Antiferromagnetic transition in $EuFe_2As_2$: A possible parent compound for superconductors

Zhi Ren,[1] Zengwei Zhu,[1] Shuai Jiang,[1] Xiangfan Xu,[1] Qian Tao,[1] Cao Wang,[1] Chunmu Feng,[2] Guanghan Cao,[1,*] and Zhu'an Xu[1,†]

[1]*Department of Physics, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China*

[2]*Test and Analysis Center, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China*

(Received 24 June 2008; revised manuscript received 11 July 2008; published 5 August 2008)

Ternary iron arsenide $EuFe_2As_2$ with $ThCr_2Si_2$-type structure has been studied by magnetic susceptibility, resistivity, thermopower, Hall, and specific-heat measurements. The compound undergoes two magnetic phase transitions at about 200 and 20 K, respectively. The former was found to be accompanied with a slight drop in magnetic susceptibility (after subtracting the Curie-Weiss paramagnetic contribution), a rapid decrease in resistivity, a large jump in thermopower, and a sharp peak in specific heat with decreasing temperature, all of which point to a spin-density-wave-like antiferromagnetic transition. The latter was proposed to be associated with an *A*-type antiferromagnetic ordering of Eu^{2+} moments. Comparing with the physical properties of the isostructural compounds $BaFe_2As_2$ and $SrFe_2As_2$, we expect that superconductivity could be induced in $EuFe_2As_2$ through appropriate doping.

DOI: 10.1103/PhysRevB.78.052501 PACS number(s): 74.10.+v, 74.25.Fy, 74.25.Dw

Superconductivity in iron-based oxyarsenides has recently become a hot topic in the condensed-matter physics community. The excitement was initiated by the observation of 26 K superconductivity in $LaFeAsO_{1-x}F_x$.[1] Following this discovery, T_c was raised quickly above 40 K by replacing La with other lanthanides.[2–5] Recently, T_c has achieved 56 K in Th^{4+} doped GdFeAsO.[6] These T_c values surpass any other superconductors except high-T_c cuprates, indicating the emergence of a class of high-temperature superconductors. The parent compounds of these superconductors LnFeAsO (Ln = lanthanides) adopt the ZrCuSiAs-type structure,[7,8] which consists of alternating stacking $[Ln_2O_2]^{2+}$ and $[Fe_2As_2]^{2-}$ layers. X-ray and neutron-diffraction studies indicate that the parent compound LaFeAsO undergoes a structural phase transition from tetragonal to orthorhombic at 155 K,[9,10] followed by a spin-density-wave (SDW) antiferromagnetic (AFM) transition below 137 K.[9] The electron doping onto the $[Fe_2As_2]^{2-}$ layers via heterovalent chemical substitution at $[Ln_2O_2]^{2+}$ layers suppresses the phase transitions and induces superconductivity. Hence the iron-based oxyarsenide superconductors provide a platform to study the interplay between magnetism and superconductivity, as shown by many theoretical studies.[11–13]

Ternary iron arsenides AFe_2As_2 (A=Sr, Ba) (Refs. 14 and 15) crystallize in $ThCr_2Si_2$-type structure, which is built up with identical $[Fe_2As_2]^{2-}$ layers separated by A^{2+} instead of $[Ln_2O_2]^{2+}$ layers. In analogy with LnFeAsO, AFe_2As_2 undergoes a structural phase transition with a symmetry reduction from tetragonal to orthorhombic, accompanied by the anomalies in electrical resistivity, magnetic susceptibility, and specific heat.[16,17] Substitution of K^+ for A^{2+} suppresses the phase transition and results in the occurrence of superconductivity at about 38 K.[18–20]

$EuFe_2As_2$ is another member of the ternary iron arsenide family;[21] however, only few works were performed on this material. Mössbauer and magnetic-susceptibility studies[22] indicated that $EuFe_2As_2$ experienced two magnetic transitions. The first one around 200 K was due to the AFM transition in the iron sublattice. The second one at 19 K arose from the AFM ordering of Eu^{2+} magnetic moments. No other physical properties of $EuFe_2As_2$ have been reported. In order to assess the potential of inducing superconductivity in this compound, we have carried out a systematic study of the physical properties of $EuFe_2As_2$. We found that the transition at about 200 K was accompanied by a rapid decrease in resistivity, a large jump in thermopower, and a sharp peak in specific heat. In addition, a slight drop in magnetic susceptibility was observed after subtracting the Curie-Weiss paramagnetic contribution of Eu^{2+} magnetic moments. These properties are quite similar with those of $BaFe_2As_2$ and $SrFe_2As_2$, suggesting that $EuFe_2As_2$ is another possible parent compound in which superconductivity may be found by proper doping.

Polycrystalline samples of $EuFe_2As_2$ were synthesized from stoichiometric amounts of the elements as reported previously.[21] Fresh Eu grains, Fe powders, and As grains were mixed in a ratio of 1:2:2, sealed in an evacuated quartz tube, and sintered at 773 K for 12 h then 1073 K for another 12 h. After cooling, the reaction product was thoroughly ground in an agate mortar and pressed into pellets under a pressure of 2000 kg/cm^2 in an argon-filled glove box. The pellets were annealed in an evacuated quartz tube at 1123K for 12 h and furnace cooled to room temperature. The $EuFe_2As_2$ samples were obtained as black powders, which are stable in air.

Powder x-ray diffraction (XRD) was performed at room temperature using a D/Max-rA diffractometer with Cu-$K\alpha$ radiation and a graphite monochromator. Lattice parameters were refined by a least-squares fit using at least 15 XRD peaks. The electrical resistivity was measured using a standard four-probe method. The temperature dependence of dc magnetization was measured on a Quantum Design magnetic property measurement system (MPMS-5). Resistivity, Hall, and specific-heat measurements were performed on a Quantum Design physical property measurement system (PPMS-9). Thermopower measurements were carried out in a cryogenic refrigerator down to 14 K by a steady-state technique with a temperature gradient ~1 K/cm.

Figure 1 shows an XRD pattern for the $EuFe_2As_2$ sample. Most of the diffraction peaks can be indexed based on the $ThCr_2Si_2$-type structure. The refined lattice parameters are

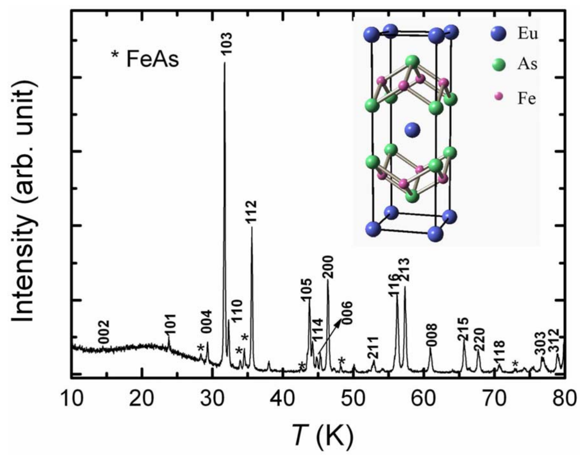

FIG. 1. (Color online) X-ray powder-diffraction pattern at room temperature for the $EuFe_2As_2$ sample. A small amount of FeAs impurity was identified. The inset shows schematic crystal structure of $EuFe_2As_2$.

$a=3.9104$ Å and $c=12.1362$ Å, in agreement with the previous report.[21] A small amount of FeAs impurity was also observed in the XRD pattern, which may arise from the loss of Eu during the high-temperature sintering process.

Figure 2(a) shows magnetic-susceptibility (χ) measurement on the $EuFe_2As_2$ sample. The data of 20 K$<T<200$ K obey the Curie-Weiss law,

$$\frac{1}{\chi} = \frac{T+\theta}{C}, \qquad (1)$$

where C denotes the Curie-Weiss constant and θ the Weiss temperature. The fitted parameters are $C=7.58$emu K/mol and $\theta=-19.7$ K. The calculated effective magnetic moment is 7.79 μ_B per formula unit, which is close to the theoretical value of 7.94 μ_B for a free Eu^{2+} ion. The χ data above 200 K deviate slightly from the Curie-Weiss formula, as can be seen in the plot of $1/\chi$ versus T. After subtraction of the above Curie-Weiss contribution, a small drop in χ at 200 K can be found. This behavior resembles those observed in $BaFe_2As_2$ (Ref. 16) and $SrFe_2As_2$,[17] which were ascribed to a SDW transition. Below 20 K, χ decreases sharply, consistent with the previous report.[22] ^{151}Eu Mössbauer spectroscopy indicated that the transition was due to the AFM ordering of Eu^{2+} moments. However, the Neel transition disappears under strong magnetic field.

Figure 2(b) shows the field-dependent magnetization for the $EuFe_2As_2$ sample at various temperatures. A slope change in the M-H curve at 2 K can be seen clearly at $\mu_0H=0.65$ T. In the range of $0.65\text{T}<\mu_0H<1.0\text{T}$, the magnetization increases rapidly with the field, suggesting a metamagnetic transition. The magnetization saturates for $\mu_0H\geq 1.6$ T, corresponding to an effective magnetic moment of 6 μ_B/f.u. Though this value was underestimated owing to the presence of a small amount of FeAs impurity, the actual saturated moment would be still smaller than the expected value of 7 ($=gS$) μ_B/f.u. This deviation of magnitude of Eu^{2+} moments was observed in Eu metal[23] and $EuZn_2Sb_2$,[24] which may be due to the crystal-field interactions. The metamagnetic transition reminisces the A-type antiferromagnetism in layered systems such as $La_{2-x}Sr_{1+x}Mn_2O_7$ (Ref. 25) and $Na_{0.85}CoO_2$.[26] Note that the above Curie-Weiss fit gives a negative value of θ, which means ferromagnetic interaction among the Eu^{2+} moments. We propose that the AFM ordering of Eu^{2+} spins is of A type, i.e., the Eu^{2+} moments parallel in a ab plane but antiparallel along the c axis. Further study is needed to understand this interesting issue.

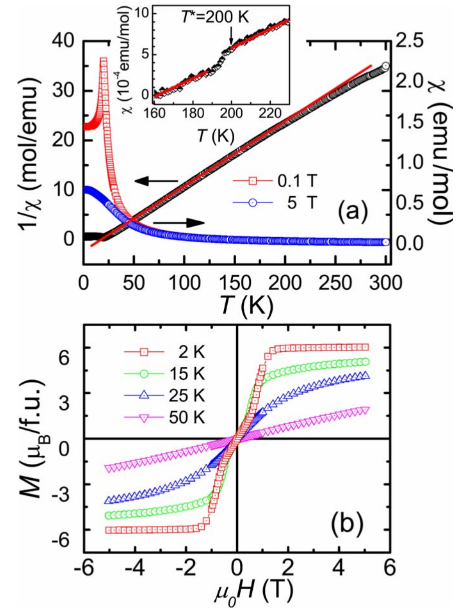

FIG. 2. (Color online) (a) Temperature dependence of magnetic susceptibility for the $EuFe_2As_2$ sample. The inset shows a drop in χ at $T^*=200$ K after subtraction of the Curie-Weiss contribution of Eu^{2+} moments. The red lines are the guide to the eyes. (b) Field dependence of magnetization at low temperatures for the $EuFe_2As_2$ sample.

The transport properties of the $EuFe_2As_2$ sample are summarized in Fig. 3. All these data demonstrate an anomaly at 200 K, in correspondence with the above magnetic measurements. The resistivity (ρ) value at room temperature is $\sim$1 mΩ cm, comparable to those of $SrFe_2As_2$ (Ref. 17) and $BaFe_2As_2$ (Ref. 16) but much smaller than that of LaFeAsO.[27] With decreasing temperature, ρ decreases slightly. Below 200 K, a sudden slope change appears in the ρ-T curve. Around 20 K, a kink is evident in the inset of Fig. 3(a), which is related to the AFM ordering of Eu^{2+} ions. No resistivity anomaly can be detected around 77 K [the AFM transition temperature of FeAs (Ref. 28)] indicating no significant effect of the FeAs impurity on the resistivity behavior. Under a magnetic field of 8 T, there is no observable variation in ρ above 200 K. Below 200 K, however, we observed a positive magnetoresistance (MR), which increases with decreasing temperature. This phenomenon can be explained in terms of the enhancement of spin scattering due to the suppression of AFM SDW order by external magnetic field, similar to that in LaFeAsO.[27] Below 19 K, the MR increases steeply and achieves 80% at 5 K. We also note that the resistivity kink at 19 K under zero field is totally suppressed by the strong field. This phenomenon coincides with the magnetic structure proposed above because the in-

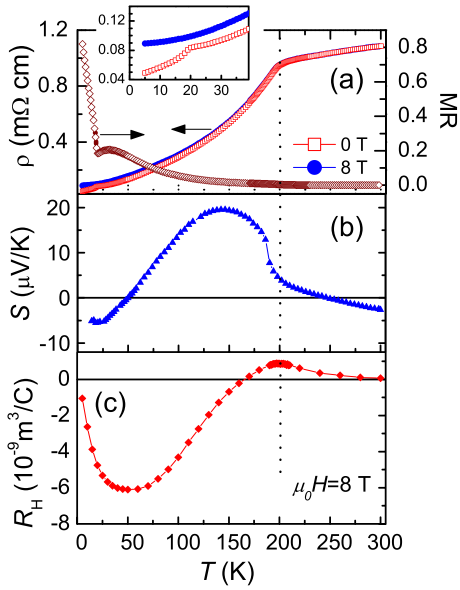

FIG. 3. (Color online) Temperature dependences of (a) resistivity, (b) thermopower, and (c) Hall coefficient for the $EuFe_2As_2$ sample. The inset of (a) is an expanded plot for showing low-temperature data.

terlayer AFM coupling is relatively weak and can be easily destroyed by the external magnetic field.

Figure 3(b) plots the thermopower (S) as a function of temperature. With decreasing temperature, S is seen to change its sign from negative to positive, then to negative again. This behavior strongly suggests a multiband characteristic in $EuFe_2As_2$. In Fig. 3(c), a sign reversal in the Hall coefficient (R_H) with decreasing temperature was also observed, further supporting the multiband scenario. At 200 K, a jump in S and a turning point in R_H are clearly seen, suggesting a substantial change of electronic states at the Fermi level. The positive sign of R_H above 200 K indicates that the dominant carriers are holelike, which is in contrast with that in LaFeAsO.[27] It is noted here that the Hall voltage is nonlinear with the applied field below 50 K, which is probably related to the nonlinearity in the above M-H curves. Thus the values of R_H below 50 K are not well defined.

Figure 4 shows the specific heat as a function of temperature. A sharp peak appears at 200 K, which points to a first-order phase transition. However, no thermal hysteresis was

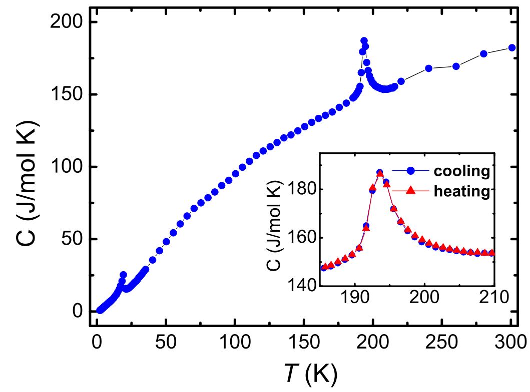

FIG. 4. (Color online) Temperature dependence of specific heat for the $EuFe_2As_2$ sample. The inset is an expanded plot, showing no detectable thermal hysteresis around 200 K.

found within the experimental precision. We thus speculate that the latent heat is quite small. Another specific-heat anomaly at 19 K is due to the AFM ordering of Eu^{2+} moments. Because of the influence of this transition, the electronic specific-heat coefficient γ cannot be extracted reliably.

In summary, we have performed a systematic physical property measurement on an $EuFe_2As_2$ polycrystalline sample. It is found that the magnetic transition at 200 K is very similar to those of $BaFe_2As_2$ and $SrFe_2As_2$, both of which become superconductors upon doping with some alkaline elements.[18–20] Therefore, superconductivity may be induced by suppressing the SDW transition through appropriate doping in $EuFe_2As_2$. The Eu^{2+} moments in $EuFe_2As_2$ are expected to be compatible with superconductivity, in analogy with $CeFeAsO_{1-x}F_x$.[3] Hall measurements[19,20] indicated that the superconductivity in K-doped $BaFe_2As_2$ and $SrFe_2As_2$ was induced by hole doping. Meanwhile, attempts to introduce superconductivity in $BaFe_2As_2$ by electron doping through substitution of La^{3+} for Ba^{2+} were not successful.[20] Owing to the dominant holelike carriers in $EuFe_2As_2$, we speculate that superconductivity may also be realized by hole doping in $EuFe_2As_2$ systems.

The authors thank Ying Liu for helpful discussions. This work is supported by the National Basic Research Program of China (Contracts No. 2006CB601003 and No. 2007CB925001) and the PCSIRT of the Ministry of Education of China (Contract No. IRT0754).

*ghcao@zju.edu.cn
†zhuan@zju.edu.cn
[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
[2] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature (London) **453**, 761 (2008).
[3] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. **100**, 247002 (2008).
[4] Z. A. Ren, J. Yang, W. Lu, W. Yi, G. C. Che, X. L. Dong, L. L. Sun, and Z. X. Zhao, arXiv:0803.4283 (unpublished).
[5] Z. A. Ren, J. Yang, W. Lu, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao, Europhys. Lett. **82**, 57002 (2008).
[6] C. Wang, L. J. Li, S. Chi, Z. W. Zhu, Z. Ren, Y. K. Li, Y. T. Wang, X. Lin, Y. K. Luo, S. Jiang, X. F. Xu, G. H. Cao, and Z. A. Xu, arXiv:0804.4290 (unpublished).
[7] V. Johnson and W. Jeitschko, J. Solid State Chem. **11**, 161 (1974).
[8] P. Quebe, L. J. Terbuchte, and W. Jeitschko, J. Alloys Compd. **302**, 70 (2000).

[9] C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff II, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and Pengcheng Dai, Nature (London) **453**, 899 (2008).
[10] T. Nomura, S. W. Kim, Y. Kamihara, M. Hirano, P. V. Sushko, K. Kato, M. Takata, A. L. Shluger, and H. Hosono, arXiv:0804.3569 (unpublished).
[11] K. Haule, J. H. Shim, and G. Kotliar, Phys. Rev. Lett. **100**, 226402 (2008).
[12] C. Cao, P. J. Hirschfeld, and H. P. Cheng, Phys. Rev. B **77**, 220506(R) (2008).
[13] D. J. Singh and M. H. Du, Phys. Rev. Lett. **100**, 237003 (2008).
[14] M. Pfisterer and G. Nagorsen, Z. Naturforsch. B **35**, 703 (1980).
[15] M. Pfisterer and G. Nagorsen, Z. Naturforsch. B **38**, 811 (1983).
[16] M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes, and R. Pöttgen, Phys. Rev. B **78**, 020503(R) (2008).
[17] C. Krellner, N. Caroca-Canales, A. Jesche, H. Rosner, A. Ormeci, and C. Geibel, arXiv:0806.1043 (unpublished).
[18] M. Rotter, M. Tegel, and D. Johrendt, arXiv:0805.4630v1 (unpublished); N. Ni, S. L. Budko, A. Kreyssig, S. Nandi, G. E. Rustan, A. I. Goldman, S. Gupta, J. D. Corbett, A. Kracher, and P. C. Canfield, Phys. Rev. B **78**, 014507 (2008).
[19] G. F. Chen, Z. Li, G. Li, W. Z. Hu, J. Dong, X. D. Zhang, P. Zheng, N. L. Wang, and J. L. Luo, arXiv:0806.1209 (unpublished); K. Sasmal, B. Lv, B. Lorenz, A. Guloy, F. Chen, Y. Xue, and C. W. Chu, arXiv:0806.1301 (unpublished).
[20] G. Wu, R. H. Liu, H. Chen, Y. J. Yan, T. Wu, Y. L. Xie, J. J. Ying, X. F. Wang, D. F. Fang, and X. H. Chen, arXiv:0806.1459 (unpublished).
[21] R. Marchand and W. Jeitschko, J. Solid State Chem. **24**, 351 (1978).
[22] H. Raffius, E. Mörsen, B. D. Mosel, W. Müller-Warmuth, W. Jeitschko, L. Terbüchte, and T. Vomhof, J. Phys. Chem. Solids **54**, 135 (1993).
[23] N. G. Nereson, C. E. Olsen, and G. P. Arnold, Phys. Rev. **135**, A176 (1964).
[24] F. Weber, A. Cosceev, S. Drobnik, A. Faisst, K. Grube, A. Nateprov, C. Pfleiderer, M. Uhlarz, and H. v. Löhneysen, Phys. Rev. B **73**, 014427 (2006).
[25] T. Kimura and Y. Tokura, Annu. Rev. Mater. Sci. **30**, 451 (2000).
[26] J. L. Luo, N. L. Wang, G. T. Liu, D. Wu, X. N. Jing, F. Hu, and T. Xiang, Phys. Rev. Lett. **93**, 187203 (2004).
[27] J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Z. Hu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, Z. Fang, and N. L. Wang, Europhys. Lett. **83**, 27006 (2008).
[28] K. Selte, A. Kjekshus, and A. Andresen, Acta Chem. Scand. (1947-1973) **26**, 3101 (1972).