 761 (2008).
3. Z. A. Ren et al., Europhys. Lett. 83, 17002 (2008).
4. M. Rotter et al., Phys. Rev. Lett. 101, 107006 (2008).
5. X. F. Wang et al., Phys. Rev. Lett. 102, 117005 (2009).
6. Athena S. Sefat et al., Phys. Rev. Lett. 101, 117004 (2008).
7. S. R. Saha et al., arXiv:1105.4798
8. Zhaoshun Gao et al., EPL, 95, 67002 (2011).
9. B. Lv et al., Proc. Nat. Acad. Sci. 108, 15705 (2011).
10. Yanpeng Qi et al., arXiv:1106.4202
11. Zhi Ren et al., Phys. Rev. B 78, 052501 (2008).
12. Nobuyuki Kurita et al., Phys. Rev. B 83, 214513 (2011).
13. Zhi Ren et al., Phys. Rev. Lett. 102, 137002 (2009).
14. C. F. Miclea et al., Phys. Rev. B 79, 212509 (2009).
15. J. J. Ying et al., Phys. Rev. B 81, 052503 (2010).
16. Y. He et al., J. Phys.: Condens. Matter 22, 235701 (2010).
17. T. Wu et al., J. Mag. Mag. Mat. 321, 3870-3874 (2009).
18. H. Chen et al., EPL, 85, 17006 (2009).
19. X. F. Wang et al., New J. Phys. 11, 045003 (2009).
20. Tyson Park et al., J. Phys.: Condens. Matter 20, 322204.
[21] Patricia L Alireza et al., J. Phys.: Condens. Matter 21, 012208 (2009).

[22] Rongwei Hu et al., Phys. Rev. B 83, 094520 (2011).